1224 *Organometallics* **2011,** *30,* 1224–1230
DOI: 10.1021/om101169x

ORGANOMETALLICS
Article

Reactivity Differences of Palladium(II) Dimers Bearing Heterocyclic Carbenes with Two, One, or No α-Nitrogen Atoms toward Isocyanides

Yuan Han, Dan Yuan, Qiaoqiao Teng, and Han Vinh Huynh*

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

Received December 11, 2010

Pd(II) dimers $[PdI_2(r\text{NHC})]_2$ (**1a**,**b**) of pyrazole-based *remote* N-heterocyclic carbenes (*r*NHCs) have been synthesized through oxidative addition of 4-iodopyrazolium iodides (**A, B**) to $[Pd_2(dba)_3]$. Reaction of **1a** with aromatic (CN-Xyl) or aliphatic (CN-Cy) isocyanides led to the template-assisted formation of novel Pd(II) dimers **8** and **9** bearing betainic *C*-imino ligands via isocyanide insertion into $Pd-C_{r\text{NHC}}$ bonds and subsequent dimerization. In contrast, both isocyanides reacted with the dimers $[PdI_2(Me_2\text{-indy})]_2$ (**2**) and $[PdI_2(Me_2\text{-bimy})]_2$ (**3**) bearing indazolin-3-ylidenes and benzimidazolin-2-ylidenes with formation of mononuclear mixed carbene/isocyanide complexes **4**−**7**. Notably, only dimer **8** underwent further bridge cleavage with excess isocyanide, yielding the mixed *C*-imino/CN-Xyl complex **10**, while dimer **9** remained intact. These results highlight the uniquely different reactivities of complexes with carbenes having no α-nitrogen versus those with one or two α-nitrogen atoms, as a result of their decreasing donor abilities.

Introduction

N-heterocyclic carbenes (NHCs) have met spectacular success in organometallic chemistry and transition-metal-mediated catalysis, primarily due to their strong electron-donating nature.[1] The stability of such classical NHCs has been primarily attributed to the push−pull electronic effect exerted by two α-nitrogen atoms. The more recent search for even stronger organometallic ligands has led to the discovery of nonconventional carbenes, including one-N, six-membered *remote* NHCs (*r*NHCs) by Raubenheimer et al.[2] and "carbodicarbenes" (CDCs) by Bertrand et al.,[3] in which the carbon donors do not contain any α-heteroatoms. As our contribution toward this development, we introduced two-N, five-membered *r*NHCs derived from pyrazole (pyrazolin-4-ylidenes) that are isomeric with classical imidazolin-2-ylidenes.[4] Likewise, these *r*NHC ligands contain carbon donors without adjacent α-nitrogen atoms. Instead, the electron-withdrawing heteroatoms are located two bonds away from the carbenoid center, which makes them strongly donating ligands. Since then, we have reported a series of structurally diverse mono-, di-, and tetranuclear Pd(II) complexes with mono- and bidentate bridging *r*NHC ligands that were obtained via oxidative addition of 4-iodopyrazolium salts to zerovalent palladium precursors in the presence of additional donors such as phosphine and pyridine.[5] Due to the fact that it is not possible to represent these pyrazolin-4-ylidenes with any neutral carbene resonance structure, they were classified as "*abnormal*" carbenes. However, it was recently suggested to use the more appropriate term "*mesoionic*" to describe such species.[6]

In our search for carbenes that are more donating than classical NHCs, we have also communicated the versatile coordination chemistry of indazolin-3-ylidenes.[7] In contrast, their carbon donor is adjacent to only one α-nitrogen atom, making them ligands with reduced heteroatom stabilization.[8]

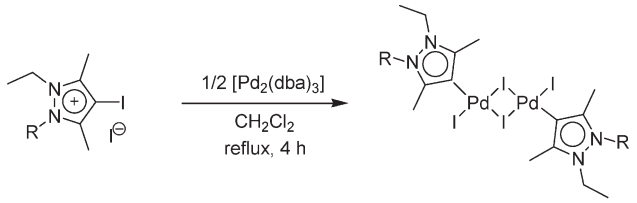
Mesoionic carbenes and carbenes with reduced heteroatom stabilization are increasingly gaining attention, and there are

*To whom correspondence should be addressed. E-mail: chmhhv@nus.edu.sg.

(1) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.
(2) (a) Meyer, W. H.; Deetlefs, M.; Pohlmann, M.; Scholz, R.; Esterhuysen, M. W.; Julius, G. R.; Raubenheimer, H. G. *Dalton Trans.* **2004**, 413. (b) Schneider, S. K.; Roembke, P.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2005**, 2973. (c) Schneider, S. K.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Dalton Trans.* **2006**, 1226.
(3) (a) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206. (b) Kaufhold, O; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4057.
(4) Han, Y.; Huynh, H. V. *Chem. Commun.* **2007**, 1089.
(5) (a) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 6581. (b) Han, Y.; Lee, L. J.; Huynh, H. V. *Organometallics* **2009**, *28*, 2778. (c) Han, Y.; Lee, L. J.; Huynh, H. V. *Chem. ur. J.* **2010**, *16*, 771. (c) Han, Y.; Huynh, H. V. *Dalton Trans.* **2011**, DOI: 10.1039/c0dt01037e.
(6) (a) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 4759. (b) Iglesias, M.; Albrecht, M. *Dalton Trans.* **2010**, *39*, 5213.
(7) Jothibasu, R.; Huynh, H. V. *Chem. Commun.* **2010**, *46*, 2986.
(8) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445.
(9) (a) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046. (b) Prades, A.; Viciano, M.; Sanaú, M.; Peris, E. *Organometallics* **2008**, *27*, 4254. (c) Yang, L.; Krüger, A.; Neels, A.; Albrecht, M. *Organometallics* **2008**, *27*, 3161. (d) Kong, Y.; Ren, H.; Xu, S.; Song, H.; Liu, B.; Wang, B. *Organometallics* **2009**, *28*, 5934. (e) Heckenroth, M.; Kluser, E.; Neels, A.; Albrecht, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6293. (f) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5282. (g) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albrecht, M. *Chem. Eur. J.* **2009**, *15*, 9375. (h) Stander-Grobler, E.; Schuster, O.; Heydenrych, G.; Cronje, S.; Tosh, E.; Albrecht, M.; Frenking, G.; Raubenheimer, H. G. *Organometallics* **2010**, *29*, 5821. (i) Raubenheimer, H. G.; Cronje, S. *Dalton Trans.* **2008**, 1265.

