ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Novel Palladium–Aminocarbene Species Derived from Metal-Mediated Coupling of Isonitriles and 1,3-Diiminoisoindoline: Synthesis and Catalytic Application in Suzuki–Miyaura Cross-Coupling

Rogério S. Chay,[†] Konstantin V. Luzyanin,*[,†,‡] Vadim Yu. Kukushkin,[‡,§] M. Fátima C. Guedes da Silva,[†,⊥] and Armando J. L. Pombeiro*[,†]

[†]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Avenida Rovisco Pais, 1049-001, Lisbon, Portugal

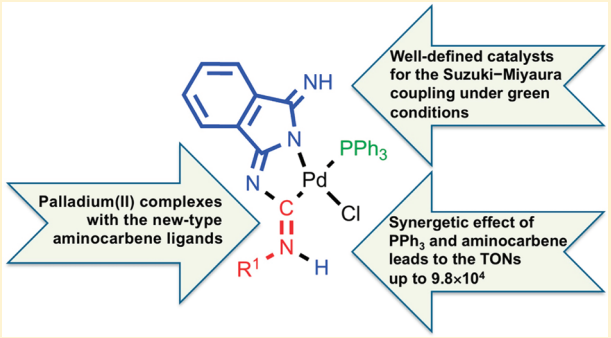
[‡]St.Petersburg State University, 198504 Stary Petergof, Russian Federation

[§]Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoii Pr. 31, 199004 St.Petersburg, Russian Federation

[⊥]Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon, 1749-024 Lisbon, Portugal

Supporting Information

ABSTRACT: The reaction between metal-bound isonitriles in *cis*-$[PdCl_2(CNR^1)_2]$ [R^1 = cyclohexyl (Cy) **1**, Bu^t **2**, $C_6H_4(2,6\text{-}Me_2)$ (Xyl) **3**, $CMe_2CH_2CMe_3$ **4**] and 1,3-diiminoisoindoline (**9**) in $CHCl_3$ under reflux for 4 h provides the carbene species $[Pd\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)R^1\}_2]^{a-b}$ (R^1 = Cy **10**, 82% isolated yield) or *cis*-$[PdCl\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)R^1\}(CNR^1)]^{a-b}$ (R^1 = Bu^t **11**, 78%; Xyl **12**, 84%; $CMe_2CH_2CMe_3$ **13**, 79%), derived from the addition of two or one equivs of **9** to the starting **1**–**4**, respectively. The corresponding integration of *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ (R^1 = Cy **5**, Bu^t **6**, $CMe_2CH_2CMe_3$ **8**) with 1 equiv of **9** in $CHCl_3$ under reflux for 4 h affords the carbene species *cis*-$[PdCl\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)R^1\}(PPh_3)]^{a-b}$ (R^1 = Cy **14**, 84%; Bu^t **15**, 76%; $CMe_2CH_2CMe_3$ **16**, 75%). Complexes **10**–**16** were characterized by elemental analyses (C, H, N), ESI^+-MS, IR, and 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC, ^1H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of aminocarbene complexes **10** and **12** were elucidated by X-ray diffraction. The catalytic properties of **10**–**16** in the Suzuki–Miyaura cross-coupling of aryl halides, viz., 4-$R^2C_6H_4X$ (X = I, R^2 = OMe; X = Br, R^2 = Me, OMe, and NO_2), with phenylboronic acid (in EtOH as solvent, K_2CO_3 or Cs_2CO_3 as base, 80 °C) yielding biaryl species 4-$R^2C_6H_4Ph$, were evaluated. Complexes **14**–**16** exhibit a high catalytic activity (yields up to 98%, TONs up to 9.8×10^4, TOFs up to 3.9×10^4).



INTRODUCTION

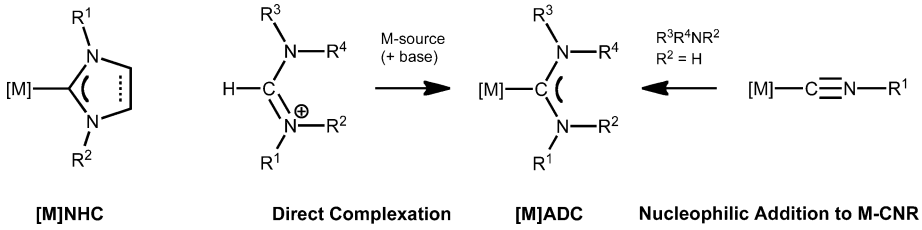
Acyclic diaminocarbenes (ADCs)[1−3] are structural analogues of the corresponding *N*-heterocyclic carbene species (NHCs);[4−12] the latter compounds have revolutioned organometallic catalysis (Scheme 1). ADCs exhibit a similar electronic stabilization (delocalization of the electron density within the carbene moiety) and possess comparable (equal bond lengths) or slightly different (wider angles around the carbene carbon) structural characteristics and coordination abilities as the related NHCs.[13−16] Metal complexes with ADC ligands[1−3,13−15,17−24] are typically generated via two distinct synthetic protocols, i.e., by (i) a direct complexation of the generated *in situ* free carbene species to a metal center[1] or through (ii) a metal-mediated nucleophilic attack on an isonitrile (Scheme 1).[1,2] In the latter approach, amines or hydrazines (sp^3-*N* nucleophiles) are commonly employed as nucleophiles.

Despite the appealing characteristics and similarities between these two types of aminocarbene species, ADCs have so far attracted much less attention as ancillary ligands in the cross-coupling transformations as compared to the related *N*-heterocyclic analogues. To date, only a few reports on catalytic applications of palladium-ADCs in intermolecular Heck,[25,26] Buchwald–Hartwig,[25] Sonogashira,[26,27] and Suzuki–Miyaura[26,28−31] cross-coupling and several intramolecular cyclization reactions[32−41] have been published, whereas the corresponding [Pd]NHC species have found a broad application as catalysts for such coupling reactions.[4,6,7]

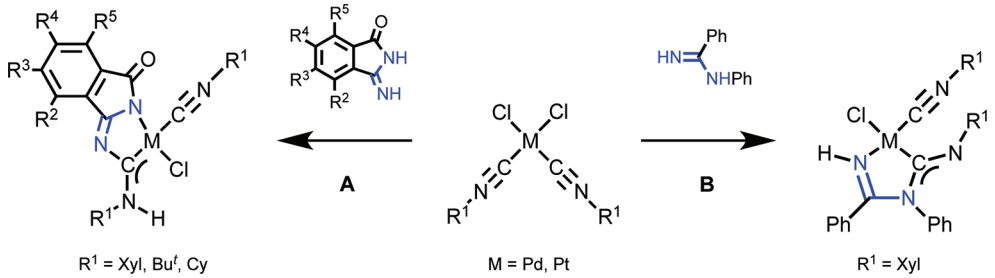
Recently, we have reported on the first examples of novel-type aminocarbene ligands derived from the coupling of palladium-bound isonitriles with sp^2-*N* [imines, e.g., 3-

Received: January 10, 2012
Published: March 5, 2012

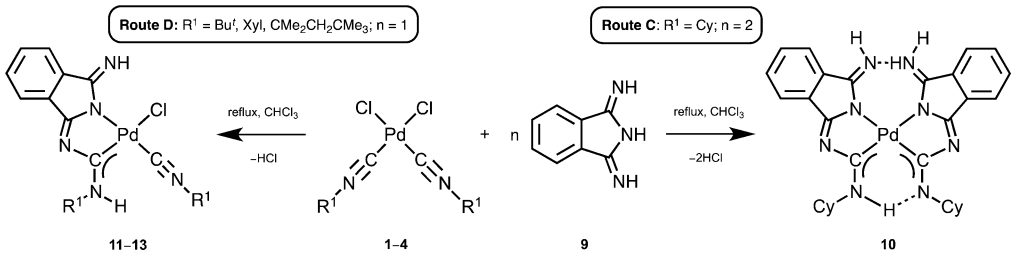
Scheme 1. Complexes with *N*-Heterocyclic Carbene ([M]NHC) and Acyclic Diaminocarbene ([M]ADC) Ligands and Main Routes for the Preparation of [M]ADC



