ORGANOMETALLICS
Article

Organometallics **2011,** *30,* 863–874 863
DOI: 10.1021/om101041g

Substituent R-Dependent Regioselectivity Switch in Nucleophilic Addition of *N*-Phenylbenzamidine to Pd^{II}- and Pt^{II}-Complexed Isonitrile RN≡C Giving Aminocarbene-Like Species

Alexander G. Tskhovrebov,[†] Konstantin V. Luzyanin,[†,‡] Maxim L. Kuznetsov,[‡] Viktor N. Sorokoumov,[†] Irina A. Balova,[†] Matti Haukka,[§] and Vadim Yu. Kukushkin*[,†,⊥]

[†]*St. Petersburg State University, Universitetskii Pr. 26, 198504 Stary Petergof, Russian Federation,* [‡]*Centro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049−001 Lisbon, Portugal,* [§]*Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101, Joensuu, Finland, and* [⊥]*Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoii Pr. 31, 199004 St. Petersburg, Russian Federation*

Received November 4, 2010

Metal-mediated coupling between one or two isonitrile ligands in *cis*-[$MCl_2(C{\equiv}NR)_2$] [M = Pd, Pt; *R* = 2,6-$Me_2C_6H_3$ (Xyl), Bu^t, cyclohexyl (Cy)] and *N*-phenylbenzamidine, HN=C(Ph)NHPh, proceeds with different regioselectivity upon varying R group. When the aromatic isonitrile is used (R = Xyl), *N*-phenylbenzamidine is coordinated to a metal by the HN=C moiety, and the nucleophilic attack proceeds via the NHPh center of the benzamidine giving [MCl{*C*(N(Ph)C(Ph)=*N*H)=NXyl}(C≡NXyl)]. For R = Bu^t, HN=C(Ph)NHPh is coordinated to a metal by the NHPh center, and the addition occurs via the HN=C center of the nucleophile to afford [MCl{*C*(NC(Ph)=*N*Ph)=NBu^t}(C≡NBu^t)]. With R = Cy, a mixture of two products that are derived from the addition of *N*-phenylbenzamidine by two nucleophilic centers was detected. The substituent *R* dependent reactivity was explored using theoretical (DFT) methods and interpreted as a result of the steric repulsions in one of the regioisomers of the addition products, when R = Cy and Bu^t. All prepared species were fully characterized by elemental analyzes (C, H, N), high resolution ESI^+−MS, IR, 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC, ^1H,^{13}C-HMBC) NMR spectroscopies, and by X-ray diffraction for four complexes. The latter studies indicate that in the case of XylNC, the corresponding carbene species possess distinct consequence of double and single bonds in the MCN_2 fragment and, therefore, belong to a novel family of *aminocarbene-like ligands*, while in the case of Bu^tNC, the carbene ligand is of the *classical* diaminocarbene type with bond delocalization in the MCN_2 functionality. The catalytic properties of systems based on two representative species, *i.e.*, [PdCl{*C*(N(Ph)C(Ph)=*N*H)=NXyl}(C≡NXyl)] (**10**) and [PdCl{*C*(NC(Ph)=NPh)=N(H)Bu^t}(C≡NBu^t)] (**16**)—that are derived from the addition of HN=C(Ph)NHPh to a Pd^{II}-bound isonitrile by its different nucleophilic centers — in Sonogashira cross-coupling of 4-$NO_2C_6H_4I$ with oct-1-yne (in EtOH as a solvent, K_2CO_3 as a base, 60 °C) yielding 1-nitro-2-(oct-1-ynyl)benzene, were evaluated indicating that the system involving **16** exhibit slightly higher catalytic efficiency (yields up to 99%, TONs up to 2000; TOFs up to 280) as compared to the system based on **10** (yields up to 99%, TONs up to 1400; TOFs up to 120). Moreover, catalytic activities of both systems are substantially higher than the conventional one based on [$PdCl_2(PPh_3)_2$] (yield 40%, TON 400; TOF 22). We also employed **16** for the synthesis of 1-(dodeca-1,3-diyn-1-yl)-2-nitrobenzene from 1-iodo-2-nitrobenzene and dodeca-1,3-diyne (in EtOH as a solvent, K_2CO_3 as a base, 50 °C), and found that aminocarbene complex **16** is significantly more efficient precatalysts for Sonogashira reaction with diynes [as compared to the previously used $Pd(OAc)_2$] providing 1-(dodeca-1,3-diynyl)-2-nitrobenzene in 97% yield with TON up to 1400.

Introduction

Metal complexes with *N*-heterocyclic carbenes (heterocyclic aminocarbenes or NHCs, Scheme 1A) are widely employed in catalysis of various organic transformations as a powerful alternative to the commonly used phosphine complexes.[1−3] However, NHCs possess certain disadvantages mostly regarding to the fact that the preparation of the vast majority of these species (and/or their precursors) for the further

*Corresponding author. kukushkin@VK2100.spb.edu.

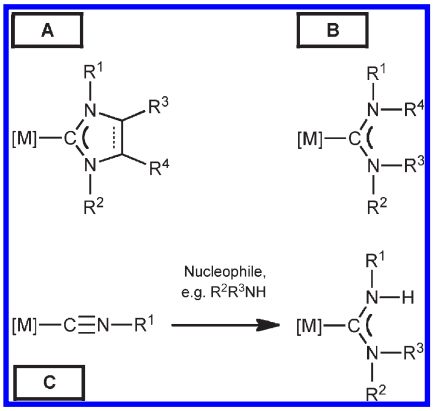
(1) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172.

(2) Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862–892.

(3) Herrmann, W. A.; Elison, M.; Fischer, J.; Koecher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371–2374.

Published on Web 01/28/2011

Scheme 1. Examples of Metal Complexes with NHCs (A) and Acyclic Aminocarbenes (B) and Preparation of Acyclic Aminocarbene Complexes *via* a Metal-Mediated Nucleophilic Addition to Isonitriles (C)



coordination to metals represents a harsh synthetic task.[4−6] In particular, when the target NHC species are unsymmetrically substituted,[7] preparative difficulties limit the possibilities for the precise tuning of the steric properties for these ligands, as it may be performed for the phosphines. In addition, despite the fact that NHC ligands are able to exhibit donor abilities comparable to phosphines,[8−12] rational tuning of prepared metallocarbenes toward selected catalytic application, is mostly achieved via the empiric variation of the carbene structure. The latter may be justified by the complexity and insufficient knowledge of mechanisms (the so-called "black-box" character) of cross-coupling processes. Hence, a continuous search for novel carbene-based species and optimization of their properties toward selected catalytic applications is an important task.

Surprisingly, *acyclic* aminocarbene species, structurally related to *cyclic* NHCs, (Scheme 1B) have not yet attracted the same attention in the catalysis despite their very long history.[13] It is important to point out that acyclic aminocarbenes possess similar electronic stabilization as nonaromatic NHCs, but their wider range of net electron-donor properties and steric flexibility as compared to NHCs allow greater control of both donor and steric properties.[14−17] In addition, complexes with acyclic aminocarbene ligands can be prepared via an efficient reaction based on a metal-mediated nucleophilic addition to isonitriles (Scheme 1C).[18,19]

As far as the generation of acyclic aminocarbene metal species is concerned, most of the known protocols are based on the addition of monofunctional (amines, alcohols) or bifunctional (hydrazines, diamines, or amidines) nucleophiles to RNC ligands (see Results and Discussion).[19] However, addition of unsymmetrical bifunctional nucleophiles, i.e. containing two distinct nucleophilic centers in one molecule, to coordinated isonitriles providing two regioisomers was never previously reported. It is important that the coupling with such nucleophiles, *e.g.*, unsymmetrically substituted amidines, may proceed via different routes affording structurally different products (Scheme 2; the chelates are conditionally represented in the classical diaminocarbene form with bond delocalization in the MCN_2 fragment).

In order to obtain the first example of regioselectivity in the addition to metal-activated isonitriles, we decided to employ the unsymmetrical amidine, *viz*., *N*-phenylbenzamidine, for the coupling with both aromatic and aliphatic isonitriles ligated to palladium- and platinum centers. Our goals were 3-fold: (*i*) to study the regioselectivity of the coupling between Pd^{II} and Pt^{II}-bound isonitriles and *N*-phenylbenzamidine and to understand factors affecting the coupling and its regioselectivity at both experimental and theoretical levels, (*ii*) to verify structural features of thus prepared aminocarbene species, and (*iii*) to evaluate the catalytic properties of the aminocarbenes in Sonogashira cross-coupling and to compare catalytic efficiencies for complexes derived from the addition of *N*-phenylbenzamidine by its different nucleophilic sites. Our results are consecutively uncovered in this article.

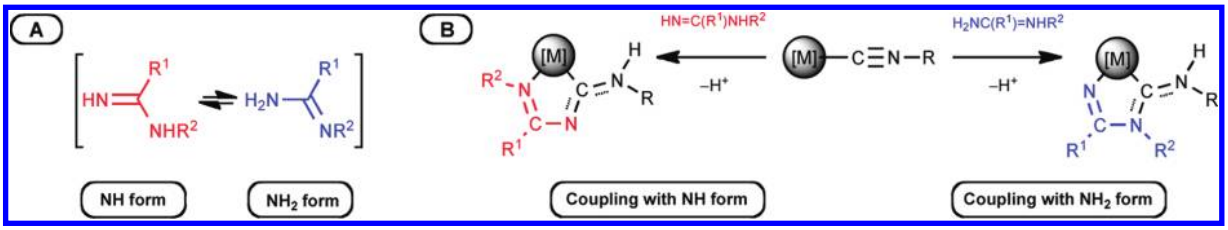
Results and Discussions

The predominate part of reports on generation of acyclic aminocarbene metal species via nucleophilic addition to metal-activated isonitriles deal with the coupling of RNC ligands and nucleophiles containing one or two equal sp^3-N- or O-donor centers, *viz*. amines/hydrazines and alcohols, resulting in diaminocarbene $C(NR^1R^2)N(H)R$ and oxyaminocarbene $C(OR^1)N(H)R$ ligands, correspondingly.[18,19] Recently, we also provided examples for the addition of sp^2-N nucleophiles such as acyclic (benzophenone imine[20]) and heterocyclic (3-iminoisoindolin-1-one[21]) imines, and also nucleophiles having an intermediate sp^3/sp^2-N hybridization of the N donor site (hydrazones[22]) affording novel aminocarbene-like complexes.