 Published on Web 02/10/2011

Scheme 1. Synthesis of Dimeric Pd(II) Pyrazolin-4-ylidene Complexes 1a,b



A: R = Me
B: R = Ph

1a: R = Me
1b: R = Ph

several studies, mainly on the catalytic activities, comparing them to classical NHCs.[9,6b] Apart from catalysis, we are not aware of any unified study on the different chemical reactivities of all three types of carbenes bearing two, one, or no α-nitrogen atom. Herein, we report on the syntheses and stabilities of phosphine- and pyridine-free pyrazolin-4-ylidene Pd(II) dimers, which broadens the structural scope of these unique ligands. Furthermore, we compare their reactivity toward isocyanides with that of their analogues bearing either NHCs with reduced heteroatom stabilization (indazolin-3-ylidene) or classical NHCs (benzimdazolin-2-ylidene). The different reactivities of Pd(II) pyrazolin-4-ylidene dimers shown here highlight their nature as one of the strongest neutral carbon donors known to date.

Results and Discussion

Palladium(II) Pyrazolin-4-ylidene Dimers. We previously reported the successful preparation of pyrazolin-4-ylidene complexes by oxidative addition of 4-iodopyrazolium iodide salts to $[Pd_2(dba)_3]$ in the presence of PPh_3 or pyridine as supporting ligand.[4,5] In the absence of any additional ligand, the formation of iodo-bridged dimeric complexes of the type $[PdI_2(rNHC)]_2$ is anticipated. Indeed, the reaction of 2 equiv of 4-iodopyrazolium iodides (**A**, **B**) with 1 equiv of $[Pd_2(dba)_3]$ in dry CH_2Cl_2 under reflux conditions proceeded smoothly to yield the desired dimeric products $[PdI_2(rNHC)]_2$ (*r*NHC = 1-ethyl-2,3,5-trimethylpyrazolin-4-ylidene (**1a**), 2-ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene (**1b**)) as red-brown solids in high yields of 75 and 86%, respectively (Scheme 1).

The air- and moisture-stable complexes **1a**,**b** are generally soluble in chlorinated and polar coordinating solvents such as CH_2Cl_2, CH_3CN, and DMSO but insoluble in the nonpolar solvents diethyl ether and toluene. Their identities were supported by the positive ESI mass spectra, which show isotopic envelopes centered at *m*/*z* 871 (**1a**) and 995 (**1b**), respectively, corresponding to the $[M - I]^+$ fragments. Their ^1H NMR spectra show little changes compared to those of their precursor salts (**A**, **B**). In the ^{13}C NMR spectrum of complex **1b,** the carbenoid signal was found at 112.7 ppm, which is more upfield than those of the complexes $[Pd(O_2CCF_3)_2(rNHC)(PPh_3)]$ (115.1 ppm) and $[PdI(rNHC)(PPh_3)_2]^+OTf^-$ (128.2 ppm) with the same pyrazolin-4-ylidene ligand,[4,5a] in line with a more Lewis acidic metal center due to the absence of additional phosphine donors. Nevertheless, this C4 signal in **1b** is still significantly more downfield by 40.1 ppm compared to the analogous resonance of the precursor salt **B**, suggesting a successful coordination of the pyrazolin-4-ylidene ligand. On the other hand, the ^{13}C carbene signal for complex **1a** could not be resolved, despite prolonged acquisition time, due to its poor solubility.

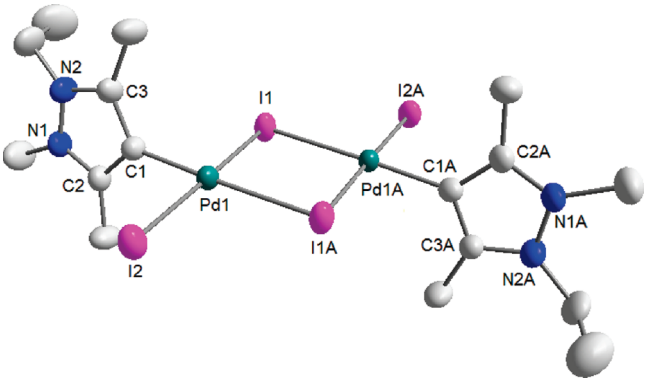


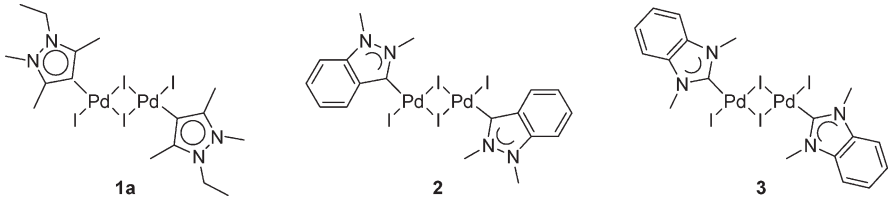
Figure 1. Molecular structure of **1a**·$4CH_2Cl_2$ showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 1.980(6), Pd1−I1 2.5719(15), Pd1−I2 2.5572(15), Pd1−I1A 2.6774(17), C1−C2 1.354(9), C1−C3 1.374(9), C3−N2 1.334(8), C2−N1 1.321(8), N1−N2 1.361(8); C1−Pd1−I1 89.25(19), C1−Pd1−I2 89.10(19), I1−Pd1−I1A 87.76(5), I2−Pd1−I1A 93.90(5), C2−C1−C3 106.0(6).