Scheme 2. Generation of Novel-Type Aminocarbenes via Addition of 3-Iminoisoindolin-1-one (Route A) and *N*-Phenylbenzamidine (Route B) to Metal-Bound Isonitrile



Scheme 3. Reaction of 1,3-Diiminoisoindoline (9) with the Isonitriles in *cis*-$[PdCl_2(CNR^1)_2]$ (1−4)



iminoisoindolin-1-one][42,43] or mixed sp^2/sp^3-*N* [amidines, e.g., *N*-phenylbenzamidine][27] type nucleophiles. Two of the studied reactants, i.e., 3-iminoisoindolin-1-one and *N*-phenylbenzamidine, possess one *amidine*-type reaction center [HN═C(NH), Scheme 2] that in the reaction with metal-bound isonitrile behaves as both a nucleophile (via the imine NH) and a chelator (via the amide HN), affording a bidentate carbene-amide ligand.

Following our ongoing project on the design of novel carbene ligands,[28,42−44] and in order to extend the family of acyclic aminocarbene species, we decided to employ in the reactions with various palladium−isonitrile species a structurally related nucleophile bearing fused *amidine* and *imine* functions in one molecule, viz., 1,3-diiminoisoindoline [HN═CC_6H_4C(═NH)NH, see Scheme 3]. In addition, taking into account that the catalytic properties of metal-ADC species are much less explored as compared to the corresponding metal-NHCs, we have also evaluated the catalytic efficiency of the newly generated palladium carbenes in Suzuki−Miyaura cross-coupling. The results of our study are disclosed in the sections that follow.

RESULTS AND DISCUSSIONS

Metal-Mediated Coupling of 1,3-Diiminoisoindolines with Palladium-Bound Isonitriles. For this study we employed 1,3-diiminoisoindoline[45] (**9**) as the nucleophile. In accord with literature sources,[46−48] this species exists in the tautomeric equilibrium between the amino and imino forms (Figure 1). Theoretical[47,48] and X-ray diffraction[46] studies

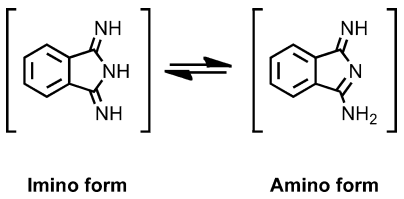


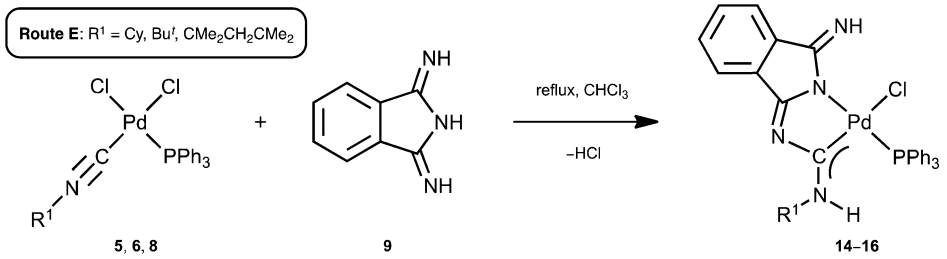
Figure 1.

clearly indicate that the imino form possesses lower energy, being the predominant one in solution, while the amino form is prevalent in the solid state, where its stabilization is explained mostly by intermolecular hydrogen bonding.

As electrophilic reagents, we addressed the known palladium(II) isonitrile complexes *cis*-$[PdCl_2(CNR^1)_2]$ [R^1 = cyclohexyl (Cy) **1**, Bu^t **2**, C_6H_4(2,6-Me_2) (Xyl) **3**] and *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ [R^1 = cyclohexyl (Cy) **5**, Bu^t **6**, C_6H_4(2,6-Me_2) (Xyl) **7**].[49−53] In addition, we also prepared two new palladium species, viz., *cis*-$[PdCl_2(CNCMe_2CH_2CMe_3)_2]$ (**4**) and *cis*-$[PdCl_2(CNCMe_2CH_2CMe_3)(PPh_3)]$ (**8**), bearing 2-isocyano-2,4,4-trimethylpentane ligands. The latter were synthesized via slightly modified procedures applied for the preparation of **1**−**3** and **5**−**7**, correspondingly, i.e., by replacement of two acetonitrile ligands in $[PdCl_2(NCMe)_2]$ by 2-isocyano-2,4,4-

dx.doi.org/10.1021/om300020j | *Organometallics* 2012, 31, 2379−2387

Scheme 4. Reaction of 1,3-Diiminoisoindoline (9) with the Ligated Isonitrile in *cis*-[$PdCl_2(CNR^1)(PPh_3)$] (5, 6, and 8)



trimethylpentane (2 equiv), affording **4** (90%), or by the reaction of **4** with PPh_3 (1 equiv) that furnishes **8** (87%).

In the initial experiments, we did not observe any reaction between equimolar amounts of the uncomplexed isonitriles and **9**. Under refluxing $CHCl_3$, in the absence of any Pd complex, only the starting materials were detected in the mixture after 2 d. This observation suggests that the addition of **9** to the isonitrile CN triple bond described in the following sections has a metal-mediated character.

The reactions between **1**–**8** and **9** in $CHCl_3$ (Schemes 3, 4 and 1S of the Supporting Information) were studied at different temperatures employing various ratios of reagents, and details of these studies are provided in the Supporting Information.

The reaction between a metal-bound isonitrile in **1** and 2 equiv of **9** proceeds efficiently under $CHCl_3$ reflux conditions for 4 h (Scheme 3, route C), and the subsequent workup provides the carbene species $[Pd\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)Cy\}_2]^{a-b}$ (**10**) in 82% isolated yield. When 1 equiv of **9** was employed, complex **10** was formed in ca. 40% yield, and unreacted starting isonitrile complex **1** (ca. 35%) was detected in the reaction solution along with yet unidentified species (three spots with close retention on TLC). The corresponding reaction between a metal-bound isonitrile in each of **2**–**4** and 1 equiv of **9** proceeds in $CHCl_3$ under reflux for 4 h (Scheme 3, route D), and the subsequent workup provides the carbene species *cis*-$[PdCl\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)R^1\}(CNR^1)]^{a-b}$ (**11**–**13**) isolated in 78–84% yield. When 2 equivs of **9** were employed, complexes **11**–**13** were formed in the same yield, although being strongly contaminated with excess **9**, **9**·HCl, and other yet unidentified species (four spots on TLC in each case).

Furthermore, the reaction between **5**, **6**, and **8** and 1 equiv of **9** in $CHCl_3$ under reflux for 4 h (Scheme 4, route E) provides the carbene species *cis*-$[PdCl\{\underline{C}(N{=}C^a(C_6H_4CNH\underline{N}^b)){=}N(H)R^1\}(PPh_3)]^{a-b}$ (**14**–**16**) in 80–85% isolated yields. When 2 equiv of **9** was employed, the reaction proceeds with a similar rate, but the formed complexes **14**–**16** (ca. 80–85%) were contaminated with unreacted **9**, **9**·HCl, and other byproduct (five spots on TLC). The reaction between *cis*-$[PdCl_2(CNXyl)(PPh_3)]$ (**7**) and 1 equiv of **9** in $CHCl_3$ under reflux for 4 h affords a mixture of species (five spots on TLC), which were not separated.

Characterization of Aminocarbene Complexes 10–16. Complexes **10**–**16** were characterized by elemental analyses (C, H, N), ESI^+-MS, IR, and 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC, ^1H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of **10** and **12** were elucidated by X-ray diffraction.