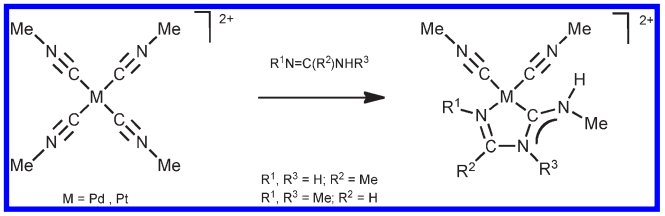
Regarding to addition of amidines to metal-bound isonitriles, the known reactions of $[M(CNMe)_4]^{2+}$ (M = Pd^{II}, Pt^{II}) species with *symmetrical* amidines (such as acetamidine or *N*,*N*′-dimethylformamidine) allows the generation of the chelating aminocarbene ligands (Scheme 3).[23] Note, despite the fact that amidines given in Scheme 3 are shown as

(4) Glorius, F. *Top. Organomet. Chem.* **2007**, *21*, 1–20.
(5) Marion, N.; Nolan, S. P., *Acc. Chem. Res.* **2008**, *41*, 1440−1449, and references therein.
(6) Peris, E. *Top. Organomet. Chem.* **2007**, *21*, 83–116.
(7) Furstner, A.; Alcarazo, M.; Cesar, V.; Lehmann, C. W. *Chem. Commun* **2006**, 2176–2178.
(8) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461–2468.
(9) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437–2448.
(10) Kelly, R. A., III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202–210.
(11) Diéz-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874–883.
(12) Tolman, C. A. *Chem. Rev.* **1977**, 313–348.
(13) Tschugajeff(Chugaev), L.; Skanawy-Grigorjewa, M. *J. Russ. Chem. Soc.* **1915**, *47*, 776.
(14) Rosen, E. L.; Sanderson, M. D.; Saravanakumar, S.; Bielawski, C. W. *Organometallics* **2007**, *26*, 5774–5777.
(15) Frey, G. D.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 2465–2478.
(16) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235–248.
(17) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219–224.
(18) Vignolle, J.; Catton, X.; Bourissou, D. *Chem. Rev.* **2009**, *109*, 3333–3384.
(19) Michelin, R. A.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75–112.
(20) Luzyanin, K. V.; Guedes da Silva, M. F. C.; Kukushkin, V. Y.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2009**, *362*, 833–888.
(21) Luzyanin, K. V.; Pombeiro, A. J. L.; Haukka, M.; Kukushkin, V. Y. *Organometallics* **2008**, *27*, 5379–5389.
(22) Luzyanin, K. V.; Tskhovrebov, A. G.; Carias, M. C.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Kukushkin, V. Y. *Organometallics* **2009**, *28*, 6559–6566.
(23) Balch, A. L.; Parks, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 4114–4121.

Scheme 2. Routes for the Regioselective Addition of the Unsymmetrically Disubstituted Amidines to Metal-Bound Isonitriles



Scheme 3. Reported Examples for the Coupling between Isonitrile Ligands and Amidines



unsymmetrical species, two N centers are symmetric due to the tautomeric effect (see later). In addition, structural features of the product were not verified[23] and it conditionally represented in Scheme 3 as the classical aminocarbene with the bond delocalization in the CN_2 fragment.

For our study we addressed, on one hand, the known palladium(II) and platinum(II) isonitrile complexes *cis*-[$MCl_2(C{\equiv}NR)_2$] [M = Pd, R = $C_6H_3(2,6\text{-}Me_2)$ (Xyl) (**1**), Bu^t (**2**), cyclohexyl (Cy) (**3**); M = Pt, R = Xyl (**4**), Bu^t (**5**), Cy (**6**)][24−29] and, on the other hand, usymmetrical monosubstituted amidine containing aromatic substituents, *viz*., *N*-phenylbenzamidine (**7**) [HN=C(Ph)NHPh, IUPAC name:[30] *N*-phenylbenzimidamide], previously employed for metal-mediated coupling with nitrile ligands.[31,32] The latter species represents an easily accessible solid amidine, which can be handled as a stable free base, whereas most of amidines are only available as amidinium salts.

It is well-documented that amidines exist in a tautomeric equilibrium in solution, which is believed to be an intramolecular process of proton transfer between two N centers (Scheme 2A), and the presence of these forms was unambiguously proved by a series of chemical and physicochemical experiments.[33,34] The ^1H NMR spectrum of **7** in $CDCl_3$ at 20−25 °C indicated the presence of a single tautomer, which was identified as the NH_2 form (Scheme 2A) by both 1D and 2D NMR methods. This observation is in complete agreement with the previous studies on tautomerism of amidines,[33−35] demonstrating that for *N*-substituted species (bearing an electron-acceptor substituent at one of the N atoms) the tautomer in which the C=N bond is conjugated with this substituent, i.e. the NH_2 form, usually predominates.[34,35]

Reaction of Metal-Complexed Isonitriles with *N*-Phenylbenzamidine. We started our studies from an attempt to perform the reaction between an uncomplexed isonitrile (C≡NCy) and **7**. In this blank experiment, no reaction was observed upon reflux of the reactants in $CHCl_3$ for 2 d, and this indicates that the addition of **7** along the C≡N triple bond of an isonitrile described below and depicted in Schemes 4−6, has a metal-mediated character.

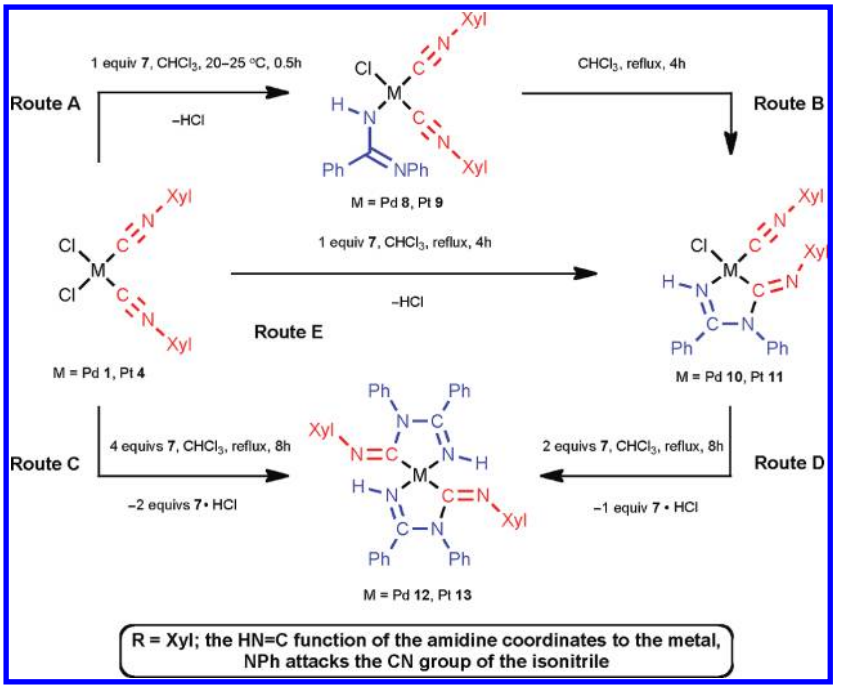
It is known, that the reactivity of metal-bound RN≡C species toward nucleophiles strongly depends on a metal center. Previously, we observed that the coupling of sp^2-N nucleophiles (imines) with both palladium(II) and platinum(II)-bound isonitriles, proceeds faster and with the higher selectivity for the palladium-mediated reaction.[21] Thus, we decided to study in details the reaction between both Pd^{II} and Pt^{II}-complexed isonitriles, *viz*., *cis*-[$MCl_2(C{\equiv}NR)_2$] (**1**−**6**) and **7** at different temperatures and varying ratios of the reactants (Schemes 4−6).

(i). Reaction of *cis*-[$MCl_2(C{\equiv}NXyl)_2$] [M = Pd (1), Pt (4)] with 7 (Scheme 4). After addition of 1 equiv of **7** to *cis*-[$MCl_2(C{\equiv}NXyl)_2$] (M = Pd (**1**), Pt (**4**)) (**Route A**), the reaction mixtures rapidly (*ca*. 5 min, 20−25 °C) changed their color from pale yellow to yellow. In the case of Pd^{II}, the progress of the reaction was monitored by IR, ESI−MS, and ^1H NMR (for the latter method $CDCl_3$ was used instead of $CHCl_3$) and, after *ca*. 30 min, the monitoring allowed the identification of only one formed complex **8** (*ca*. 95% NMR yield); **8** originates from the replacement of a chloride with deprotonated **7**. Complex **8** undergoes slow decomposition, when this reaction mixture was left to stand for 1 d at 20−25 °C giving a mixture of yet unidentified species (6 spots on TLC). In the case of Pt^{II}, we observed a similar substitution reaction but it proceeds slower (2 h for platinum complex **4** vs 5 min for palladium complex **1**) and with a lower selectivity as compared to the palladium(II) system. Thus, **9** is formed in *ca*. 80% NMR yield, in a mixture with two unidentified compounds (detected by TLC).