The identity of **1a** could be confirmed by an X-ray diffraction analysis on single crystals obtained by slow evaporation of a saturated CH_2Cl_2 solution. As depicted in Figure 1, each of the two Pd(II) centers is coordinated by one *r*NHC ligand and one terminal iodo and two bridging iodo ligands in a square-planar fashion. As is commonly observed, the *r*NHC ligands are oriented almost perpendicularly to the coordination plane with a dihedral angle of 77.45°. The $Pd-C_{carbene}$ bond length of 1.980(6) Å is identical with those found in the mononuclear phosphine complexes $[PdI_2(rNHC)(PPh_3)]$ (1.996(7) Å) and $[PdI(rNHC)(PPh_3)_2]^+OTf^-$ (2.004(9) Å) with the same *r*NHC ligand within the 3σ limit.[4,5a] Furthermore, among the three different types of Pd−I bonds, those trans to the *r*NHC ligand are significantly longer than the other two types due to the strong trans influence of the *r*NHC ligand.

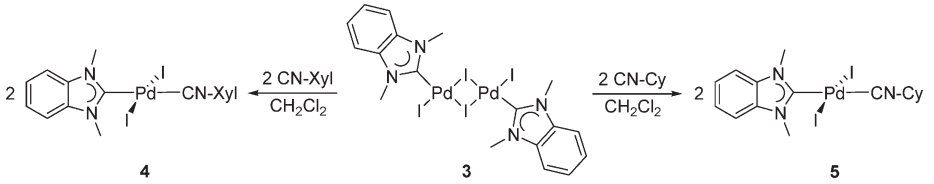
Reactivity of Palladium(II) Dimers toward Isocyanides. Monocarbene palladium(II) dimers can be easily cleaved by various donors to give mixed carbene/coligand complexes[10] that can be employed as useful precatalysts for certain organic transformations.[11] A range of such complexes bearing a constant carbene probe has also been synthesized to determine the donor strength of the respective coligand.[12] Of particular interest is the bridge-cleavage reaction with isocyanides, giving complexes with two different types of palladium−carbon bonds.[13] Alternatively, such complexes have also been synthesized through template-assisted reaction pathways.[14] In certain cases, insertion reactions of isocyanides into metal−carbon bonds have been observed. Such insertions have been extensively studied since the 1960s, owing to their fundamental importance in

(10) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267.
(11) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768.
(12) Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395.
(13) Han, Y.; Huynh, H. V. *Dalton Trans.* **2009**, 2201.
(14) (a) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175. (b) Tamm, M.; Hahn, F. E. *J. Chem. Soc., Chem. Commun.* **1995**, 569. (c) Flores-Figueroa, A.; Kaufhold, O.; Feldmann, K; Hahn, F. E. *Dalton Trans.* **2009**, 9334.

Chart 1. Dimeric Monocarbene Complexes with Different Degrees of Heteroatom Stabilization



Scheme 2. Bridge-Cleavage Reactions of a Dimeric Pd(II) Benzimidazolin-2-ylidene Complex



metal-mediated polymerization reactions.[15] Most studies in this field involved insertions into metal−aryl or metal−alkyl bonds, and only limited examples have been reported involving metal−carbene[16] and metal−heteroaryl compounds.[17] Therefore, we became interested in investigating how the Pd−C bond of the pyrazolin-4-ylidene dimer **1a** would interact with aromatic and aliphatic isocyanides, in comparison with its analogues **2**[7] and **3** bearing indazole- and benzimidazole-derived carbenes (Chart 1).

Palladium(II) Benzimidazolin-2-ylidene Dimer. The previously unknown dimer $[PdI_2(Me_2\text{-bimy})]_2$ (**3**; Me_2-bimy = 1,3-dimethylbenzimidazolin-2-ylidene) was straightforwardly synthesized by reacting 1 equiv of 1,3-dimethylbenzimidazolium iodide with 1 equiv of $Pd(OAc)_2$ with the addition of 4 equiv of NaI in DMSO at 90 °C, in analogy to the procedure for a bromido derivative.[10] The subsequent reaction of **3** with 2 equiv of 2,6-dimethylphenyl or cyclohexyl isocyanide (CN-Xyl or CN-Cy) in CH_2Cl_2 at ambient temperature afforded the mononuclear mixed carbene/isocyanide complexes *trans*-$[PdI_2(CN\text{-}Xyl)(Me_2\text{-bimy})]$ (**4**) and *trans*-$[PdI_2(CN\text{-}Cy)(Me_2\text{-bimy})]$ (**5**) in high yields of 80 and 94%, respectively (Scheme 2). A color change from red-brown to orange optically indicates the successful bridge-cleavage reactions.

These reactions turned out to be very selective, giving rise to only trans isomers, which is in stark contrast to analogous reactions of the bromido-bridged dimer $[PdBr_2(^iPr_2\text{-bimy})]_2$ ($^iPr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene), which always afforded mixtures of cis and trans isomers despite containing a more bulky NHC ligand.[13] It appears that the larger and more electron rich iodido ligands prefer a trans arrangement. The successful cleavage reaction with trans selectivity is supported by ^1H and ^{13}C NMR spectra of both compounds, which show only one set of signals for the carbene and isocyanide ligands, respectively. Upon coordination of the latter, the carbene signal in both complexes shifted significantly downfield to 171.3 ppm ($\Delta\delta$ = 14.3 ppm), indicating a more electron rich palladium center. In addition, strong absorption bands observed at 2189 cm^{-1} (**4**) and 2216 cm^{-1} (**5**) by IR spectroscopy (KBr pellet) indicate the presence of coordinated isocyanides.

The identities of **4** and **5** as trans complexes were further confirmed by X-ray diffraction analyses on single crystals obtained by slow evaporation of saturated dichloromethane solutions.[18]

Palladium(II) Indazolin-3-ylidene Dimer. Indazolin-3-ylidenes are isomeric with benzimidazolin-2-ylidenes but possess stronger donor ability due to the presence of only one electron-withdrawing α-nitrogen with respect to the carbene carbon.[7,12] In order to evaluate if such changes would induce any reactivity differences, the palladium(II) indazolin-3-ylidene dimer $[PdI_2(Me_2\text{-indy})]_2$ (**2**; Me_2-indy = 1,2-dimethylindazolin-3-ylidene) was also treated with 2 equiv of CN-Xyl and CN-Cy, respectively. In analogy to its isomer **3**, bridge-cleavage reactions of the brown complex **2** were observed for both isocyanides, giving the two new mixed indazolin-3-ylidene/isocyanide complexes *trans*-$[PdI_2(CN\text{-}Xyl)(Me_2\text{-indy})]$ (**6**) and *trans*-$[PdI_2(CN\text{-}Cy)(Me_2\text{-indy})]$ (**7**), which were isolated as yellow powders in yields of 83 and 65%, respectively (Scheme 3). In comparison to the parent dimer **2**, the solubilities of **6** and **7** in common organic solvents, with the exception of nonpolar hexane and diethyl ether, have also improved significantly.