Compounds **10**–**16** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulations of the complexes, while ESI^+-MS of **10**–**16** display molecular ion peaks and/or a fragmentation corresponding to the loss of Cl's from the molecular ion, viz., $[M - nCl]^+$, with the characteristic isotopic distribution.

The examination of the IR spectra of **10** and **14**–**16** revealed no $\nu(C{\equiv}N)$ in the range between 2270 and 2150 cm^{-1}, indicating the complete transformation of the isonitrile species. Meanwhile, the IR spectra of **11**–**13** exhibit one strong $\nu(C{\equiv}N)$ stretching vibration at ca. 2210 cm^{-1}, which is in agreement with the presence of one unreacted isonitrile ligand in this complex [the starting *cis*-$[MCl_2(CNR^1)_2]$ (M = Pd, Pt) complexes usually display two overlapped stretches in the 2250–2150 cm^{-1} interval]. In the formed $C{=}N(H)R^1$ carbene moiety, $\nu(N{-}H)$ bands emerge in the 3211–3052 cm^{-1} range, while the corresponding very strong bands due to $\nu(C{=}N)$ appear between 1545 and 1522 cm^{-1}. The medium/weak-intensity bands in the 2988–2824 cm^{-1} range are characteristic of $\nu_s(C{-}H)$ and $\nu_{as}(C{-}H)$ vibrations, while medium-intensity bands due to δ(C–H from Ar) appear in the interval 778–692 cm^{-1}.

The ^1H NMR spectra of carbenes **10**–**16** display a broad peak in the range δ 8.74–9.79, assigned to the $M{-}C_{carbene}{=}N(H)R^1$ proton, while the corresponding $C_{carbene}{=}NH$ ^{13}C signals, in the $^{13}C\{^1H\}$ NMR spectra of **10**–**16**, were found to resonate in the 175–202 ppm range. These signals are approximately 80–90 ppm downfield shifted in comparison with the starting (isonitrile)M^{II} complexes (e.g., 115 ppm for C≡N in *cis*-$[PdCl_2(CNCy)_2]$) and agree with those previously observed in the related palladium aminocarbene complexes $[PdCl\{\underline{C}(N{=}C^a(C_6R^2R^3R^4R^5CO\underline{N}^b)){=}N(H)R^1\}(CNR^1)]^{a-b}$.[42] Moreover, in the ^1H NMR spectra of **11**–**16** the presence of an additional distinct NH signal—that belongs to the imine group of the unreacted iminoisoindoline moiety—was detected, and this suggests that **11**–**16** in solution are stabilized in the imino form, in contrast to the solid state, where the amino form was identified by X-ray diffraction (see below). The ^1H and ^{13}C signal assignments were performed by interpretation of gradient-enhanced two-dimensional ^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC, and ^1H,^{13}C-HMBC NMR spectroscopy. Thus, the long-range shift correlation experiments via $^2J_{H,C}$ and $^3J_{H,C}$ coupling (^1H,^{13}C-HMBC) allowed the discrimination of the $C_{carbene}$ signal of the newly formed carbene species from the C=N carbon of the imine moiety. The $^{31}P\{^1H\}$ NMR spectra of mixed carbene–phosphine complexes **14**–**16** contain one sharp resonance at ca. 25.0 ppm for the PPh_3 ligand, indicating the presence of a single isomer for each of **14**–**16**.

The crystallographic data and processing parameters for **10** and **12** are summarized in Table 1S (see Supporting Information), while the corresponding molecular structure plots can be found in Figures 2 and 3, and bond lengths and angles are given in the legends of these figures. In the

dx.doi.org/10.1021/om300020j | *Organometallics* 2012, 31, 2379–2387

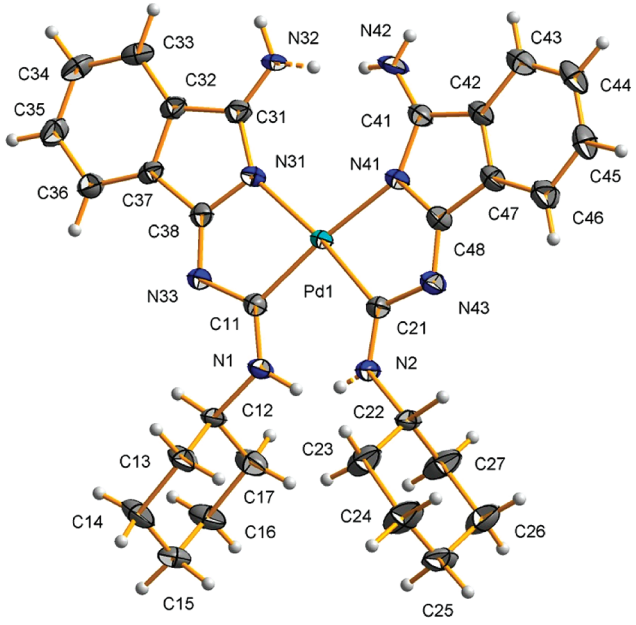


Figure 2. View of **10** with the atomic numbering scheme and with disordered models at the N1, N2, N32, and N42 protons. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pd1−C11 2.001(3), Pd1−C21 2.002(3), Pd1−N31 2.113(2), Pd1−N41 2.112(2), C11−N1 1.298(3), C11−N33 1.414(4), C21−N2 1.288(3), C21−N43 1.411(3), N33−C38 1.292(3), C38−N31 1.386(3), N43−C48 1.305(3), C48−N41 1.370(4), N31−C31 1.363(3), C31−N32 1.268(4), N41−C41 1.372(3), C41−N42 1.276(4), C11−Pd1−N31 78.27(10), C21−Pd1−N41 78.81(9), N2−C21−N43 117.9(2), N1−C11−N33 117.8(2).

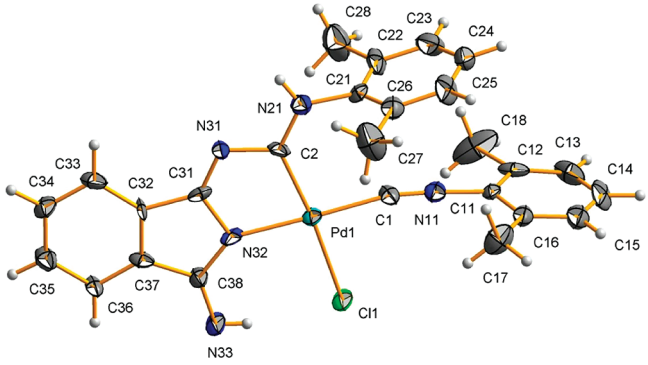


Figure 3. View of one of the two symmetry-independent molecules in **12** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pd1−Cl1 2.403(2), Pd1−C2 2.015(9), Pd1−N32 2.021(9), Pd1−C1 1.961(11), C2−N21 1.293(11), C2−N31 1.434(12), C1−N11 1.138(12), N31−C31 1.287(12), C31−N32 1.403(11), N32−C38 1.354(12), C38−N33 1.315(11), C2−Pd1−N32 79.2(4), Cl1−Pd1−C1 85.4(3), Cl1−Pd1−N32 95.3(2), N21−C2−N31 113.4(8).

asymmetric unit of **12**, there are two symmetry-independent complex molecules, which differ in the PdNCC torsion angles, averaging 173.5° and 162.1° (for Pd1- and Pd2-containing molecules, correspondingly), thus showing that the latter is clearly bent relatively to the former. In addition, the $NC_{carbene}N$ angle in the Pd2 molecule is wider as compared to that of Pd1 [113.4(8)° against 115.0(8)°]. In **10**, the PdNCC torsion and the $NC_{carbene}N$ angles adopt average values of 177.3° and 117.8°, respectively.