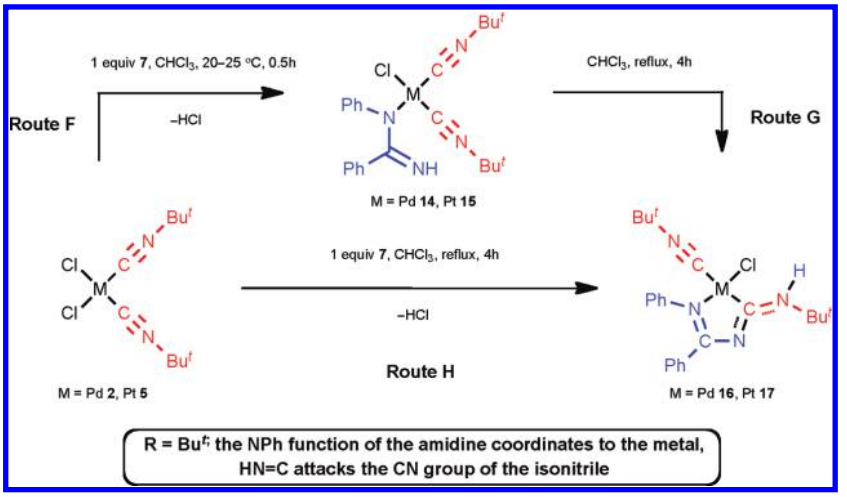
Evaporation of the latter reaction mixtures led to the solids, that were subjected to ESI^+−MS, IR, and ^1H NMR spectroscopy (upon redissolution in $CDCl_3$) and the physicochemical data allows the formulation of amidinato complexes **8** and **9** (see Supporting Information for details). However,

(24) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251–256.
(25) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021–2025.
(26) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809–2815.
(27) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85–92.
(28) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93–99.
(29) 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.
(30) http://www.iupac.org/nomenclature/index.html
(31) Bokach, N. A.; Kuznetsova, T. V.; Simanova, S. A.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Y. *Inorg. Chem.* **2005**, *44*, 5152–5160.
(32) Sarova, G. H.; Bokach, N. A.; Fedorov, A. A.; Berberan-Santos, M. N.; Kukushkin, V. Y.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Dalton Trans.* **2006**, 3798–3805.
(33) Shriner, R. L.; Neumann, F. W. *Chem. Rev.* **1944**, *35*, 351–425.
(34) Granik, V. G. *Russ. Chem. Rev.* **1983**, *52*, 377–393.
(35) Cook, M. J.; Katritzky, A. R.; Nadji, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 211–214.

Scheme 4. Reaction of *cis*-[$MCl_2(C{\equiv}NXyl)_2$] (M = Pd (1), Pt (4)) with 7



Scheme 5. Reaction of *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] (M = Pd (2), Pt (5)) with 7



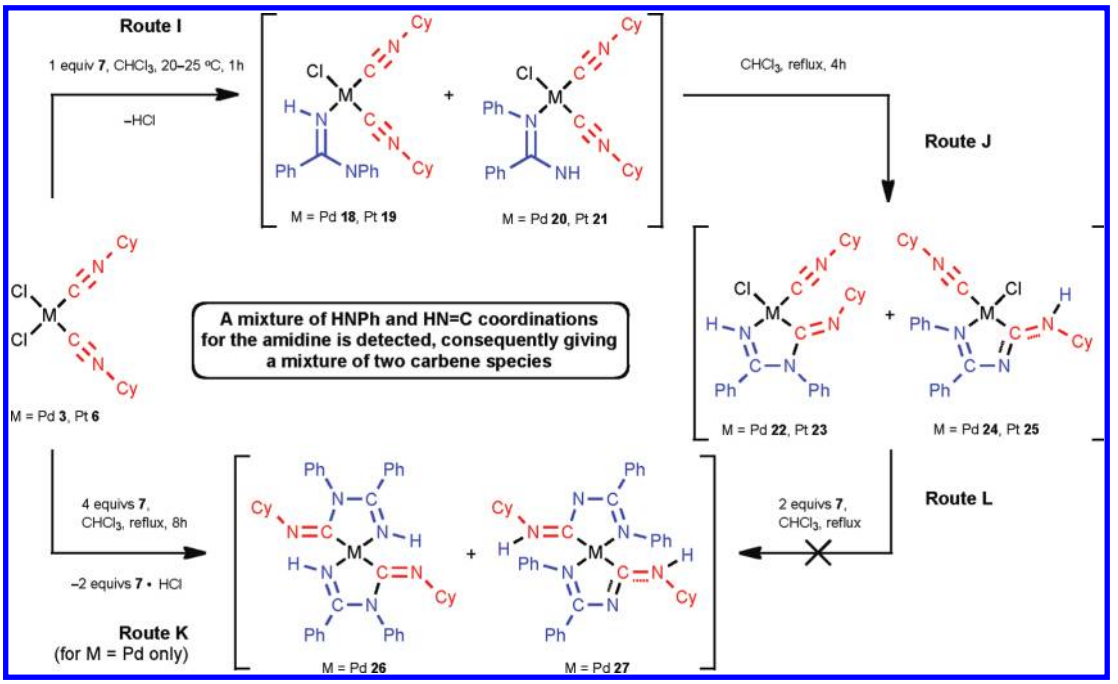
we were unable to isolate analytically pure **8** and **9** due to their insufficient stability even at room temperature gradually converting to **10** and **11**.

Complexes **10** and **11** were also prepared by a single-pot procedure upon reflux of a mixture of the equimolar amounts of *cis*-[$MCl_2(C{\equiv}NXyl)_2$] and **7** in $CHCl_3$ for *ca.* 4 h (**Route E**). When a 1:2 mixture of *cis*-[$MCl_2(C{\equiv}NXyl)_2$] (M = Pd (**1**), Pt (**4**)) and **7** in $CHCl_3$ was used, no significant difference in the reaction rates for **Route A** was observed at 20−25 °C, but formed **8** and **9** (*ca.* 85% and 75% yields, respectively) were strongly contaminated with starting **7**, its hydrochloride, and also with **10** and **11** (*ca.* 5% each), along with some other yet unidentified species.

When a 1:4 mixture of *cis*-[$MCl_2(C{\equiv}NXyl)_2$] and **7** was refluxed in $CHCl_3$ for *ca.* 8 h, the formation of bright yellow complexes **12** (or **13**) was accomplished in *ca.* 65% yield, accompanied by precipitation of **7**•HCl (**Route C**). Slightly higher yields of **12** and **13** (*ca.* 70%) were achieved upon reflux of a mixture of **10** (or **11**) with 2 equiv of **7** in $CHCl_3$ for *ca.* 8 h (**Route D**).

(ii). Reaction of *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] [M = Pd (2), Pt (5)] with 7 (Scheme 5). In this case, both Pd^{II}- and Pt^{II}-mediated reactions proceed significantly slower than the corresponding processes with complexes **1** and **4** bearing XylNC (see above). Thus, when a mixture of the equimolar amounts of *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] (M = Pd (**2**), Pt (**5**)) and **7** in $CHCl_3$ were used, the solution gradually (*ca.* 30 min for **2** and 3 h for **5**; 20−25 °C) changed their color from pale yellow to yellow. In the case of Pd^{II}, the monitoring demonstrated the presence of only one complex **14** (*ca.* 95% NMR yield) derived from the replacement of one chloride ligand with deprotonated **7** (**Route F**); no further changes in the system were observed even after its keeping for 1 d at 20−25 °C. In the case of platinum complex **5**, corresponding product **15** was obtained in *ca.* 75% NMR yield in a mixture with two unidentified compounds (detected by TLC). Complexes **14** and **15** were further refluxed in $CHCl_3$ for 4 h accomplishing **16** and **17** in

Scheme 6. Coupling of *cis*-[$MCl_2(C{\equiv}NCy)_2$] (M = Pd (3), Pt (6)) with 7



ca. 85% isolated yield (**Route G**). Complexes **16** and **17** were also prepared without intermediate isolation of **14** and **15** upon reflux of *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] and **7** in $CHCl_3$ for *ca.* 4 h (**Route H**). When a 1:2 (or 1:4) mixture of *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] and **7** in $CHCl_3$ was used, no significant difference in the reaction rate for **Route F** was observed, but formed **14** and **15** (*ca.* 85% and 75% yields, respectively) were strongly contaminated with an excess of starting **7**, **7**•HCl, and other yet unidentified species. Attempts to prepare complexes structurally relevant to **12** and **13** (Scheme 4), were unsuccessful even upon a broad modification of reaction conditions, *e.g.*, reflux in either $CHCl_3$ or $MeNO_2$ and variation of molar ratios of reagents up to 1:8.

(iii). Reaction of *cis*-[$MCl_2(C{\equiv}NCy)_2$] [M = Pd (3), Pt (6)] with 7 (Scheme 6). When a mixture of the equimolar amounts of the complexes *cis*-[$MCl_2(C{\equiv}NCy)_2$] (M = Pd (**3**), Pt (**6**)) and **7** in $CHCl_3$ were used, the reaction mixtures rapidly at 20−25 °C (*ca.* 5 min for palladium complex **3** and 1 h for platinum complex **6**) changed their color from pale yellow to yellow. The monitoring after 1 h indicated the presence of a mixture of two complexes, *i.e.* **18** and **20** (for Pd^{II}) or **19** and **21** (for Pt^{II}), formed in *ca.* 95% overall NMR yield and in *ca.* 1:1 ratio. (**Route I**).