ESI mass spectrometry and ^1H and ^{13}C NMR spectroscopy corroborated the similar reactivities, including trans selectivities, of the isomeric Pd(II) dimers **2** and **3**. For example, a pronounced downfield shift of the carbene resonance from 148.8 ppm (**2**)[7] to 164.9 (**6**) and 165.1 ppm (**7**), respectively, was also observed upon formation of the mononuclear complexes. The molecular structure of **6** (Figure 2),

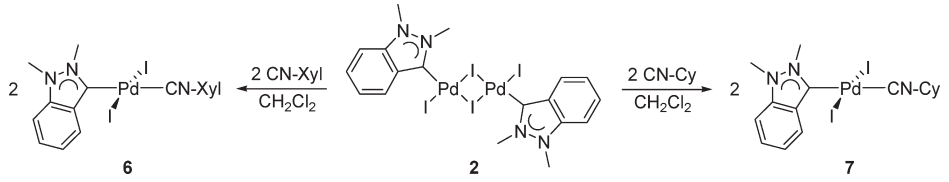
(15) (a) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225. (b) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 439. (c) Yamamoto, Y.; Tanase, T.; Yanai, T.; Asano, T.; Kobayashi, K. *J. Organomet. Chem.* **1993**, *456*, 287. (d) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L.; van Neer, F. J. P. *Organometallics* **1997**, *16*, 2948. (e) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587.

(16) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. (b) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 912. (c) Mitsudo, T.-A.; Watanabe, H.; Komiya, Y.; Watanabe, Y.; Takaegami, Y.; Nakatsu, K.; Kinoshita, K.; Miyagawa, Y. *J. Organomet. Chem.* **1980**, *190*, C39. (d) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. S. H.; Rettig, S. J.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 1707. (e) Cadierno, V.; García-Álvarez, J.; Gimeno, J.; Rubio-García, J. *J. Organomet. Chem.* **2005**, *690*, 5856. (f) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886. (g) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J. *Organometallics* **2008**, *27*, 1809.

(17) (a) Bertani, R.; Berton, A.; Bianca, D. F.; Crociani, B. *J. Organomet. Chem.* **1986**, *303*, 283. (b) Crociani, B.; Sala, M. *Organometallics* **1986**, *5*, 1369.

(18) The molecular structures of **4** and **5** are discussed separately in the Supporting Information.

Scheme 3. Bridge-Cleavage Reactions of a Dimeric Pd(II) Indazolin-3-ylidene Complex



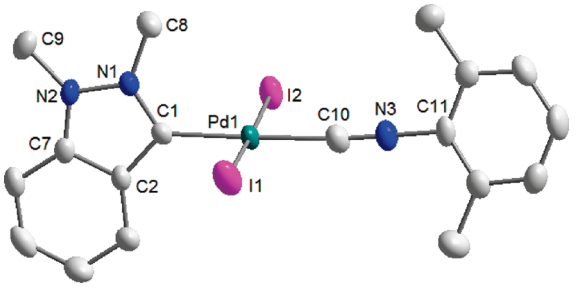


Figure 2. Molecular structure of complex **6** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 2.002(5), Pd1−C10 1.993(5), Pd1−I1 2.5925(6), Pd1−I2 2.5991(6), N1−C1 1.333(6), N1−C8 1.462(6), N1−N2 1.377(5), N2−C9 1.455(6), N2−C7 1.350(6), C7−C2 1.406(7), C10−N3 1.136(6), N3−C11 1.409(6); C1−Pd1−I1 89.01(14), C1−Pd1−I2 89.96(14), C10−Pd1−I1 89.95(17), C10−Pd1−I2 91.03(17), N1−C1−C2 105.0(4), C10−N3−C11 175.0(6).

determined by X-ray diffraction on single crystals obtained from a saturated dichloromethane solution, confirms the trans arrangement of the indazolin-3-ylidene and the isocyanide ligand around a square-planar palladium center with Pd−$C_{carbene}$ and Pd−C_{CN} bonds of 2.002(5) and 1.993(5) Å, respectively. The carbene plane is oriented almost perpendicularly to the PdC_2I_2 coordination plane with an angle of 83.42°. These and all other bond parameters are essentially in the range of those observed for benzimidazolin-2-ylidene analogues **4** and **5** and require no further comments.

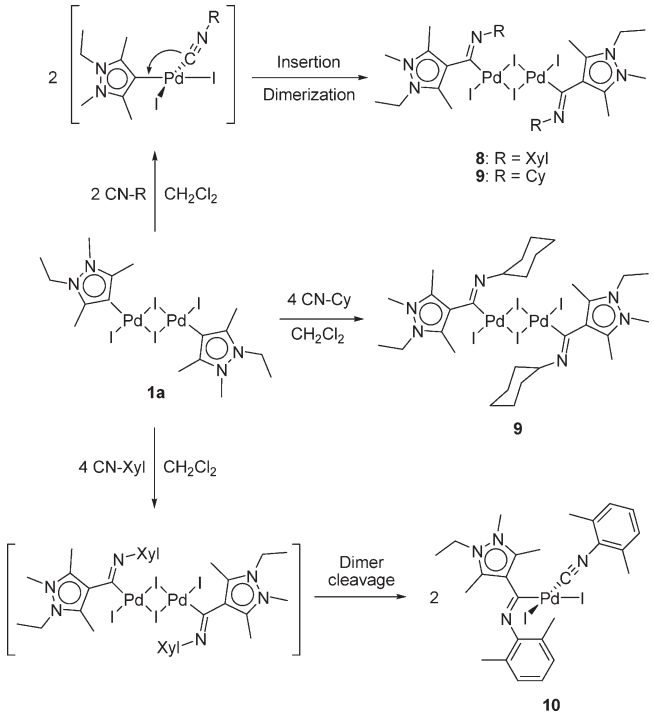
From these results it can be concluded that the increased donor ability of carbenes with reduced heteroatom stabilization compared to their classical NHC counterparts is still insufficient to induce different reactivities toward isocyanides.