In both crystal structures of **10** and **12**, the metal center adopts a distorted square-planar geometry. In **10**, both $C_{carbene}$=N moieties of the two bidentate carbene ligands $\{\underline{C}(N{=}C^{a}(C_6H_4CNH\underline{N}^{b})){=}N(H)R^{1}\}^{a-b}$ are in *cis* position to each other. In the metallacycles formed upon coordination of the bidentate carbene species to the metal center, the angles around the metal [av 78.8°] are similar to those previously observed in the related palladium complexes with chelating carbenes $[PdCl\{\underline{C}(N{=}C^{a}(C_6R^2R^3R^4R^5CO\underline{N}^{b})){=}N(H)Cy\}(CNCy)]^{a-b}$.[42] The carbene ligands are in the *E*-configuration in **10** and in the *Z*-configuration in **12**, and the Pd−$C_{carbene}$ bond distances [av 2.002(3) (**10**) and 2.018(9) (**12**) Å] are similar to those reported for the related palladium carbene complexes $[PdCl\{\underline{C}(N{=}C^{a}(C_6R^2R^3R^4R^5CO\underline{N}^{b})){=}N(H)Cy\}(CNCy)]^{a-b}$ (2.001(3) Å),[42] *cis*-$[PdCl_2\{\underline{C}(OMe){=}N(H)Me\}_2]$ (1.953−1.972 Å),[54] and *cis*-$[PdCl_2\{\underline{C}(=NHCy)NHNH\underline{C}(=NHCy)\}_2]$ (1.958−1.964 Å).[31]

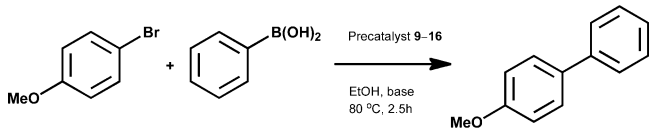
In each MCN_2 fragment, one of the CN bonds has a double-bond character [**10**: C11−N1 1.298(3), C21−N2 1.288(3) Å; **12**: C2−N21 1.293(11), C5−N51 1.308(11) Å], with bond distances in accord with those found in the above-mentioned carbene complexes (1.29−1.33 Å),[27,42] while the other CN bonds have values of a typical single bond [**10**: C11−N33 1.414(4), C21−N43 1.411(3) Å; **12**: C2−N31 1.434(12), C5−N61 1.398(12) Å]. In **10**, two hydrogen bonds were detected, one being intramolecular and involving the disordered proton from the $C_{carbene}$=N(H)R carbene groups [d(N1···N2) 2.654(3), ∠N1···H*n*···N2 142(6)° (n = 1 or 2, see below)] and the other being intermolecular and involving the disordered NH proton of the iminoisoindoline groups [d(N42···N32) 2.711(4), ∠(N42···H*n*B···N32) 172(6)° (n = 32) or 159(7)° (n = 42)]. These hydrogen bonds were observed in the solid state, suggesting the presence of two unsymmetrically protonated carbene ligands. However, in accord with the ^{1}H and $^{13}C\{^{1}H\}$ NMR data, both carbene ligands in **10** are similar in solution, therefore reinforcing the disordered model incorporated in the crystal structure. In **12**, the iminoisoindoline moieties are caught up in both intra- and intermolecular hydrogen bond interactions, the former with the chloride ligand [d(N33···Cl1) 3.160(10) Å, ∠(N33−H33A···Cl1) 166.3°; d(N63···Cl2) 3.187(10) Å, ∠(N63−H63A···Cl2) 162.6°] and the latter with the N carbene atoms [d(N21···N63) 2.930(11) Å, ∠(N21−H21···N63) 163.1°; d(N51···N33) 2.898(12) Å, ∠(N51−H51···N33) 164.1°].

All the other bond lengths in **10** and **12** are of normal values and agree with those reported for related palladium(II) complexes.[27,28,42]

Application of the Prepared Aminocarbene Complexes As Catalysts for Suzuki−Miyaura Cross-Coupling. In recent reports, we[28] and others[26,30,31] have demonstrated that palladium(II) complexes with ADC ligands display high/moderate catalytic activity in Suzuki−Miyaura reaction. In pursuit of the ongoing research in our laboratory on novel efficient and green cross-coupling catalytic systems, we decided to evaluate the catalytic properties of the aminocarbene complexes, prepared in this study, toward that cross-coupling reaction.

As a model system, we have chosen the commonly used reaction of 4-methoxybromobenzene (4-bromoanisole) with phenylboronic acid, accomplishing 4-methoxybiphenyl. Preliminary optimization of the reaction conditions performed as previously reported by us for other Pd−aminocarbene species [ref 28] allowed us to conclude that ethanol could be used as

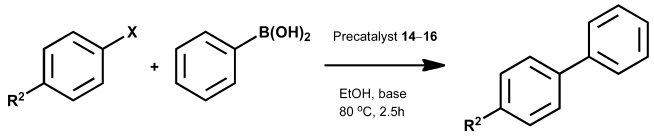
Table 1. Screening of the Catalytic Efficiency for 9−16 in the Suzuki−Miyaura Cross-Coupling System[a]



		yield with the selected base, %	
entry	precatalyst	K_2CO_3	Cs_2CO_3
1		4	4
2	**10**	70	4
3	**11**	63	4
4	**12**	32	4
5	**13**	27	4
6	**14**	77	81
7	**15**	67	84
8	**16**	86	93
9	*cis*-$[PdCl_2(PPh_3)_2]$	8	13

[a]Base (1.5×10^{-4} mol, 1.5 equiv), 4-bromoanisole (1.0×10^{-4} mol, 1 equiv), phenylboronic acid (1.2×10^{-4} mol, 1.2 equiv); precatalysts (**9−16**, 1×10^{-8} mol); EtOH (1 mL).

Table 2. Screening of the Catalytic Efficiency for 9−16 in the Suzuki−Miyaura Cross-Coupling System[a]



		yield with the selected catalyst and base, %					
		14		**15**		**16**	
entry	aryl halide	K_2CO_3	Cs_2CO_3	K_2CO_3	Cs_2CO_3	K_2CO_3	Cs_2CO_3
1	4-$MeOC_6H_4I$	96	62	99	82	99	88
2	4-$MeOC_6H_4Br$	77	81	67	64	86	93
3	4-MeC_6H_4Br	69	50	98	82	93	85
4	4-$NO_2C_6H_4Br$	95	84	99	99	99	93
5	4-$MeOC_6H_4I$	98	24	39	80	58	85
6	4-$MeOC_6H_4Br$	9	9	4	4	53	58
7	4-MeC_6H_4Br	5	4	4	4	69	26
8	4-$NO_2C_6H_4Br$	97	4	40	11	95	77

[a]Base (1.5×10^{-4} mol, 1.5 equiv), aryl halide (1.0×10^{-4} mol, 1 equiv), phenylboronic acid (1.2×10^{-4} mol, 1.2 equiv); precatalysts **14−16** (1×10^{-8} mol) for entries 1−4 and (1×10^{-9} mol) for entries 5−8; EtOH (1 mL).

an appropriate solvent for our catalytic runs. In refluxing EtOH, the conversion of 4-bromoanisole is essentially complete after ca. 2.5 h, furnishing the biaryl product (4-$MeOC_6H_4Ph$) in ca. 86−93% yield (for precatalyst **16**), without visible catalyst decomposition. In addition, K_2CO_3 and Cs_2CO_3 were found to be the most appropriate bases for the studied catalytic system. The efficiencies of all the prepared Pd−aminocarbene complexes (**10−16**) in the Suzuki−Miyaura cross-coupling reaction using the mentioned model coupling reaction were estimated, and the results are summarized in Table 1.