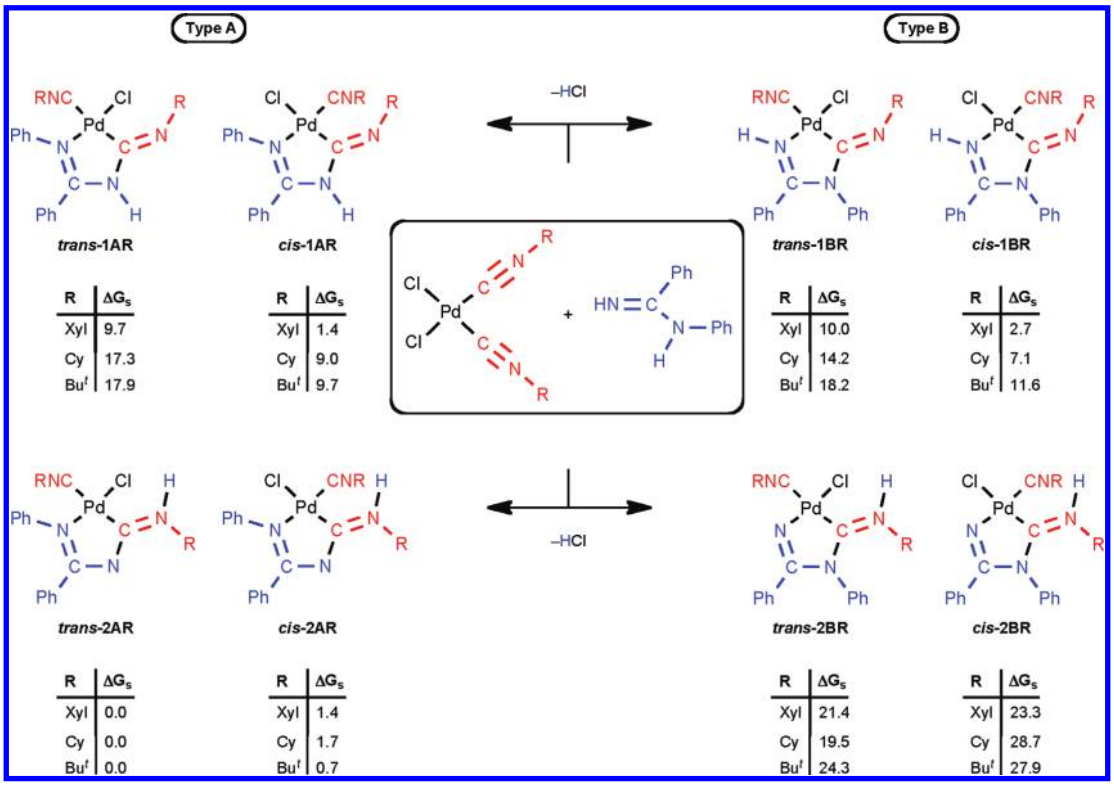
Attempts of the isolation of **18**−**21** as pure species failed due to their slow transformation even at 20−25 °C to aminocarbene complexes **22**−**25**. At room temperature the reactions are rather slow (*ca.* 5% of **22**−**25** were formed for 3 h), and do not accomplish high yields of the target species even after 1 week at 20−25 °C. In order to increase the rate, the reaction mixtures containing **18**−**21** were further refluxed in $CHCl_3$ giving **22**−**25** in *ca.* 65% isolated yield after *ca.* 4 h (**Route J**) in a mixture with other yet unidentified compounds (4 spots on TLC). When a 1:2 mixture of *cis*-[$MCl_2(C{\equiv}NCy)_2$] and **7** in $CHCl_3$ was used, no significant difference in the reaction rate for **Route I** was observed, but the precipitate of **7**·HCl was isolated.

When a 1:4 mixture of *cis*-[$MCl_2(C{\equiv}NCy)_2$] (M = Pd **3**) and **7** in $CHCl_3$ was used under reflux conditions, the formation of a bright yellow mixture of **26** and **27** was accomplished after 8 h in *ca.* 45% isolated yield, accompanied by precipitation of **7**·HCl (**Route K**) and formation of other yet unidentified species (4 spots on TLC). Our efforts to obtain the corresponding platinum-based products via **Route K** were unsuccessful. Moreover, no conversions of any complexes **22**−**25** to **26** and **27** (expected **Route L**) were observed under various reaction conditions (2−4 equivs **7**, reflux, 12−24 h) and molar ratios of reagents (up to 1:8). Thus, upon reflux of **22**−**25**, only gradual decomposition of these species providing a broad mixture of yet unidentified species (6 spots on TLC) was detected.

Theoretical Calculations. The substituent *R* dependent reactivity of the ligated isonitriles in *cis*-[$MCl_2(C{\equiv}NR)_2$] toward **7** prompted us to use quantum-chemical methods (DFT, B3LYP functional) for the estimate of thermodynamic characteristics of the monochelated products derived from the coupling. The calculations were performed for possible products *trans*-/*cis*-**1AR**, *trans*-/*cis*-**2AR**, *trans*-/*cis*-**1BR**, and *trans*-/*cis*-**2BR** (R = Xyl, Bu^t, Cy) depicted in Scheme 7.

For each reaction, two regioisomers (types A and B) with various location of the amidine H atom (*i.e.*, at the endocyclic or exocyclic N atoms) and both *trans*- and *cis*-configuration of the ligands were calculated. The results indicate the following. First, for each R, the most stable isomers of type A are *trans*-**2AR**. These isomers correspond to product **16** isolated experimentally upon the reaction of **2** (R = Bu^t) with **7**. Second, the most stable isomers of type B are *cis*-**1BR** corresponding to complex **10** obtained upon the reaction of **1** (R = Xyl) with **7**. Third, the *relative* stability of *trans*-**2AR** *vs* *cis*-**1BR** clearly decreases along the sequence of R = Bu^t > Cy > Xyl (Scheme 8) well correlating with the experimental observations. Such a trend may be explained by a destabilization of *cis*-**1BCy** and, in particular, *cis*-**1BBu^t** due to steric repulsions between hydrogen(s) atom(s) of R and the metal-bound carbon atom of the isonitrile ligand (Figure 1) (see Supporting Information for details).

Scheme 7. Possible Products of the Reaction between *cis*-$[PdCl_2(CNR)_2]$ and 7[a]



[a] The ΔG_s values (in kcal/mol) are indicated relative to the most stable isomer.

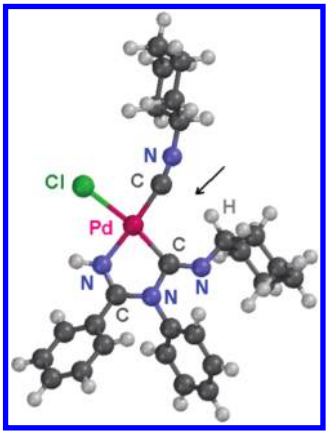


Figure 1. Equilibrium structure of *cis*-**1BCy**. The steric repulsion between the C and the H atoms (indicated by the arrow) provides the destabilization of the structure.

Fourth, as can be inferred from the inspection of the X-ray data for **10** and **11**, the hydrogen atom in the structures of type B is localized at the endocyclic N atom. However, the site of the hydrogen location in the complexes of type A was not elucidated by the X-ray diffraction (see below). The theoretical calculations allow to clarify this situation and indicate that in the complexes of type A the protonation of the exocyclic N is preferable (structures *trans*-/*cis*-**2AR**) except pair *cis*-**1AXyl**-*cis*-**2AXyl** with the same stability of both species. This is conceivably accounted for by intramolecular interactions. Namely, in the pairs *trans*-**1AR**/*trans*-**2AR**, structures *trans*-**2AR** are stabilized by the intramolecular H-bond with the Cl atom. In the pairs *cis*-**1AR**/*cis*-**2AR**, structures *cis*-**1ABu^t** and *cis*-**1ACy** are destabilized by steric repulsions between hydrogen atoms at the endocyclic N atom and the R group (see Supporting Information). In contrast, the structures of type B having the protonated endocyclic nitrogen (*trans*-/*cis*-**1BR**) were found to be more stable than *trans*-/*cis*-**2BR**, in agreement with X-ray data for **10** and **11**.

Fifth, for the structures with the protonated exocyclic nitrogen, *trans*-isomers *trans*-**2AR** and *trans*-**2BR** are more stable than corresponding *cis*-isomers *cis*-**2AR** and *cis*-**2BR**. For the complexes with the protonated endocyclic nitrogen, the opposite was found. This correlates with the experimental isolation of *cis*-**10** and explains the observed geometrical isomerization upon the reaction of *cis*-**2** with **7** giving *trans*-**16**.

Characterization of Synthesized Complexes. Diaminocarbene and aminocarbene-like (**10**−**13**, **16**, **17**, and **22**−**27**) species were fully characterized by elemental analyzes (C, H, N), high-resolution ESI^+−MS, IR, and 1D ^1H and $^{13}C\{^1H\}$ and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC/^1H,^{13}C-HSQC, ^1H,^{13}-C-HMBC) NMR spectroscopies (for detailed description of this characterization as well as characterization of the intermediate amidinato species (**8**, **9**, **14**, **15**, **18**−**21**) see Supporting Information). Four complexes (**10**, **11**, **16**, and **28**) were characterized by a single crystal X-ray diffraction (Figures 2 and 3; **Figures 1S** and **2S** and **Tables 1S**−**3S** of **Supporting Information**). A rather poor quality of structure of **16** (crystals are heavily twinned) allowed just the confirmation of the basic structure of **16**, but not precise inspection of its geometric parameters. However, we succeeded in isolation from the same reaction (Scheme 5, **Route G**) a few X-ray quality crystals of a minor product (**28**), *i.e.*, the complex obtained by the replacement of the isonitrile ligand in **16** with one molecule of **7**. High crystallographic quality structure of **28** allows the qualitative comparison of bond lengths and angles.

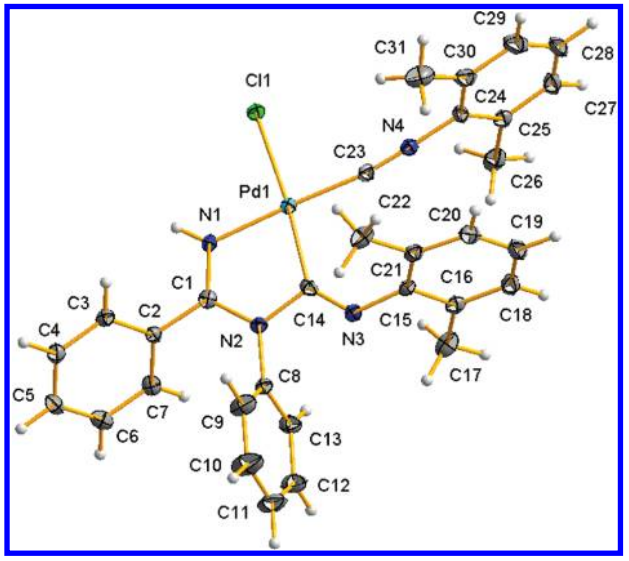


Figure 2. View of **10** with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels were omitted for simplicity, and only one molecule from the dimeric unit is shown.