Palladium(II) Pyrazolin-4-ylidene Dimer. Although pyrazolin-4-ylidenes and related ligands are among the strongest neutral donors reported to date, their chemistry is still underdeveloped. In this context, the question arises whether the superior electron donation would translate into any unique reactivity of their complexes. Thus, reactions of the dimeric pyrazolin-4-ylidene complex **1a** with 2 equiv of CN-Xyl and CN-Cy were carried out under the same conditions as described for dimers **2** and **3** (Scheme 4).

A distinct color change from red-brown **1a** to orange was observed for both isocyanides, indicating a successful reaction. However, the orange products **8** and **9** exhibit much poorer solubilities in comparison to the mixed carbene/isocyanide complexes **4**−**6** and precipitate from dichloromethane. Nevertheless, they can be dissolved in polar coordinating solvents, i.e. CH_3CN, DMSO, and DMF, which resembles properties of the dimeric Pd(II) complexes **1a**, **2**, and **3**.

More strikingly, their IR spectra show strong bands at 1627 and 1617 cm^{-1} indicative for C=N double bonds, while

Scheme 4. Insertion of Isocyanides into a Pd−*r*NHC Bond



bands for isocyanide C≡N triple bonds are absent. Furthermore, the values of these bands fall within the commonly observed range (1550−1650 cm^{-1}) for products resulting from isocyanide insertion into Pd−C bonds.[15c−e,17a,17b] Additional support for an isocyanide insertion was found in the ^1H NMR spectra of complexes **8** and **9**, which show downfield-shifted resonances for the pyrazole moiety with respect to those in the parent complex **1a**. The ^{13}C NMR signal for the new *C*=N−Xyl function of complex **8** arises at 148.7 ppm, whereas that for *C*=N−Cy in **9** was not resolved. Overall, these spectroscopic data in combination with the complex properties suggest that **8** and **9** are dimeric species, which have formed via isocyanide precoordination,[15d] isocyanide insertion, and subsequent dimerization (Scheme 4).

A final confirmation for this proposal was obtained by X-ray diffraction analysis on single crystals of the complex **9**·4CH_3CN, grown by slow evaporation of a CH_3CN solution, and its molecular structure is shown in Figure 3.

To our surprise, the dimeric structure of **9** was not cleaved by CH_3CN upon standing in solution for a few days. This is in contrast to our previously reported dimeric Pd(II) benzimidazolin-2-ylidene complex $[PdBr_2(^iPr_2\text{-bimy})]_2$, which could be easily cleaved by CH_3CN to form $[PdBr_2(CH_3CN)(^iPr_2\text{-bimy})]$.[10] Apparently, this Pd(II) dimer with iodido bridges is more stable than bromido analogues, possibly due to stronger soft−soft attractive interactions. In complex **9**, each palladium is surrounded by one newly formed *C*-imino and one terminal iodido and two bridging iodido ligands in a

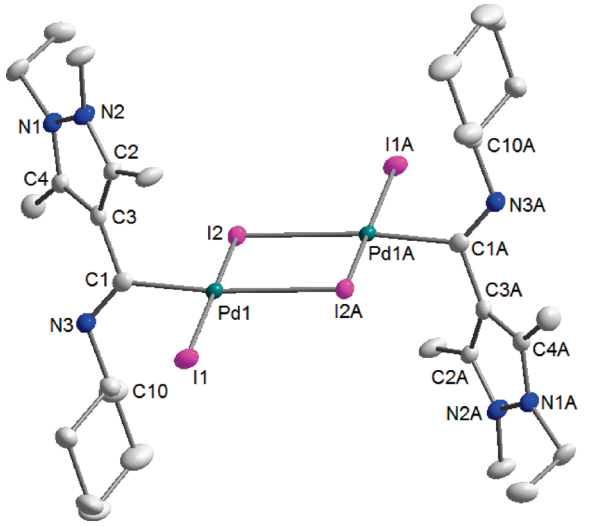


Figure 3. Molecular structure of $\mathbf{9}\cdot 4CH_3CN$ showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 1.980(4), Pd1−I1 2.6271(4), Pd1−I2 2.6290(4), Pd1−I2A 2.7765(4), C1−C3 1.489(5), C1−N3 1.261(5), C10−N3 1.466(5), N1−N2 1.361(4), N1−C4 1.350(4), N2−C2 1.346(4), C2−C3 1.407(5), C3−C4 1.401(5); C1−Pd1−I1 90.42(10), C1−Pd1−I2 86.91(10), I1−Pd1−I2A 95.230(14), I2−Pd1−I2A 87.937(13), C3−C1−N3 118.3(3), C1−N3−C10 120.9(3), C2−C3−C4 106.2(3).

nearly perfect square-planar fashion. The C3−C1−N3 imino plane forms a torsion angle of 75.20° relative to the $[PdCI_3]$ coordination plane. The Pd−C_{imino} bond length of 1.980(4) Å is essentially identical with the Pd−$C_{carbene}$ bond (1.980(6) Å) in **1a**. The Pd−I bond trans to the *C*-imino ligand, amounting to 2.7765(4) Å, is significantly longer than in the parent *r*NHC complex **1a** (2.6774(17) Å), indicating a stronger trans influence of the *C*-imino ligand. All bond parameters of the five-membered pyrazole moiety indicate aromatic character and are essentially the same as observed for pyrazolin-4-ylidenes. The C1−C3 bond that has newly formed through isocyanide insertion into the *r*NHC ligand amounts to 1.489(5) Å, which is in the range of a typical $C_{sp2}-C_{sp2}$ single bond. On the other hand, the C1−N3 distance of 1.261(5) Å has substantial double-bond character, which is also in line with the observed sp-to-sp^2 rehybridization of this CN fragment. Overall, the newly formed *C*-imino ligand can be considered as a betaine, in which the anionic C-donor atom is charge-separated from the cationic pyrazolium moiety.