The obtained data clearly demonstrated that the palladium aminocarbene/phosphine species **14−16** are good catalyst precursors (with either K_2CO_3 or Cs_2CO_3 as a base) of the studied reaction, while the other complexes exhibit moderate (**10** or **11**; both with the K_2CO_3 as a base) or low (**12** or **13**) activity. In addition, we also compared the catalytic activity of **14−16** with the commonly used *cis*-$[PdCl_2(PPh_3)_2]$ (Table 1, entry 9) and found that under our experimental conditions the mixed aminocarbene/phosphine species are ca. 10 times more efficient.

For further screening of the catalytic activity, the most promising precatalysts (**14−16**) were used. At the next step, we checked the effect of the substituent of the aryl halide and found that various substituted aryl bromides 4-$R^2C_6H_4Br$ or aryl iodides 4-$R^2C_6H_4I$ react with phenylboronic acid to give excellent yields of biphenyl species, thus showing a valuable versatility of our catalytic system (Table 2). Note, for entries 1−4 (catalyst loading 1×10^{-8} mol), the yields of the products correspond to nearly quantitative conversions of the starting materials, indicating that no side-reactions involving the substrates occur under the described conditions.

Finally, we also examined the effect of catalyst loading in the catalytic system and found that a maximum TON of 5.8×10^4 for the described model reaction (and a maximum TON of 9.8×10^4 with 4-$R^2C_6H_4I$ as a substrate) was obtained even at catalyst loadings as low as 10^{-5} mol per mole of substrate.

Furthermore, it is important to mention that all the catalytic runs were performed in nondried EtOH and in air. When the runs were additionally performed under dinitrogen and in dried EtOH, the obtained results were nearly identical with those

dx.doi.org/10.1021/om300020j | *Organometallics* 2012, 31, 2379−2387

presented in Tables 1 and 2, showing that the system is air/humidity insensitive.

FINAL REMARKS

The results of this work may be considered from at least two perspectives. First, in the course of this study, we have discovered that the metal-mediated coupling between 1,3-diiminoisoindoline and isonitriles in *cis*-$[PdCl_2(CNR^1)_2]$ or *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ opens up a route to palladium complexes containing novel aminocarbene ligands (Schemes 3 and 4). In this reaction, 1,3-diiminoisoindoline behaves as both nucleophile (via the imine NH) and chelator (via the amide HN), affording a bidentate carbene species.

Second, we found that the newly prepared aminocarbene complexes display a high activity in Suzuki−Miyaura cross-coupling of aryl bromides and iodides with phenylboronic acids. In particular, the catalytic systems based on **14**−**16** [which contain one aminocarbene and one phosphine ligand] with an environmentally benign solvent (EtOH) exhibit higher efficiencies in terms of yields/TONs (yields up to 93%, TONs up to 5.8×10^4 with 4-$MeOC_6H_4Br$ as a substrate) than the majority of those reported for acyclic aminocarbenes. Thus, the procedure introduced by Dhudshia and Thadani[26] employs toxic solvents (toluene/THF) and demands high catalyst loading (0.5 mol % based on Pd), while the scheme described by Slaughter and colleagues[30,31] requires a high catalyst loading (1 mol % based on Pd) and a long reaction time (24 h). Furthermore, we believe that a superior catalytic activity of mixed aminocarbene/phosphine complexes (**14**−**16**) as compared to bis-aminocarbene (**10**), mixed aminocarbene/isonitrile (**11**−**13**), and bis-phosphine (i.e., *cis*-$[PdCl_2(PPh_3)_2]$) can be, at least partially, rationalized by a synergetic effect of two catalytically important ligands, viz., aminocarbene and phosphine species in **14**−**16**. Despite the latter, the catalytic system studied in this work exhibits comparable activity with that based on structurally related acyclic aminocarbenes reported recently by some of us [yields up to 88%, with a TON up to 8.8×10^5].[28,55]

Currently, we are seeking novel metal-mediated couplings between other sp^2-N nucleophiles and isonitriles, with a particular emphasis on those mediated by Pd, Pt, and Au metal centers in view of potential catalytic applications of the derived aminocarbene complexes of these metals.

EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents, $PdCl_2$, PPh_3, isonitriles, and all reagents for catalytic studies were obtained from commercial sources and used as received, apart from chloroform and ethanol, which were purified by conventional distillation over calcium chloride and activated magnesium, correspondingly. 1,3-Diiminoisoindoline (**9**)[45] and complexes $[PdCl_2(NCMe)_2]$,[52] *cis*-$[PdCl_2(CNR^1)_2]$ (R^1 = Cy **1**, Bu^t **2**, Xyl **3**),[49−53] and *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ (R = Cy **5**, Bu^t **6**, Xyl **7**)[49−53] were prepared as previously reported. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI^+ mass spectra were obtained on a Varian 500-MS LC ion trap mass spectrometer in MeOH (ion spray voltage: +5 kV, capillary voltage: 30 V, RF loading: 100%). Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^1H, $^{13}C\{^1H\}$, DEPT, and $^{31}P\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC and ^1H,^{13}C-HMBC) NMR spectra were measured on Bruker Avance II+ 500 MHz (UltraShield Plus Magnet) spectrometers at ambient temperature. Supporting Information for this article contains Table 1S (crystallographic parameters for structures **10** and **12**) and a description of additional experiments performed between **1**−**8** and **9** at different conditions.

X-ray Structure Determinations. Single crystals of **10** and **12** were obtained as indicated below. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo Kα (λ 0.71073) radiation. Data were collected at 150 K using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[56] on all the observed reflections. Absorption corrections were applied using SADABS.[57] Structures were solved by direct methods by using the SHELXS-97 package[58] and refined with SHELXL-97.[59] Calculations were performed using the WinGX System, Version 1.80.03.[60] The hydrogen atoms attached to carbon atoms were placed in calculated positions and refined by using a riding model. In both structures the hydrogen atoms bonded to the nitrogen atoms were located from the difference Fourier synthesis and included, in the final refinement, at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. However, in **10** the hydrogen atom bonded to N1 and N2 and that bonded to N32 and N42 were disordered over two positions by using the PART instruction; the occupancies of H1 and H2 refined to a ratio of 49% and 51%, the same occurring for the occupancies of H32B and H42B. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. For **10** and **12**, where disordered molecules in voids were detected, PLATON/SQUEEZE[61] was used to correct the data. Total potential volumes of 574.4 (**10**) and 137.4 (**12**) $Å^3$ were found and 119 (**10**) or 32 (**12**) electrons per unit cell worth of scattering were located in the voids. CCDC-847294 and -847295 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Work. *Preparation of cis-[$PdCl_2(CNCMe_2CH_2CMe_3)_2$] (**4**).* This complex was prepared using a modified procedure previously employed for the preparation of *cis*-$[PdCl_2(CNR^1)_2]$ (R^1 = Cy **1**, Bu^t **2**, Xyl **3**).[49−53] Thus, a solution of 2-isocyano-2,4,4-trimethylpentane (0.557 g, 4.0 mmol) in 5 mL of $CHCl_3$ was slowly (ca. 30 min) added to a suspension of $[PdCl_2(NCMe)_2]$ (0.519 g, 2.0 mmol) in $CHCl_3$ (15 mL) under vigorous stirring. The reaction mixture was kept additionally for 4 h at 20−25 °C and then filtered off to remove some insoluble material. The filtrate was evaporated to dryness under a stream of dinitrogen, producing a colorless precipitate of **4**. It was then washed with two 5 mL portions of Et_2O, two 5 mL portions of iPr_2O, and again two 5 mL portions of Et_2O and dried *in vacuo* at 20−25 °C. Yield is 90% (0.820 g), based on Pd. ^1H NMR (DMSO-d_6, δ): 1.73 (s, 4H, CH_2), 1.56 (m, 12H, Me), 1.05 (s, 18H, Me). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 113.9 (C≡N), 62.8 (CH_2), 51.9 (CMe_2), 31.4 (CMe_3), 30.6 (CMe_2C), 29.8 (CMe_3). IR (KBr, selected bands, cm^{-1}): 2954 m, 2906 mw ν(C−H); 2247 s, 2231 s ν(C≡N); 1478 s δ(C−H in Bu^t); 729 s δ(C−H). ESI^+-MS, *m*/*z*: 455 $[M + H]^+$, 419 $[M - Cl]^+$. Anal. Calcd for $C_{18}H_{34}N_2Cl_2Pd$: C, 47.43; H, 7.52; N, 6.15. Found: C, 47.48; H, 7.45; N, 6.10.