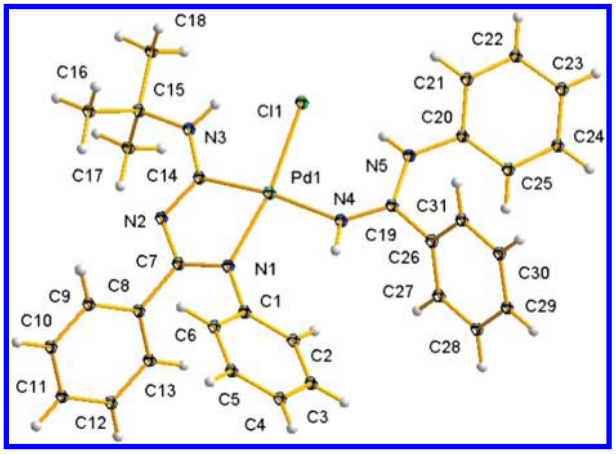


Figure 3. View of **28** with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels were omitted for simplicity, and only one molecule from the dimeric unit is shown.

Figures 2 (and 1S, Supporting Information) and 3 (and 2S) represent two types of complexes generated from the nucleophilic addition of **7** to the isonitrile complexes. The first type (compounds **10**−**13**; Scheme 4, Figure 2) includes the complexes formed via the addition by the NHPh center, while the second type comprises complexes (**16**, **17**, and **28**; Scheme 2, Figure 3) generated via the addition by the HN=C center. All these structural data support our ideas on the substituent dependent regioselectivity of the coupling. Detailed description of X-ray data can be found in Supporting Information and here one should stress one important issue. When complexes with the aromatic XylNC were employed, obtained carbene ligands exhibit distinct consequence of the double and the single bonds in the MCN_2 fragment. We previously observed this unusual phenomenon for the relevant [MCl{*C*(N=C($C_6R^1R^2R^3R^4$CO*N*))=N(H)R}(C≡NR)] (M = Pd, Pt; R = Cy, Bu^t, Xyl; R_1−R_4 = H; R_1, R_3, R_4 = H, R_2 = Me; R_1, R_4 = H, R_2, R_3 = Cl) complexes[21] and those compounds along with the current examples provide a novel family of *aminocarbene-like species* (Scheme 8). For aliphatic Bu^{t}NC, corresponding carbene possess bond delocalization in the MCN_2 functionality and belong to the *classical diaminocarbene* systems (Scheme 8).

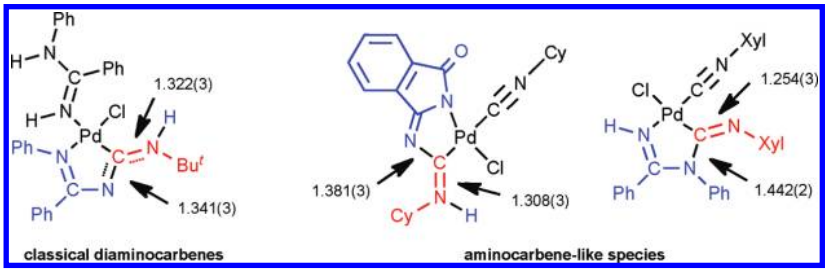
Evaluation of the Catalytic Properties of Systems on the Basis of the Novel Diaminocarbene/Aminocarbene-Like Species in Sonogashira Cross-Coupling. Having two structural types of aminocarbene ligands at our disposal, it was tempting to get initial data on their catalytic activity in some organic transformations. Taking into account our experience in the alkyne chemistry,[36−38] it is not surprising that Sonogashira reaction was selected as the starting point for these studies. Previously palladium-catalyzed Sonogashira cross-coupling system has been widely used for the synthesis of internal alkynes starting from the terminal C≡C species.[39,40] Although many palladium catalysts bearing nitrogen and phosphorus ligands have been studied as catalysts for this reaction, only few systems involving Pd^{II} species with NHCs have been employed.[41−52] Moreover, despite evident resemblance between *N*-heterocyclic and acyclic diaminocarbenes (see Introduction), examples for Sonogashira reaction catalyzed by acyclic diaminocarbene palladium complexes are scarce and represented by only one report emerged until the current study.[53]

The catalytic part consists of two subsections. First, we employed a model Sonogashira reaction to evaluate the difference in catalytic properties for systems based on two types of palladium aminocarbene species (represented by **10** and **16**). Second, we applied the most efficient precatalyst for the cross-coupling involving diynes; these difficult-to-obtain substrates are very little explored in Sonogashira reaction. Our results are disclosed in two subsections that follow.

(i). Systems Based on 10 and 16 in the Model Sonogashira Cross-Coupling. Many recent studies have demonstrated that the cyclization of substituted aryl- and hetarylacetylenes (in particular, those containing *ortho*-substituents in the aromatic

(36) Balova, I. A.; Morozkina, S. N.; Sorokoumov, V. N.; Vinogradova, O. V.; Knight, D. W.; Vasilevsky, S. F. *Eur. J. Org. Chem.* **2005**, 882–888.
(37) Vinogradova, O. V.; Sorokoumov, V. N.; Vasylevsky, S. F.; Balova, I. A. *Tetrahedron Lett.* **2007**, *48*, 4907–4909.
(38) Vinogradova, O. V.; Sorokoumov, V. N.; Balova, I. A. *Tetrahedron Lett.* **2009**, *50*, 6358–6360.
(39) Sonogashira, K., *Metal-Catalyzed Cross-Coupling Reactions*. In Stang, P. J.; Diederich, F., Eds. Wiley: Weinheim, Germany, 1998; pp 203−229.
(40) Anastasia, L.; Negishi, E.-I. *Chem. Rev.* **2003**, *103*, 1979–2018.
(41) Gu, S.; Chen, W. *Organometallics* **2009**, *28*, 909–914.
(42) Ray, L.; Barman, S.; Shaikh, M. M.; Ghosh, P. *Chem.—Eur. J.* **2008**, *14*, 6646–6655.
(43) Kim, J. H.; Lee, D. H.; Jun, B. H.; Lee, Y., S. *Tetrahedron Lett.* **2007**, *48*, 7079–7084.
(44) Altenhoff, G.; Würtz, S.; Glorius, F. *Tetrahedron Lett.* **2006**, *47*, 2925–2928.
(45) Sommer, W., J.; Weck, M. *Adv. Synth. Catal.* **2006**, *348*, 2101–2113.
(46) Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566–1568.
(47) Mas-Marza, L.; Segarra, A., M.; Claver, C.; Peris, E.; Fernandez, E. *Tetrahedron Lett.* **2003**, *44*, 6595–6599.
(48) Eckhardt, M.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 13642–13643.
(49) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002**, *4*, 1411–1414.
(50) Yang, C.; Nolan, S., P. *Organometallics* **2002**, *21*, 1020–1022.
(51) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748.
(52) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93–96.
(53) Dhudshia, B.; Thadani, A. N. *Chem. Commun* **2006**, 668–670.

Scheme 8. Bond Distances (Å) in Classical Diaminocarbene *vs* Novel Aminocarbene-like Species



Scheme 9. Model Sonogashira Catalytic System Employed for Our Studies

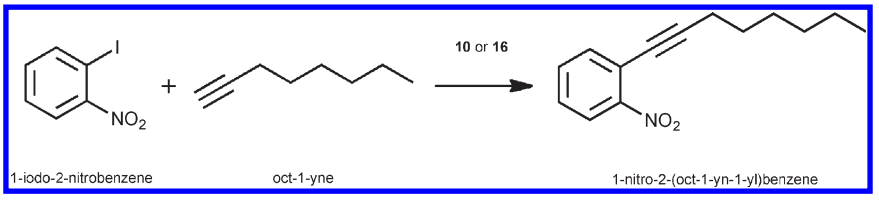


Table 1. Evaluation of the Catalytic Properties of 10 and 16 in Sonogashira Coupling

Entry	Catalyst	Catalyst loading, mol %	Solvent	Base	Time, h	Yield (isolated yield), %	TON	TOF, h^{-1}
1	**10**	0.07	THF	Et_3N	96	99 (94)	1400	15
2	**16**	0.07	THF	Et_3N	68	99	1400	15
3	**10**	0.07	THF	Et_3N	24	99	1400	60
4	**16**	0.07	THF	Et_3N	12	99	1400	120
5	**10**	0.07	THF	Et_3N	24	20	290	12
6	**10**	0.07	EtOH	K_2CO_3	24	–	–	–
7	**16**	0.07	EtOH	K_2CO_3	24	10	140	6
8	**10**	0.07	EtOH	K_2CO_3	14	99 (96)	1400	100
9	**16**	0.07	EtOH	K_2CO_3	5	99	1400	280
10	$[PdCl_2(PPh_3)]_2$	0.1	EtOH	K_2CO_3	18	40	400	22
11	**10**	0.1	EtOH	K_2CO_3	18	99	990	55
12	**16**	0.1	EtOH	K_2CO_3	4	99	990	250
13	**16**	0.05	EtOH	K_2CO_3	18	99	1980	110

For all runs, 1-iodo-2-nitrobenzene (0.610 g, 2.45 mmol) and oct-1-yne (0.550 g, 5.00 mmol) were used. For all runs, except 6 and 7, CuI (0.045g, 9.60 mmol %) was added as co-catalyst, and for all runs except 5, PPh_3 (0.030 g, 4.60 mmol %) was used as the catalyst activator. All runs were performed at 60 °C, except 1 and 2 (those were performed at 20 °C) until disappearance of the starting 1-iodo-2-nitrobenzene. Yields are based on ^1H NMR integration.

ring, *e.g.* 2-nitroarylacetylens[54]) represents an efficient route for the preparation a wide range of pharmacologically important heterocycles such as indoles, indolo[1,2-c]quinazolines, quinolines/isoquinolines, furopyridine, and pyrazolopyridines (for a recent review see ref55). This fact provided a motivation to investigate an interplay between 1-iodo-2-nitrobenzene and oct-1-yne accomplishing 1-nitro-2-(oct-1-ynyl)benzene as a model reaction for our catalytic studies (Scheme 9). As components of catalytic systems we addressed **10** and **16**, derived from the addition of **7** via its different nucleophilic centers to $(RNC)Pd^{II}$ species as depicted in Schemes 4 and 5.