As noted above, the iodido bridges of dimer **9** are very strong and remain intact in the presence of weak donors such as CH_3CN. This low tendency to undergo bridge-cleavage reactions may be explained by the increased electron density around the palladium center as a result of coordination of the very strongly donating *C*-imino ligand in **9**. In comparison, the *C*-imino ligand in **8**, containing a less electron donating xylyl group, should be a slightly weaker σ donor, which in turn may lead to a different reactivity. To test this concept, the bridge-cleavage reaction of **1a** was repeated, except with 4 equiv of both isocyanides (Scheme 4).

Interestingly, these isocyanides indeed reacted differently. In the reaction with 2,6-dimethylphenyl isocyanide, the monomeric complex **10** was isolated in a high yield of 70%, while the reaction with cyclohexyl isocyanide primarily afforded the dimeric complex **9** along with some unidentified byproduct. This may be due to the stronger $+I$ effect and more pronounced steric bulk of the cyclohexyl substituent compared to the 2,6-dimethylphenyl substituent. It is anticipated that the formation of **10** occurs through insertion of the aromatic isocyanide, giving rise to dimeric complex **8**, which is cleaved in situ by a second isocyanide. In its ^{1}H NMR spectrum, all resonances arising from the pyrazole moiety are shifted slightly downfield compared to those in **1a**. The resonances for all methyl groups of the two xylyl groups in complex **10** coincidentally overlapped, giving rise to one singlet at 2.19 ppm that integrates to 12 protons. The ^{13}C NMR signal for the *C*-imino donor was detected at 151.3 ppm. Furthermore, the IR spectrum of complex **10** shows two strong absorption bands at 2170 and 1623 cm^{-1} characteristic of the σ-coordinated isocyanide and the *C*-imino ligand, respectively. The formation of **10** is also supported by ESI mass spectrometry, which shows an isotopic pattern centered at m/z 633 for the $[M - I]^+$ complex fragment.

Due to the aforementioned reasons, in situ bridge cleavage reactions of dimeric **9** did not take place, which again highlights that changes in ligand donor ability can lead to significantly different reactivities of the resulting complexes.

Conclusion

In an attempt to broaden the structural and chemical scope of *r*NHC complexes, we have successfully prepared the iodido-bridged Pd(II) dimers $[PdI_2(rNHC)]_2$ (**1a**,**b**) with terminal monodentate pyrazolin-4-ylidene ligands via direct oxidative addition of 4-iodopyrazolium salts to Pd(0) in the absence of additional supporting ligands. Further treatment of complex **1a** with CN-Xyl and CN-Cy led to the formation of Pd(II) dimers **8** and **9**, bearing novel betainic *C*-imino ligands through isocyanide insertions. In contrast, analogous reactions of the Pd(II) dimers $[PdI_2(Me_2\text{-bimy})]_2$ (**3**) and $[PdI_2(Me_2\text{-indy})]_2$ (**2**), containing classical NHCs (benzimidazolin-2-ylidenes) and NHCs with reduced heteroatom stabilization (indazolin-3-ylidenes), respectively, afforded mixed NHC/isocyanide Pd(II) complexes **4**−**7** via simple bridge-cleavage reactions. The remarkably different reactivity of **1a** is attributed to the superior donor ability of pyrazolin-4-ylidenes with no α-nitrogen atoms compared to that of indazolin-3-ylidenes and benzimdazolin-2-ylidenes with one and two electron-withdrawing α-nitrogen atoms, respectively. Efforts to reveal further differences or similarities between nonclassical carbenes and their well-known conventional NHC counterparts are underway.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air or moisture, and all solvents and chemicals were used as received without any further treatment. If required, CH_2Cl_2 was dried over calcium hydride and distilled under nitrogen prior to use. Tris(dibenzylideneacetone)dipalladium(0) was received from Alfa Aesar. 1-Ethyl-4-iodo-2,3,5-trimethylpyrazolium iodide (**A**),[5a] 2-ethyl-4-iodo-3,5-dimethyl-1-phenylpyrazolium iodide (**B**),[5a] 1,3-dimethylbenzimidazolium iodide (**C**),[19] and the dimeric indazolin-3-ylidene complex **2**[7] were prepared according to reported procedures. ^{1}H and ^{13}C NMR spectra were recorded

(19) (a) Fischer, O. *Chem. Ber.* **1901**, *34*, 930. (b) Begtrup, M.; Larsen, P. *Acta Chem. Scand.* **1990**, *44*, 1050.

on a Bruker ACF 300 or AMX 500 spectrometer, and the chemical shifts (δ) were internally referenced to the residual protio solvent signals relative to tetramethylsilane. Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Infrared spectra were recorded with a Varian 3100 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Bis(μ-iodo)bis(1-ethyl-2,3,5-trimethylpyrazolin-4-ylidene)diiododipalladium(II) (1a). Tris(dibenzylideneacetone)dipalladium(0) (92 mg, 0.1 mmol) and **A** (78 mg, 0.2 mmol) were dissolved in dry CH_2Cl_2 (30 mL) and heated under reflux for 4 h under an inert nitrogen atmosphere. After it was cooled to ambient temperature, the resulting mixture was filtered through Celite, and the filtrate was extracted with H_2O (4 × 30 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was washed with pentane (3 × 30 mL) and dried in vacuo to give the crude product as a red-brown powder. Diffusion of pentane into a concentrated $CHCl_3$ solution afforded the pure product as a red-brown solid. Yield: 75 mg, 0.075 mmol, 75%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.11 (m, ^3J(H,H) = 7.2 Hz, 4 H, CH_2), 3.70 (s, 6 H, NCH_3), 2.59 (s, 6 H, CH_3), 2.58 (s, 6 H, CH_3), 1.30 (t, ^3J(H,H) = 7.2 Hz, 6 H, CH_2CH_3). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): 147.7, 146.9 (CCH_3), 42.2 (CH_2), 33.6 (NCH_3), 16.3, 16.0, 14.7 (CH_3), carbene signal not detected. Anal. Calcd for $C_{16}H_{28}I_4N_4Pd_2$: C, 19.28; H, 2.83; N, 5.62. Found: C, 19.31; H, 2.85; N, 5.53. MS (ESI): m/z 871 $[M - I]^+$.