*Reaction of **1** with 1,3-Diiminoisoindoline (**9**).* Solid 1,3-diiminoisoindoline (0.029 g, 0.20 mmol) was added to a solution of *cis*-$[PdCl_2(CNCy)_2]$ (0.040 g, 0.10 mmol) in $CHCl_3$ (10 mL), and the reaction mixture was refluxed for 4 h. During this period, the color of the mixture gradually turned from light yellow to orange followed by precipitation of a yellowish-orange solid. After 4 h, the reaction mixture was filtered off, and the precipitate was washed with two 5-mL portions of cold (5 °C) $CHCl_3$ and with five 5 mL portions of Et_2O and then dried *in vacuo* at 20−25 °C. Yield of **10** was 82% (0.050 g), based on Pd.

Complex 10. ^1H NMR (DMSO-d_6, δ): 8.28, 8.23 (s, br, 2H, C═NH), 8.11 (s, br, 2H, C_{carb}═NH), 7.96−7.71 (m, 8H, aryls), 4.54 (m, 2H, C*H*-Cy), 1.79−1.42 (m, 20H, CH_2-Cy). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 197.3 (C_{carb}═N), 176.3, 168.9 (C═NH), 136.2, 134.6, 133.1, 132.2, 123.8, 122.1 (aryls), 54.6 (CH-Cy), 31.5, 30.7, 24.6 (CH_2−-Cy).

dx.doi.org/10.1021/om300020j | *Organometallics* 2012, 31, 2379−2387

IR (KBr, selected bands, cm^{-1}): 3204 w ν(N−H); 2931 s, 2854 m ν(C−H); 1686 w, 1618 mw ν(C═N); 1545 s ν(N−C_{carb}); 1437 s δ(C−H from Cy); 1116 m, 1040 m ν(C═C); 776 mw, 708 s δ(C−H from aryl). ESI^+-MS, m/z: 613 $[M + H]^+$. Anal. Calcd for $C_{30}H_{34}N_8Pd$: C, 58.77; H, 5.59; N, 18.28. Found: C, 58.70; H, 5.52; N, 17.99.

*Reactions of **2**−**4** and 1,3-Diiminoisoindoline (**9**).* Solid 1,3-diiminoisoindoline (0.029 g, 0.20 mmol) was added to a solution of *cis*-$[PdCl_2(CNR^1)_2]$ (0.20 mmol) in $CHCl_3$ (10 mL), and the reaction mixture was refluxed for 4 h. During this period, the color of the mixture gradually turned from light yellow to yellowish-orange. After 4 h, the reaction mixture was evaporated to dryness, and the solid residue was extracted with five 5 mL portions of CH_2Cl_2. The extracts were combined as a yellow-orange solution, which was evaporated to dryness, and the residue was washed with two 5 mL portions of cold (5 °C) Et_2O and with five 5 mL portions of iPr_2O and then dried *in vacuo* at 20−25 °C. Yields of **11**−**13** were 78−84%, based on Pd.

Complex 11. Yield: 78%. ^1H NMR ($CDCl_3$, δ): 10.19 (s, 1H, C═NH), 9.13 (w, 1H, C_{carb}═NH), 7.85−7.61 (m, 4H, aryls), 1.74−1.54 (m, 18H, Me). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 182.2 (C_{carb}═N), 181.2 and 170.5 (C═NH), 135.4, 134.9, 134.6, 133.3, 125.7, and 122.7 (aryls), 59.9 and 59.1 (CMe_3), 29.2, 29.4, 27.6, and 24.3 (CMe_3). IR (KBr, selected bands, cm^{-1}): 3211 w ν(N−H); 2988 mw, 2924 m ν(C−H); 2202 m ν(C≡N); 1654 mw, 1618 mw ν(C═N); 1542 s ν(N−C_{carb}); 1440 s δ(C−H from Bu^t); 1116 m, 1133 s ν(C═C); 768 m, 707 s δ(C−H from aryl). ESI^+-MS, m/z: 452 $[M + H]^+$. Anal. Calcd for $C_{18}H_{24}N_5ClPd$: C, 47.80; H, 5.35; N, 15.48. Found: C, 47.58; H, 5.42; N, 15.49.

Complex 12. Yield: 84%. ^1H NMR ($CDCl_3$, δ): 9.48 (s, 1H, C═NH), 9.13 (w, 1H, C_{carb}═NH), 7.82−7.60 (m, 4H, aryls) and 7.52−7.28 (m, 6H, aryls), 2.12 (s, 6H) and 2.04 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 175.8 (C_{carb}═N), 171.5 and 168.2 (C═NH), 150.6, 135.5, 134.2, 133.4, 133.3, 132.9, 132.3, 131.4, 129.0, 127.5, 127.1, 126.0, 123.9, and 123.7 (aryls), 18.7 and 17.6 (Me). IR (KBr, selected bands, cm^{-1}): 3223 w ν(N−H); 2982 mw, 2928 m ν(C−H); 2192 m ν(C≡N); 1642 mw, 1606 mw ν(C═N); 1546 s ν(N−C_{carb}); 1122 m, 1123 s ν(C═C); 768 m, 707 s δ(C−H from aryl). ESI^+-MS, m/z: 512 $[M - Cl]^+$. Anal. Calcd for $C_{26}H_{24}N_5ClPd$: C, 56.95; H, 4.41; N, 12.77. Found: C, 56.92; H, 4.42; N, 12.49.

Complex 13. Yield: 79%. ^1H NMR (DMSO-d_6, δ): 9.93 (s, br, 2H, C═NH), 8.76 (s, br, 2H, C_{carb}═NH), 7.85−7.61 (s, 8H, aryls), 1.94 (s, 4H, CH_2), 1.94 (s, 6H), 1.62 (s, 6H), 1.03 (s, 18H, Me from $C(Me_2)CH_2CMe_3$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 197.0 (C_{carb}═N), 176.6, 171.0 (C═NH), 134.6, 132.3, 125.1 (aryls), 63.3 (CMe_2CH_2), 53.0 (CH_2), 33.0 (CMe_3), 31.8 and 29.9 (CMe_3 and CMe_2CH_2). IR (KBr, selected bands, cm^{-1}): 3186 w br ν(N−H); 2951 m br, ν(C−H); 1686 s ν(C═N); 1535 s ν(N−C_{carb}); 1431 s br δ(N−H); 1133 s, 1087 s ν(C═C); 777 m, 712 s δ(C−H from aryl). ESI^+-MS, m/z: 564 $[M]^+$. Anal. Calcd for $C_{26}H_{40}N_5ClPd$: C, 55.32; H, 7.14; N, 12.41. Found: C, 55.73; H, 7.04; N, 12.32.