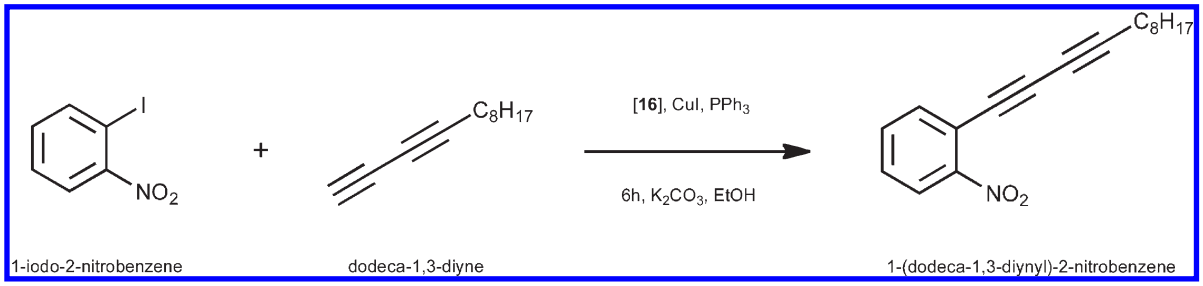
With palladium complexes **10** and **16** in hand, we first examined their catalytic activity for the coupling of the mentioned substrates under traditionally employed conditions [THF as solvent, Et_3N as a base, and CuI as a cocatalyst, and PPh_3 as a precatalyst activator[41]] (Table 1, entries 1−5) and observed the full conversion of the starting 1-nitro-2-iodobenzene within 96 h (for **10**) or 68 h (for **16**) at room temperature to furnish the target 1-nitro-2-(oct-1-ynyl)benzene in 99% yield (entries 1 and 2). Increase in the reaction temperature up to 60 °C resulted in 99% product yield accomplished for 24 h (for **10**) and 12 h (for **16**) (entries 3 and 4). We also found that the presence of PPh_3 in the system is essential for the coupling and without the added PPh_3 1-nitro-2-(oct-1-ynyl)benzene was obtained in only 20% yield after 24 h (entry 5).

We have recently reported that acyclic diaminocarbene precatalysts operate efficiently in the Suzuki−Miyaura cross-coupling under sustainable conditions (EtOH as solvent, K_2CO_3 as a base).[22] Inspired by these results, we conducted the model reaction in EtOH as solvent and using K_2CO_3 as a base (Table 1, entries 6−13). The catalytic test without addition of CuI (entries 6 and 7) afforded no target 1-nitro-2-(oct-1-ynyl)benzene (for **10**) or it was obtained in low (10%) yield (for **16**) after 24 h at 60 °C, thus suggesting that the catalytic cycle for both **10** and **16** involves CuI as the cocatalyst. Indeed, in the presence of CuI, 1-nitro-2-(oct-1-ynyl)benzene was obtained at 60 °C in 99% yield after 14 h (for **10**, entry 8) or after 5 h (for **16**, entry 9).

As the next step, we also compared the catalytic properties of **10**- and **16**-based systems with the widely used one based on $[PdCl_2(PPh_3)_2]$[56] (entries 10−12). After 3 h at 60 °C,

(54) Kim, J. S.; Han, J. H.; Lee, J. J.; Jun, Y. M.; Lee, B. M.; Kim, B. H. *Tetrahedron Lett.* **2008**, *49*, 3733–3738.
(55) Kirsch, G.; Hesse, S.; Comel, A. *Curr. Org. Synth.* **2004**, *1*, 47–63.
(56) Bailar, J. C. J.; Itatani, H. *Inorg. Chem.* **1965**, *4*, 1618–1620.

Scheme 10. Sonogashira Reaction with Dodeca-1,3-diyne Furnishing 1-(Dodeca-1,3-diynyl)-2-nitrobenzene



$[PdCl_2(PPh_3)_2]$ allowed the formation of the target product in *ca.* 35% yield, approaching the total 40% yield after next 15 h (entry 10). Under similar conditions, **10**-based system demonstrated slightly better catalytic activity providing *ca.* 40% conversion within 3 h, and increasing to *ca.* 99% after next 15 h (entry 11). At the same time, for **16** nearly quantitative conversion (99%) of substrates was achieved in 3 h (entry 12), and this explicitly indicates that **16**-based system is more catalytically efficient for the coupling as compared to both **10**- and the conventionally used one based on $[PdCl_2(PPh_3)_2]$. Finally, we also searched to optimize TON for more active complex **16** and found that maximum TON of 1980 (at 99% conversion of the substrates) is accomplished with [**16**] = 0.05 mol %.

(ii). Sonogashira Cross-Coupling with Terminal Diyne Catalyzed by 16-based System. As it was indicated previously, cyclization of the *ortho*-substituted aryl- and hetarylacetylenes allows the preparation of various heterocyclic species, while corresponding cyclization reactions of *ortho*-diynyl-substituted arenes and hetarenes are practically unexplored due to a lack of synthetic procedures and suitable catalysts (or precatalysts) for their synthesis. Following the project on chemistry of functionalized diynes conducted by two of us,[37,38] we employed **16**-based system for the synthesis of 1-(dodeca-1,3-diynyl)-2-nitrobenzene from 1-iodo-2-nitrobenzene and dodeca-1,3-diyne (Scheme 10; see Supporting Information for detailed procedure). Reaction was performed under conditions indicated in Table 1 (entry 9), but due to a poor stability of the diyne, the catalytic run was performed at lower (50 °C) temperature. The starting 1-iodo-2-nitrobenzene was fully transformed to the target 1-(dodeca-1,3-diynyl)-2-nitrobenzene (97% isolated yield) for 6 h and this reaction is characterized with TON = 1400. These results indicate that **16**, as precatalyst, gives significantly more efficient catalytic species for Sonogashira reaction with diynes as compared to the previously used[36] $Pd(OAc)_2$ [in previous work[36] with $Pd(OAc)_2$, 1-(dodeca-1,3-diynyl)-2-nitrobenzene was obtained in 80% yield and high precatalyst loading (10 mol %)].

Final Remarks. The results of this work may be considered from the following perspectives. First, searching for novel acyclic aminocarbene species, we succeeded in preparation of metal complexes containing chelating diaminocarbene or aminocarbene-like ligands via the reaction between the unsymmetrical amidine, *i.e.*, *N*-phenylbenzamidine, and one or two isonitriles in *cis*-$[MCl_2(C{\equiv}NR)]$ ($M = Pd^{II}, Pt^{II}$; R = Xyl, Bu^t, Cy) (see Schemes 4−6). The formation of these species occur via the two-step process, involving the initial coordination of *N*-phenylbenzamidinate to a metal center followed by an intramolecular attack of the remote nucleophilic center of the coordinated amidinate on the CN triple bond of the isonitrile. The products derived from XylNC exhibit distinct consequence of the double and the single bonds in the MCN_2 fragment and belong to a novel family of *aminocarbene-like species*. The carbene derived from Bu^{t}NC, exhibits the delocalization in the MCN_2 functionality and belong to the *classical diaminocarbene* systems (Scheme 1, B). Further studies on the aminocarbene-like type of ligands performed in our group will be aimed on extending number of these species, inspection of their geometrical parameters, and understanding factors that determine the preference in formation of aminocarbene-like vs. classical diaminocarbene structure.

Second, we detected the first example of regioselectivity in addition of bifunctional nucleophiles to isonitriles. Thus, the interplay between *N*-phenylbenzamidine and a metal-bound isonitrile is strongly affected by the nature of the substituent *R* of the isonitrile. When aromatic isonitrile is used (R = Xyl), *N*-phenylbenzamidine is coordinated to a metal by the HN═C moiety (Scheme 4), and the nucleophilic attack proceeds via the NHPh center of the benzamidine. For R = Bu^t, *N*-phenylbenzamidine is coordinated to a metal by the NHPh center, and the addition occurs via the HN═C center of the nucleophile (Scheme 5). When R = Cy, we observed a mixture of two regioisomers that are derived from the addition of *N*-phenylbenzamidine by two nucleophilic centers (Scheme 6). This experimentally observed substituent *R* dependent reactivity of isonitriles in *cis*-$[MCl_2(C{\equiv}NR)_2]$ toward *N*-phenylbenzamidine was explored using the theoretical (DFT) methods and interpreted as a result of the steric repulsions in one of the regioisomers of the addition products, when R = Cy and Bu^t. The thermodynamic stability of various isomers of the reaction products was calculated and analyzed. It is important to point out that examples for the metal-mediated regioselective addition to C≡N triple bond are scarce, and the formation of two different products was observed only for the addition of *N*,*N*′-diphenylguanidine to metal-bound dialkylcyanamides, $R_2NC{\equiv}N$.[57] To the best of our knowledge, no regioselective additions to *isonitriles RNC* were reported before this study.

Third, we evaluated catalytic properties for systems based on two types of palladium aminocarbene species, i.e. **10** and **16**, derived from the regioselective addition of *N*-phenylbenzamidine to Pd^{II}-bound isonitrile by its different nucleophilic centers. We found that both systems exhibit catalytic activities in Sonogashira cross-coupling of 4-$NO_2C_6H_4I$ with oct-1-yne yielding 1-nitro-2-(oct-1-ynyl)benzenes (yields are up to 99%, TONs up to 2000), under relatively mild and sustainable conditions (in non-dried EtOH as a solvent, K_2CO_3 as a base, air, 60 °C). Moreover, we found that **16**-based system exhibits slightly higher catalytic efficiency (yields up to 99%, TONs up to 2000; TOFs up to 280) as compared to one based on **10**

(57) Gushchin, P. V.; Kuznetsov, M. L.; Haukka, M.; Wang, M.-J.; Gribanov, A. V.; Kukushkin, V. Y. *Inorg. Chem.* **2009**, *48*, 2583–2592.