Bis(μ-iodo)bis(2-ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene)-diiododipalladium(II) (1b). 1b was prepared analogously to **1a** from tris(dibenzylideneacetone)dipalladium(0) (92 mg, 0.1 mmol) and **B** (91 mg, 0.2 mmol). Yield: 97 mg, 0.086 mmol, 86%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64−6.62 (m, 6 H, Ar H), 7.31−7.30 (d, 4 H, Ar H), 3.91 (m, ^3J(H,H) = 7.2 Hz, 4 H, CH_2), 2.71 (s, 6 H, CH_3), 2.37 (s, 6 H, CH_3), 1.11 (t, ^3J(H,H) = 7.2 Hz, 6 H, CH_2CH_3). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 150.1, 149.6 (CCH_3), 133.7, 132.4, 131.2, 129.1 (Ar−C), 112.7 ($C_{carbene}$), 43.1 (CH_2), 17.2, 17.0, 15.5 (CH_3). Anal. Calcd for $C_{26}H_{32}I_4N_4Pd_2$: C, 27.86; H, 2.88; N, 5.00. Found: C, 27.32; H, 2.80; N, 4.54%. MS (ESI): m/z 995 $[M - I]^+$.

Bis(μ-iodo)bis(1,3-dimethylbenzimidazolin-2-ylidene)diiododipalladium(II) (3). A mixture of 1,3-dimethylbenzimidazolium iodide (**C**; 165 mg, 0.5 mmol), $Pd(OAc)_2$ (113 mg, 0.5 mmol), and NaI (300 mg, 2 mmol) in DMSO (10 mL) was stirred at 90 °C for 24 h. The reaction mixture was filtered over Celite, and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was washed with H_2O (4 × 20 mL) and dried in vacuo to afford the product as a red-brown solid (177 mg, 0.18 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (dd, 4 H, Ar H), 7.35 (dd, 4 H, Ar H), 4.02 (s, 12 H, NCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 157.0 ($C_{carbene}$), 134.3, 123.1, 110.5 (Ar C), 35.4 (NCH_3). Anal. Calcd for $C_{18}H_{20}I_4N_4Pd_2$: C, 21.35; H, 1.99; N, 5.53. Found: C, 21.45; H, 2.04; N, 5.16. MS (ESI): m/z 1035 $[M + Na]^+$.

Diiodo(1,3-dimethylbenzimidazolin-2-ylidene)(2,6-dimethylphenyl isocyanide)palladium(II) (4). 2,6-Dimethylphenyl isocyanide (26 mg, 0.20 mmol) was added to a suspension of **3** (101 mg, 0.10 mmol) in dichloromethane (12 mL). The reaction mixture was stirred at ambient temperature for 24 h. The volatiles were removed under reduced pressure. The residue was washed with hexane (3 × 15 mL) and dried in vacuo to afford the product as an orange solid (102 mg, 0.16 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (dd, 2 H, Ar H), 7.31 (dd, 2 H, Ar H), 7.22 (ps. dd, 1 H, Ar H), 7.12 (ps. d, 2 H, Ar H), 4.07 (s, 6 H, NCH_3), 2.56 (s, 6 H, Ar CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 171.3 ($C_{carbene}$), 137.1, 135.8, 130.6, 128.7, 126.4, 123.8, 110.7 (Ar C), 36.1 (NCH_3), 19.7 (Ar CH_3). The C≡N signal could not be detected. IR (KBr pellet): 2189 cm^{-1} (s, C≡N). Anal. Calcd for $C_{18}H_{19}I_2N_3Pd$: C, 33.91; H, 3.00; N, 6.59. Found: C, 33.88; H, 2.85; N, 6.58. MS (ESI): m/z 656 $[M + NH_4]^+$.

Diiodo(cyclohexyl isocyanide)(1,3-dimethylbenzimidazolin-2-ylidene)palladium(II) (5). Complex **5** was prepared analogously to **4** from **3** (101 mg, 0.10 mmol) and cyclohexyl isocyanide (25 μL, 0.20 mmol), yielding the product as an orange solid (116 mg, 0.19 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (dd, 2 H, Ar H), 7.27 (dd, 2 H, Ar H), 4.01 (s, 6 H, NCH_3), 3.97 (m, 1 H, C≡NCH), 1.95−1.74 (br m, 6 H, CH_2), 1.52−1.36 (br m, 4 H, CH_2). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 171.3 ($C_{carbene}$), 135.6 (Ar C), 128.0 (br t, C≡N), 123.6, 110.6 (Ar C), 55.0 (C≡N*C*), 36.0 (NCH_3), 32.3, 25.4, 22.9 (CH_2). IR (KBr pellet): 2216 cm^{-1} (s, C≡N). Anal. Calcd for $C_{16}H_{21}I_2N_3Pd$: C, 31.22; H, 3.44; N, 6.83. Found: C, 31.29; H, 3.38; N, 6.77. MS (ESI): m/z 597 $[M - I + C_7H_{11}N]^+$.

Diiodo(1,2-dimethylindazolin-3-ylidene)(2,6-dimethylphenyl isocyanide)palladium(II) (6). 2,6-Dimethylphenyl isocyanide (14 mg, 0.108 mmol) was added to a suspension of indazolin-3-ylidene Pd(II) dimer **2** (55 mg, 0.054 mmol) in dichloromethane (5 mL). The resulting yellow solution was stirred at ambient temperature overnight. All the volatiles were removed in vacuo, and the resulting solid was washed with diethyl ether (3 × 10 mL) to give the product as a yellow powder (57 mg, 0.089 mmol, 83%) upon drying. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, 1 H, Ar H), 7.59 (t, 1 H, Ar H), 7.29−7.19 (m, 3 H, Ar H), 7.11 (ps. d, 2 H, Ar H), 4.35 (s, 3 H, NMe), 3.94 (s, 3 H, NMe), 2.57 (s, 6 H, Me). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 164.9 ($C_{carbene}$), 141.0, 137.1, 132.5, 131.0, 130.4, 130.0, 128.7, 126.7, 123.0, 109.3 (Ar C), 41.4, 34.1 (NCH_3), 19.8 (Me), C≡N signal could not be detected. IR (KBr pellet): 2185 (s, C≡N) cm^{-1}. Anal. Calcd for $C_{18}H_{19}I_2N_3Pd$: C, 33.91; H, 3.00; N, 6.59. Found: C, 33.85; H, 2.71; N, 6.52. MS (ESI): m/z 642 $[M - I + C_9H_9N]^+$, 1017 $[2\,M - I - C_9H_9N]^+$, 1148 $[2\,M - I]^+$.