*Preparation of cis-[$PdCl_2$(C≡$NCMe_2CH_2CMe_3$)(PPh_3)] (**8**).* This complex was prepared using a modified procedure previously employed for the preparation of *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ (R = Cy **5**, Bu^t **6**).[49−53] Thus, a solution of PPh_3 (0.262 g, 1.0 mmol) in Et_2O (2 mL) was added to solution of *cis*-$[PdCl_2(CNCMe_2CH_2CMe_3)_2]$ in $CHCl_3$ (10 mL). The reaction mixture was refluxed for 1 h and then filtered off to remove some insoluble material. The filtrate was evaporated to dryness under a stream of dinitrogen, producing a colorless precipitate of **6**. It was washed with two 5 mL portions of Et_2O, two 5 mL portions of iPr_2O, and again two 5 mL portions of Et_2O and dried *in vacuo* at 20−25 °C. Yield is 87%, based on Pd. ^1H NMR (DMSO-d_6, δ): 7.69−7.53 (m, 15H aryls); 1.32 (s, 2H, CH_3), 1.12 (s, 6H, CH_3), 0.86 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 133.9−129.1 (aryls), 62.0 (CMe_2CH_2), 51.6 (CH_2), 31.2 (CMe_3), 30.4 and 29.2 (CMe_2CH_2 and CMe_3). $^{31}P\{^1H\}$ NMR (DMSO-d_6, δ): 23.0. IR (KBr, selected bands, cm^{-1}): 2948 mw, 2905 w ν(C−H); 2228 s ν(C≡N); 1481 m δ(C−H); 1412 s δ(C−P); 749 s δ(C−H). ESI^+-MS, m/z: 578 $[M + H]^+$, 542 $[M - Cl]^+$. Anal. Calcd for $C_{27}H_{32}NCl_2PPd$: C, 56.02; H, 5.57; N, 2.42. Found: C, 56.18; H, 5.45; N, 2.30.

*Reactions of **5**, **6**, and **8** with 1,3-Diiminoisoindoline (**9**).* Solid 1,3-diiminoisoindoline (0.029 g, 0.20 mmol) was added to a solution of *cis*-$[PdCl_2(CNR^1)(PPh_3)]$ (0.20 mmol) in $CHCl_3$ (10 mL), and the reaction mixture was refluxed for 4 h. During this period, the color of the mixture gradually turned from light yellow to orange. The reaction mixture was then filtered off to remove some insoluble material, the filtrate was evaporated to dryness, and the product was extracted with three 5 mL portions of $CHCl_3$. The bright yellow solution was evaporated at room temperature to dryness under a stream of N_2, washed with five 5 mL portions of Pr^i_2O, one 1 mL portion of cold (5 °C) Et_2O, and again five 5 mL portions of Pr^i_2O, and then dried *in vacuo* at 20−25 °C. Yields of **14**−**16** were 75−84%, based on Pd. In the case of R^1 = Xyl (**7**), no isolable product was formed.

Complex 14. Yield: 84%. ^1H NMR ($CDCl_3$, δ): 10.46 (s, 1H, C═NH), 9.22 (s, 1H, C_{carb}═NH), 7.86−7.42 (m, 19H, aryls), 4.38 (s, 1H, C*H*-Cy), 1.90−1.42 (m, 10H, CH_2-Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 197.4 (C_{carb}═N) 183.1, 171.0 (C═NH), 135.4−125.0 (aryls), 55.8 (*C*H-Cy), 32.0, 24.9, 24.3 (CH_2−Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 23.3. IR (KBr, selected bands, cm^{-1}): 3054 w ν(N−H); 2930 m, 2853 m ν(C−H); 1686 w ν(C═N); 1544 s, 1527 s ν(N−C_{carb}); 1435 s δ(N−H); 1410 s ν(C−P); 1153 w, 1038 m ν(C═C); 778 w, 707 s δ(C−H). ESI^+-MS, m/z: 657 $[M]^+$. Anal. Calcd for $C_{33}H_{32}N_4ClPPd$: C, 60.28; H, 4.91; N, 8.52. Found: C, 59.74; H, 4.70; N, 8.47.

Complex 15. Yield: 76%. ^1H NMR ($CDCl_3$, δ): 10.83 (s, br, 1H, C═NH), 9.29 (s, br, 1H, C_{carb}═NH), 7.90−7.57 (s, 19H, aryls), 1.62−1.49 (m, 9H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 200.6 (C_{carb}═N) 176.1 (C═NH), 134.2−123.6 (aryls), 58.0 (CMe_3), 29.0, 28.7, 28.3 (CMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 24.3. IR (KBr, selected bands, cm^{-1}): 3052 w ν(N−H); 2972, 2932 w ν(C−H); 2226 w ν(C≡N); 1686 mw ν(C═N); 1541 s ν(N−C_{carb}); 1425 s ν(C−P); 1133 mw, 1041 w ν(C═C); 778 w, 708 s δ(C−H). ESI^+-MS, m/z: 631 $[M]^+$. Anal. Calcd for $C_{31}H_{30}N_4ClPPd$: C, 58.97; H, 4.79; N, 8.87. Found: C, 58.37; H, 4.70; N, 8.92.

Complex 16. Yield: 75%. ^1H NMR ($CDCl_3$, δ): 10.85 (s, 1H, C═NH), 8.23 (s, 1H, C_{carb}═NH), 7.78−7.52 (m, 19H, aryls), 1.62 (s, 2H, CH_2), 1.50 (s, 6H), 1.45 (s, 3H) and 1.10 (m, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 195.8 (C_{carb}═N) 176.5 (C═NH), 134.8−124.2 (aryls), 65.4 (CMe_2CH_2), 51.4 (CH_2), 31.9 (CH_2CMe_3), 15.6 and 14.3 (CMe_2CH_2 and CMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 24.5. IR (KBr, selected bands, cm^{-1}): 3057 w ν(N−H); 2960 w, ν(C−H); 1663 s ν(C═N); 1522 m ν(N−C_{carb}); 1436 s δ(C−H from Cy); 1420 m ν(C−P); 1133 mw, 1023 w ν(C═C); 750 mw, 692 s δ(C−H from aryl). ESI^+-MS, m/z: 687 $[M + H]^+$. Anal. Calcd for $C_{35}H_{38}N_4ClPPd$: C, 61.14; H, 5.57; N, 8.15. Found: C, 61.54; H, 5.58; N, 8.10.

General Procedure for the Catalytic Suzuki−Miyaura Cross-Coupling (specific conditions are provided in Tables 1 and 2). Selected base (1.5×10^{-4} mol, 1.5 equiv), aryl bromide (1.0×10^{-4} mol, 1.0 equiv) and phenylboronic acid (1.2×10^{-4} mol, 1.2 equiv) were mixed in a 5 mL Schlenk tube connected to a reflux condenser open to air. A solution of the precatalyst (1×10^{-8} mol) in nondried EtOH (1 mL) was then added. For the tests under anaerobic reactions, anhydrous EtOH was used, and the Schlenk tube was then connected to a reflux condenser bearing a take-off with a connected dinitrogen balloon. The Schlenk tube was placed in a preheated oil bath at 80 °C, stirred for 2.5 h, and then cooled to 25 °C. The reaction mixture was evaporated to dryness under a stream of dinitrogen followed by addition of 1.0 equiv of 1,2-dimethoxyethane (NMR internal standard) and extraction of the reaction mixture with three 0.20 mL portions of $CDCl_3$. All fractions were combined and subjected to ^1H NMR monitoring. The product peak assignments were based on authentic samples or on published data,[13,25,26,30,31,62] while quantifications were performed upon integration of the selected peak of the product relative to the peak of the standard. In some cases, the products were isolated by extraction of the residue after evaporation of the reaction mixture with CH_2Cl_2, followed by column chromatography on silica gel (Fluka 40/60; 10:1 hexane/ethyl acetate, v/v).

dx.doi.org/10.1021/om300020j | *Organometallics* 2012, 31, 2379−2387

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kluzyanin@ist.utl.pt; pombeiro@ist.utl.pt.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (including FCT projects PTDC/QUI-QUI/098760/2008, PTDC/QUI-QUI/109846/2009, and PEst-OE/QUI/UI0100/2011), as well as Federal Targeted Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009−2013" (contract P676 from 20/05/2010), Russian Fund of Basic Research (grants 12-03-00076 and 11-03-12044), and Saint-Petersburg State University for a research grant (2011−2013). K.V.L. expresses gratitude to the FCT and the Instituto Superior Técnico (IST) for a research contract (Ciência 2008 program), and R.S.C. to the FCT for a research grant (within FCT project PTDC/QUI-QUI/098760/2008). The authors thank the Portuguese NMR Network (IST-UTL Center) for providing access to the NMR facilities and the Portuguese MS Network (IST Node) for the ESI-MS measurements.