(yields up to 99%, TONs up to 1400; TOFs up to 120), and substantially higher activity than for the conventionally used system based on $[PdCl_2(PPh_3)_2]$ (yield 40%, TONs up to 400; TOFs up to 22). We also employed **16** for the synthesis of 1-(dodeca-1,3-diynyl)-2-nitrobenzene from 1-iodo-2-nitrobenzene and dodeca-1,3-diyne (in EtOH as a solvent, K_2CO_3 as a base, 50 °C), and found that **16** is significantly more efficient precatalysts for Sonogashira reaction with diynes [as compared to the previously used $Pd(OAc)_2$] providing 1-(dodeca-1,3-diyn-1-yl)-2-nitrobenzene in 97% yield with one of the best reported TONs of 1400. It is important to notice that the observed difference in the catalytic activity between **10** and **16** could be justified by either different steric/donor properties of the R group of the ligands and/or by the different structure of these ligands.

Finally, it is worth mentioning, that the catalytic system based on **16** or **10** is not sensitive to air and moisture, operate under mild and sustainable conditions (nondried EtOH having low environmental impact) and accomplishes the target compounds in high yields. We believe that upon proper derivatization of the carbene catalyst (e.g., by employing of other substituted amidines toward isonitriles), and further optimization of the reaction conditions, sustainable catalytic systems for Sonogashira coupling may be further developed.

Experimental Section

Materials and Instrumentation. Solvents, $PdCl_2$, $K_2[PtCl_4]$, all isonitriles and all reagents for catalytic studies were obtained from commercial sources and used as received, apart from chloroform that was purified by conventional distillation over calcium chloride. *N*-Phenylbenzamidine was prepared by the known protocol based on a nucleophilic addition of $PhNH_2$ to PhCN in the presence of $AlCl_3$.[58] The complexes *cis*-$[PdCl_2(RNC)_2]$ (R = Xyl (**1**), Bu^t (**2**), Cy (**3**)) and *cis*-$[PtCl_2(RNC)_2]$ (R = Xyl (**4**), Bu^t (**5**), Cy (**6**)) were prepared as previously reported.[24−29] C, H, and N elemental analyses were carried out by the Department of Organic Chemistry of St. Petersburg State University on a 185B Hewlett-Packard carbon hydrogen nitrogen analyzer. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI^+−MS) and the capillary exit at 70−150 V. The nebulizer gas flow was 0.4 bar and drying gas flow 4.0 L/min. For ESI species were dissolved in MeCN. In the isotopic pattern, the most intensive peak is reported. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker-DPX 300 spectrometer at ambient temperature, while 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC, ^1H,^{13}C-HSQC, and ^1H,^{13}C-HMBC) NMR spectra were acquired on Bruker Avance II+ 400 MHz (UltraShield Magnet) and Bruker Avance II+ 500 MHz (UltraShield Plus Magnet) spectrometers at ambient temperature.

X-ray Structure Determinations. The crystals of **10**, **11**, and **28** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Denzo-Scalepack*[59] or *EvalCCD*[60] program packages were used for cell refinements and data reductions. The structures were solved by direct methods using the *SIR97*[61] *or SHELXS-97*[62] program with the *WinG4*[63] graphical user interface. A semiempirical[64] (**10**) or analytical[65] (**11**) absorption correction was applied to data. Structural refinements were carried out using *SHELXL-97*.[62] In **10** and **11**, the NH hydrogen atoms were located from difference Fourier maps and refined isotropically. In **28**, the NH hydrogen atoms were also located from the difference Fourier map but constrained to ride on their parent atom U_{iso} = 1.2−1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C−*H* = 0.95−0.98 Å and U_{iso} = 1.2−1.5 U_{eq}(parent atom). The crystallographic details are summarized in Table S1 of the Supporting Information. CCDC 795512−795514 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. General Procedure for Reaction of *cis*-$[MCl_2(C{\equiv}NR)_2]$ (1−6) and HN=C(Ph)NHPh (1 equiv). Solid **7** (0.049 g, 0.250 mmol) was added to a solution (R = Bu^t, Cy) or a suspension (R = Xyl) of *cis*-$[MCl_2(RNC)_2]$ (0.250 mmol) in $CHCl_3$ (5 mL). The reaction mixture was refluxed for 4 h. During the reaction time, the color of the mixture turned from light orange to bright yellow. After 4 h, the reaction mixture was filtered off from some undissolved material and then evaporated to dryness at 40−45 °C, and the solid residue was extracted with two 5 mL portion of CH_2Cl_2. The bright yellow solution was evaporated to dryness at room temperature, washed with three 1 mL of Et_2O, and dried in air at 20−25 °C. Yields were 65−85%, based on the metal.

10. Anal. Calcd for $C_{31}H_{29}N_4ClPd$: C, 62.19; H, 4.88; N, 9.36. Found: C, 62.47; H, 4.31; N, 9.12. HRMS (ESI^+, 105 V, MeCN): found, 564.1532 $[M - Cl]^+$; calcd for $C_{31}H_{29}N_4Pd$, 564.1521. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3362 (m), ν(C−H) 2955 (m), ν(C≡N) 2191 (s), ν(N=$C_{carbene}$, N=C) 1635 (s), 1588 (s), δ(C−H from Ar) 751 (s), 695 (s). ^1H NMR ($CDCl_3$, δ): 7.35−7.28 (m), 7.24−6.94 (m), 6.66 (d), 6.11 (t, 17H, C=NH, aryls), 2.21 (s), 2.15 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 171.2 (C=N from carbene), 163.8 (C=NH), 150.6, 139.3 (C from Ph's), 134.3−123.3 (C and CH from aryls), 19.4 and 18.6 (Me's).

11. Anal. Calcd for $C_{31}H_{29}N_4ClPt$: C, 54.13; H, 4.25; N, 8.15. Found: C, 54.36; H, 4.38; N, 7.80. HRMS (ESI^+, 105 V, MeCN): found, 689.1530 $[M]^+$; calcd for $C_{31}H_{29}N_4ClPt$, 689.1753. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3437 (m), ν(C−H) 2977 (m), ν(C≡N) 2185 (s), ν(N=$C_{carbene}$, N=C) 1610 (s), 1584 (s), δ(C−H from Ar) 756 (s), 693 (s). ^1H NMR ($CDCl_3$, δ): 7.53 (s, 1H, C=NH), 7.39−7.27 (m), 7.25−6.95 (m), 6.63 (d), 6.05 (t, 16H, aryls), 2.26 (s), 2.13 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 171.7 (C=N from carbene), 162.0 (C=NH), 151.0, 139.0 (C from Ph's), 134.5−122.9 (C and CH from aryls), 19.3 and 18.6 (Me's).

16. Anal. Calcd for $C_{23}H_{29}N_4ClPd$: C, 54.96; H, 5.82; N, 11.15. Found: C, 54.93; H, 5.83; N, 11.19. HRMS (ESI^+, 105 V, MeCN): found, 506.1295 $[M + H]^+$; calcd for $C_{23}H_{30}N_4ClPd$, 506.1288. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3283 (m),

(58) Cooper, F.; Partridg, M. *Org. Synth.* **1958**, *36*, 64–65.
(59) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, J., Eds.; Methods of Enzymology 276; Academic Press: New York, Vol. *276*, pp 307−326.
(60) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220–229.
(61) Altomare, A.; Burla, M. C.; Camalli, M. C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
(62) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
(63) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
(64) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38.
(65) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

ν(C−H) 2983 (m), ν(C≡N) 2210 (s), ν(N=$C_{carbene}$, N=C) 1537 (s), 1506 (s), δ(C−H from Ar) 700 (s). ^{1}H NMR ($CDCl_3$, δ): 7.85 (s, 1H, C=NH), 7.30−7.27 (m), 7.24−6.93 (m, 10H, Ph's), 1.49 (s) and 1.17 (s, 18H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 190.4 (C=N from carbene), 180.6 (C=NH), 150.9, 146.4, 133.1−122.2 (C and CH from Ph's), 56.1 and 54.9 (C from Bu^t's), 30.2, 29.7, 29.3, and 29.0 (Me's).

17. Anal. Calcd for $C_{23}H_{29}N_4ClPt$: C, 46.68; H, 4.94; N, 9.47. Found: C, 47.05; H, 5.14; N, 9.16. HRMS (ESI$^+$, 70 V, MeCN): found, 557.2376 $[M - Cl]^+$; calcd for $C_{23}H_{30}N_4ClPt$, 557.2142. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3445 (m), ν(C−H) 2978 (m), 2931 (m), ν(C≡N) 2199 (s), ν(N=$C_{carbene}$, N=C) 1625 (s), 1519 (s), δ(C−H from Ph) 696 (s). ^{1}H NMR ($CDCl_3$, δ): 7.88 (s, 1H, C=NH), 7.14−6.64 (m, 10H, Ph's), 1.62 (s) and 1.55 (s, 18H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 180.6 (C=N from carbene), 162.7 (C=NH), 150.9 and 146.5 (C from Ph's), 130.7−122.9 (CH from Ph's), 30.3, 29.7, 29.3, and 29.1 (C from Bu^t's).

Mixture of **22** and **24**. Anal. Calcd for $C_{27}H_{33}N_4ClPd$: C, 58.46; H, 6.00; N, 10.10. Found: C, 58.64; H, 6.17; N, 10.03. HRMS (ESI$^+$, 105 V, MeCN): found, 557.1547 $[M]^+$; calcd for $C_{27}H_{33}N_4ClPd$, 557.1522. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3331 (m), ν(C−H) 2929 (s), 2853 (s), ν(C≡N) 2221 (s), ν(N=$C_{carbene}$, N=C) 1628 (s), 1593 (s), δ(C−H from Ar) 694 (s). ^{1}H NMR ($CDCl_3$, δ): 7.88 (s, 1H, C=NH), 7.54−7.31 (m), 7.23−6.24 (m, 20H, Ph's), 5.75 (s, 1H, C=NH), 4.23 (m, 2H), 4.02 (m, 1H), 3.46 (m, 1H, CH), 2.15−1.20 (m, 40H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 181.2 and 179.8 (C=N from carbene), 169.5 and 165.2 (C=NH), 157.6, 150.8, 146.4 (C from Ph's), 133.1−121.7 (Ph's), 54.9, 54.7, 53.2, 52.4 (CH from Cy's), 33.9−14.2 (CH_2).

Mixture of **23** and **25**. Anal. Calcd for $C_{27}H_{33}N_4ClPt$: C, 50.37; H, 5.17; N, 8.71. Found: C, 50.18; H, 5.42; N, 8.92. HRMS (ESI$^+$, 105 V, MeCN): found, 608.2477 $[M - Cl]^+$; calcd for $C_{27}H_{33}N_4Pt$, 608.2377. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3428 (m), ν(C−H) 2928−2853 (s), ν(C≡N) 2212 (s), ν(N=$C_{carbene}$, N=C) 1620 (s), 1569 (s), δ(C−H from Ar) 693 (s). ^{1}H NMR ($CDCl_3$, δ): 7.87 (s, br, 1H, C=NH from carbene), 7.54−7.29 (m), 7.24−6.52 (m), 6.30 (d 20H, Ph's), 4.28 (m) and 4.00−3.42 (m, 4H, CH), 2.15−1.17 (m, 40H, CH_2); *H*N=C(Ph) is not resolved. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 182.0 and 169.6 (C=N from carbene), 165.2 and 164.1 (C=NH), 148.5 and 141.3 (C from Ph's), 130.8−123.8 (Ph's), 55.1, 54.8, 52.7, and 52.9 (CH from Cy's), 33.9−14.2 (CH_2).

General Procedure for the Reaction between *cis*-[MCl_2-(C≡NR)$_2$] (1−6) and HN=C(Ph)NHPh (4 equiv). Solid **7** (0.100 g, 0.510 mmol) was added to a solution (R = Cy, Bu^t) or a suspension (R = Xyl) of *cis*-[MCl_2(RNC)$_2$] (0.127 mmol) in $CHCl_3$ (3 mL). The reaction mixture was then refluxed for *ca*. 8 h under vigorous stirring. During the reaction time, the color of the mixture turned from light orange to bright yellow and then to dark yellow. After 8 h, the reaction mixture was filtered off from the released **7**·HCl and then evaporated to dryness at 90 °C, and the solid residue was extracted with two 5 mL portions of CH_2Cl_2. The dark yellow solution was filtered off to remove some insoluble material, the filtrate was evaporated to dryness at room temperature, washed with five 1 mL of cold (5 °C) Et_2O, and dried in air at 20−25 °C. Yields were 45−65%, based on the metal.

12. Anal. Calcd for $C_{44}H_{40}N_6Pd$: C, 69.63; H, 5.31; N, 11.08. Found: C, 70.05; H, 5.22; N, 11.04. HRMS (ESI$^+$, 70 V, MeCN): found, 759.2383 $[M]^+$; calcd for $C_{44}H_{40}N_6Pd$, 759.2443. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3455 (m), ν(C−H) 2917 (m), ν(N=$C_{carbene}$, N=C) 1633 (s), 1589 (s), δ(C−H from Ar) 777 (s), 749 (s), 697 (s). ^{1}H NMR ($CDCl_3$, δ): 7.97 (s, br, 2H, C=NH), 7.70−7.28 (m), 7.23−6.57 (m, 26H, C=NH, aryls), 2.56 (s) and 2.37 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 171.2 (C=N from carbenes), 163.4 (C=NH), 145.3, 134.3 (C from Ph's), 131.8−122.5 (C and CH from aryls), 19.4 and 18.6 (Me's).

13. Anal. Calcd for $C_{44}H_{40}N_6Pt$: C, 62.33; H, 4.75; N, 9.91. Found: C, 62.35; H, 4.72; N, 10.12. HRMS (ESI$^+$, 70 V, MeCN): found, 847.2958 $[M]^+$; calcd for $C_{44}H_{40}N_6Pd$, 847.2962. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3442 (m), ν(C−H) 2912 (m), ν(N=$C_{carbene}$, N=C) 1641 (s), 1578 (s), δ(C−H from Ar) 782 (s), 740 (s), 688 (s). ^{1}H NMR ($CDCl_3$, δ): 8.02 (s, br, 2H, C=NH), 7.62−7.29 (m), 7.22−6.50 (m, 26H, C=NH, aryls), 2.54 (s) and 2.32 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 172.1 (C=N from carbenes), 164.0 (C=NH), 145.5 and 134.7 (C from Ph's), 132.9−123.5 (C and CH from aryls), 19.6 and 17.6 (Me's).

Mixture of **26** and **27**. Anal. Calcd for $C_{40}H_{44}N_6Pd$: C, 67.17; H, 6.20; N, 11.75. Found: C, 67.46; H, 6.27; N, 11.58. HRMS (ESI$^+$, 105 V, MeCN): found, 714.2648 $[M]^+$; calcd for $C_{40}H_{44}N_6Pd$, 714.2662. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3325 (m), ν(C−H) 2932 (s), ν(N=$C_{carbene}$, N=C) 1642 (s), 1585 (s), δ(C−H from Ar) 702 (s). ^{1}H NMR ($CDCl_3$, δ): 7.92 (s, br, 4H, C=NH), 7.56−7.30 (m), 7.26−6.34 (m, 40H, Ph's), 5.72 (s, br, 4H, C=NH), 4.32 (s, 2H) and 4.22 (s, 2H, CH), 2.22−1.30 (m, 40H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 178.2 and 171.5 (C=N from carbene), 168.5 and 166.4 (C=NH), 157.8, 152.7, 146.4, 142.3 (C from Ph's), 134.1−121.2 (Ph's), 52.4 and 51.0 (CH from Cy's), 34.8−21.2 (CH_2).

Computational Details. The full geometry optimization of all structures has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP)[66,67] with the help of the Gaussian-03[68] program package. This functional was found to be a quite reasonable one for the investigation of reactivity, structural and spectral properties of Pt and Pd complexes with nitriles and isonitriles.[69−72] No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic Stuttgart pseudopotential that described 28 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][73] for the palladium atom and the 6-31G basis set for other atoms. Then, single-point calculations were performed on the basis of the equilibrium geometries found using the 6-31+G(d) basis set for nonmetal atoms. The Hessian matrix was calculated analytically in order to prove the location of correct minima (no imaginary frequencies) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C.

(66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
(67) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789.
(68) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *Gaussian 03, revision C.02*; Gaussian, Inc.: Wallingford CT, 2004.
(69) Kuznetsov, M. L.; Kukushkin, V. Y.; Pombeiro, A. J. L. *Dalton Trans* **2008**, 1312–1322.
(70) Menezes, F. M. C.; Kuznetsov, M. L.; Pombeiro, A. J. L. *Organometallics* **2009**, *28*, 6593–6602.
(71) Kuznetsov, M. L.; Kukushkin, V. Y.; Pombeiro, A. J. L. *J. Org. Chem.* **2010**, *75*, 1474–1490.
(72) Kuznetsov, M. L.; Nazarov, A. A.; Kozlova, L. V.; Kukushkin, V. Y. *J. Org. Chem.* **2007**, *72*, 4475–4478.
(73) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.

The starting geometries were based on the experimental X-ray structures of **10** and **16** (this work).

Solvent effects (δE_s) were taken into account at the single-point calculations on the basis of the gas-phase geometries at the CPCM-B3LYP/6-31+G(d)//gas-B3LYP/6-31G level of theory using the polarizable continuum model in the CPCM version[74,75] with $CHCl_3$ taken as solvent. The UAKS model was applied for the molecular cavity. The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated by addition of the solvent effect δE_s to the gas-phase values H_g and G_g.

General Procedure for the Catalytic Sonogashira Cross-Coupling (Specific Conditions Provided in the Legend to Table 2 and Supporting Information). Oct-1-yne (0.550 g, 5.00 mmol), 1-iodo-2-nitrobenzene (0.610 g, 2.45 mmol), CuI (0.045 g, 9.60 mmol %) and PPh_3 (0.030 g, 4.60 mmol %) and selected base (K_2CO_3, 2.0 g, 14.5 mmol; Et_3N, 1.5 g, 14.5 mmol), were mixed in a round-bottom flask, followed by addition of a solution of the catalyst in EtOH (1 mL). All the reactions were performed under air. The flask was placed in a preheated oil bath at 60 °C and stirred for the required time. After cooling 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 joined and analyzed by ^1H NMR spectroscopy. The product peak assignments were based on authentic samples or on published data,[37,38,76,77] while quantifications were performed upon integration of the selected peak of the product relatively 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 (10:1 hexane/ethyl acetate, v/v).

Acknowledgment. This project has been supported by the Federal Aimed Program "Personnel", direction "Inorganic and Coordination Chemistry, Analytical Chemistry of Inorganic Compounds", in the framework of Subprogram 1.2.1 (Contracts P676 from 20.05.2010 and P1294 from 09.07.2010), Saint-Petersburg State University for research grant (2011), Russian Fund of Basic Research (Grants 09-03-00065 and 09-03-12173-ofi_m), and RAS Presidium Subprogram coordinated by Acad. N. T. Kuznetsov (Grant No. 18P). K.V.L. and M.L.K. express gratitude to the Fundação para a Ciência e a Tecnologia (FCT), Portugal (Project PTDC/QUI-QUI/098760/2008), and to both the FCT and the Instituto Superior Técnico (IST) for the research contracts (Ciência 2007 and 2008 Initiatives). The authors thank the Portuguese NMR Network (IST-UTL NMR Center) for providing access to the NMR facilities. Prof. V. P. Boyarskiy is thanked for stimulating discussions and valuable comments.

Supporting Information Available: Characterization of the amidinato and aminocarbene/aminocarbene-like species, X-ray crystal structure determinations of the Pd^{II} and Pt^{II} complexes with aminocarbene/aminocarbene-like ligands (including a cif file), catalytic procedures, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

(74) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027–2094.
(75) Barone, V.; Cossi, M. J. *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
(76) Urgaonkar, S.; Verkade, J. G., *J. Org. Chem.* **2004**, *69*, 5752−5755 and references therein.
(77) Liang, Y.; Xie, Y.-X.; Li, J.-H., *J. Org. Chem.* **2006**, *71*, 379−381 and references therein.