■ REFERENCES

(1) Vignolle, J.; Catton, X.; Bourissou, D. *Chem. Rev.* **2009**, *109*, 3333−3384.
(2) Michelin, R. A.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75−112.
(3) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121−1123.
(4) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.
(5) Arnold, P.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596−609.
(6) Glorius, F. *Top. Organomet. Chem.* **2007**, *21*, 1−20.
(7) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676.
(8) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172.
(9) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Fehlhammer, W. P. *Chem.—Eur. J.* **2003**, *9*, 704−712.
(10) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Van, D. L. *Angew. Chem., Int. Ed.* **2005**, 3759−3763.
(11) Hahn, F. E.; Langenhahn, V.; Pape, T. *Chem. Commun.* **2005**, 5390−5392.
(12) Hahn, F. E.; Plumed, C. G.; Münder, M.; Lügger, T. *Chem.—Eur. J.* **2004**, *10*, 6285−6293.
(13) Rosen, E. L.; Sanderson, M. D.; Saravanakumar, S.; Bielawski, C. W. *Organometallics* **2007**, *26*, 5774−5777.
(14) Frey, G. D.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 2465−2478.
(15) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235−248.
(16) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219−224.
(17) Frey, G. D.; Herrmann, W. A. *J. Organomet. Chem.* **2005**, *690*, 5876−5880.
(18) Wanniarachchi, Y. A.; Kogiso, Yu.; Slaughter, L. M. *Organometallics* **2008**, *27*, 21−24.
(19) Wanniarachchi, Y. A.; Slaughter, L. M. *Organometallics* **2008**, *27*, 1055−1062.
(20) Wanniarachchi, Y. A.; Subramanium, S. S.; Slaughter, L. M. *J. Organomet. Chem.* **2009**, *694*, 3297−3305.
(21) Rosen, E. L.; Sung, D. H.; Chen, Z.; Lynch, V.; Bielawski, C. W. *Organometallics* **2010**, *29*, 250−256.
(22) Ruiz, J.; Perandondes, B. F. *Organometallics* **2009**, *28*, 830−836.
(23) Collins, M. S.; Rosen, E. L.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2010**, *29*, 3047−3053.
(24) Droge, T.; Wanniarachchi, Y. A.; Slaughter, L. M. *Chem. Commun.* **2007**, 3294−3296.
(25) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Furstner, A. *Chem.—Eur. J.* **2005**, *11*, 1833−1853.
(26) Dhudshia, B.; Thadani, A. N. *Chem. Commun.* **2006**, *6*, 668−670.
(27) Tskhovrebov, A. G.; Luzyanin, K. V.; Kuznetsov, M. L.; Sorokoumov, V. N.; Balova, I. A.; Haukka, M.; Kukushkin, V. Yu. *Organometallics* **2011**, *30*, 863−874.
(28) Luzyanin, K. V.; Tskhovrebov, A. G.; Carias, M. C.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Organometallics* **2009**, *28*, 6559−6566.
(29) Slaughter, L. M. *Comm. Inorg. Chem.* **2008**, *29*, 46−72.
(30) Moncada, A. I.; Khanb, M. A.; Slaughter, L. M. *Tetrahedron Lett.* **2005**, *46*, 1399−1403.
(31) Moncada, A. I.; Manne, S.; Tanski, J. M.; Slaughter, L. M. *Organometallics* **2006**, *25*, 491−505.
(32) Bartolomé, C.; Ramiro, Z.; Pérez-Galán, P.; Bour, C.; Raducan, M.; Echavarren, A. M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 11391−11397.
(33) Bartolomé, C.; Ramiro, Z.; García-Cuadrado, D.; Pérez-Galán, P.; Raducan, M.; Bour, C.; Echavarren, A. M.; Espinet, P. *Organometallics* **2010**, *29*, 951−956.
(34) Bartolomé, C.; García-Cuadrado, D.; Ramiro, Z.; Espinet, P. *Organometallics* **2010**, *29*, 3589−3592.
(35) Bartolomé, C.; García-Cuadrado, D.; Ramiro, Z.; Espinet, P. *Inorg. Chem.* **2010**, *49*, 9758−9764.
(36) Hashmi, A. S. K.; Hengst, T.; Lothschütz, C.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 1315−1337.
(37) Seo, H.; Roberts, B. P.; Abboud, K. A.; Merz, K. A. Jr.; Hong, S. *Org. Lett.* **2010**, *12*, 4860−4863.
(38) Seo, H.; Snead, D. R.; Abboud, K. A.; Hong, S. *Organometallics* **2011**, *30*, 5725−5730.
(39) Hashmi, A. S. K.; Haffner, T.; Rudolph, M.; Rominger, F. *Eur. J. Org. Chem.* **2011**, 667−671.
(40) Hashmi, A. S. K.; Haffner, T.; Rudolph, M.; Rominger, F. *Chem.—Eur. J.* **2011**, *17*, 8195−8201.
(41) Handa, S.; Slaughter, L. M. *Angew. Chem., Int. Ed.* **2012**, in press (DOI: 10.1002/anie.201107789).
(42) Luzyanin, K. V.; Pombeiro, A. J. L.; Haukka, M.; Kukushkin, V. Yu. *Organometallics* **2008**, *27*, 5379−5389.
(43) Luzyanin, K. V.; Guedes da Silva, M. F. C.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2009**, *362*, 833−838.
(44) Luzyanin, K. V.; Tskhovrebov, A. G.; Guedes da Silva, M. F. C.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Chem.−Eur. J* **2009**, *15*, 5969−5978.
(45) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1952**, 5000−5007.
(46) Zhang, Zh.-Q.; Njus, J. M.; Sandman, D. J.; Guo, C.; Foxman, B. M.; Erk, P.; van Gelder, R. *Chem. Commun.* **2004**, 886−887.
(47) Lyubimtsev, A. V.; Barański, A.; Isayaikin, M. K.; Smirnov, R. P. *Chem. Heterocycl. Cmpd.* **1997**, *33*, 937−941.
(48) Acker, A.; Hofmann, H.-J.; Cimiraglia, R. *J. Mol. Struct. (THEOCHEM)* **1994**, *315*, 43−51.
(49) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809−2815.
(50) Bertani, R.; Mozzon, M.; Michelin, R. A.; Benetollo, F.; Bombieri, G.; Castilho, T. J.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1991**, *189*, 175−187.
(51) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251−256.
(52) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85−92.

(53) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021−2025.
(54) Domiano, P.; Musatti, A.; Nardelli, M.; Predieri, G. *J. Chem. Soc., Dalton Trans.* **1975**, 2165−2168.
(55) Chay, R. S.; Luzyanin, K. V. *Inorg. Chim. Acta* **2012**, *380*, 322−327.
(56) *Bruker APEX2* & *SAINT*; Bruker, AXS Inc.: Madison, WI, USA, 2004.
(57) Sheldrick, G. M. *SADABS, Bruker Nonius scaling and absorption correction*, v 2.10; Bruker AXS, Inc.: Madison, WI, USA, 2003.
(58) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.
(59) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
(60) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(61) Spek, A. L. PLATON/SQUEEZE, An effective tool for taking the contribution of disordered solvent into account in crystal structure refinement In *Bijvoet Center for Biomolecular Research*; Utrecht University: Padualaan 8, 3584 CH Utrecht, The Netherlands, 2005.
(62) Moncada, A. I.; Tanski, J. M.; Slaughter, L. M. *J. Organomet. Chem.* **2005**, *690*, 6247−6251.