Diiodo(cyclohexyl isocyanide)(1,2-dimethylindazolin-3-ylidene)-palladium(II) (7). Complex **7** was synthesized analogously to **6** by reacting cyclohexyl isocyanide (7.5 μL, 0.060 mmol) with indazolin-3-ylidene Pd(II) dimer **2** (30 mg, 0.030 mmol) in CH_2Cl_2 (5 mL) to afford a yellow solid (24 mg, 0.039 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, 1 H, Ar H), 7.57 (t, 1 H, Ar H), 7.26 (t, 1 H, Ar H), 7.18 (d, 1 H, Ar H), 4.32 (s, 3 H, NMe), 3.98 (br m, 1 H, NCH), 3.94 (s, 3 H, NMe), 1.89 (br s, 6 H, CH_2), 1.47 (br s, 4 H, CH_2). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 165.1 ($C_{carbene}$), 141.0, 132.5, 131.1, 130.1, 123.0, 109.2 (Ar C), 55.0 (CH), 41.3, 34.0 (NCH_3), 32.6, 25.6, 23.1 (CH_2), C≡N signal could not be detected. IR (KBr pellet): 2209 (s, C≡N) cm^{-1}. Anal. Calcd for $C_{16}H_{21}I_2N_3Pd$: C, 31.22; H, 3.44; N, 6.83. Found: C, 31.65; H, 3.40; N, 6.78. MS (ESI): m/z 598 $[M - I + C_7H_{11}N]^+$.

Bis(μ-iodo)bis(2,6-dimethylphenyl-*C*-imino)diiododipalladium(II) (8). 2,6-Dimethylphenyl isocyanide (20 mg, 0.15 mmol) was added to a suspension of **1a** (75 mg, 0.075 mmol) in dichloromethane (8 mL). The reaction mixture was stirred at ambient temperature for 24 h. The orange precipitate was collected by filtration, washed with small portions of dichloromethane, and then dried in vacuo to give the product as an orange powder. The dichloromethane filtrate was concentrated to 2 mL, which upon stirring at ambient temperature afforded a second crop of the product. Overall yield: 78 mg, 0.062 mmol, 83%. ^{1}H NMR (500 MHz, d_6-DMSO): δ 6.92−6.83 (m, 3 H, Ar H), 4.50 (m, ^3J(H,H) = 7.0 Hz, 2 H, CH_2), 4.00 (s, 3 H, CH_3), 2.94 (s, 3 H, $NCCH_3$), 2.92 (s, 3 H, $NCCH_3$), 2.35 (s, 6 H, CH_3), 1.33 (t, ^3J(H,H) = 7.0 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} NMR (125.76 MHz, d_6-DMSO): 148.7 (*C*=N−Xy), 143.0, 142.0 ($NCCH_3$), 128.1, 127.5, 126.5, 122.1 (Ar C), 41.4 (CH_2), 33.4 (NCH_3), 21.8, 18.0, 13.8, 13.5, 13.1 (CH_3), C4-pyr not detected. IR (KBr pellet): 1627 (s, C=N−Xy) cm^{-1}. Anal. Calcd for $C_{34}H_{46}I_4N_6Pd_2$: C, 32.43; H, 3.68; N, 6.67. Found: C, 32.22; H, 3.77; N, 6.61. MS (ESI): m/z 1261 $[M + H]^+$, 1133 $[M - I]^+$, 580 $[^1/_2\,M - I + DMSO]^+$.

Bis(μ-iodo)bis(cyclohexyl-*C*-imino)diiododipalladium(II) (9). Cyclohexyl isocyanide (19 μL, 0.15 mmol) was added to a suspension of **1a** (75 mg, 0.075 mmol) in dichloromethane (8 mL). The reaction mixture was stirred at ambient temperature for 24 h. The orange precipitate was collected by filtration, washed with small portions of dichloromethane, and then dried in vacuo to give the product as an orange powder (66 mg, 0.054 mmol, 72%). ^{1}H NMR (300 MHz, CD_3CN): δ 4.37 (m, 1 H, CH), 4.29 (m, ^3J(H,H) = 7.2 Hz, 2 H, CH_2CH_3), 3.80 (s, 3 H,

Table 1. Selected X-ray Crystallographic Data for Complexes 1a·4CH_2Cl_2, 6, and 9·4CH_3CN

	1a·4CH_2Cl_2	**6**	**9**·4CH_3CN
formula	$C_{16}H_{28}I_4N_4Pd_2 \cdot C_4H_8Cl_8$	$C_{18}H_{19}I_2N_3Pd$	$C_{30}H_{50}I_4N_6Pd_2 \cdot C_8H_{12}N_4$
fw	1336.53	637.56	1379.38
color, habit	orange, block	yellow, block	orange, block
cryst size (mm)	0.70 × 0.14 × 0.10	0.38 × 0.18 × 0.10	0.54 × 0.16 × 0.08
temp (K)	223(2)	223(2)	100(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.306(8)	17.9130(12)	8.7000(11)
b (Å)	10.916(8)	7.7294(5)	10.0247(13)
c (Å)	10.961(9)	15.4981(10)	15.825(2)
α (deg)	66.564(17)	90	81.020(3)
β (deg)	75.026(16)	107.899(2)	85.403(3)
γ (deg)	80.789(16)	90	66.200(20)
V (Å^3)	984.9(13)	2042.0(2)	1247.1(3)
Z	1	4	1
D_c (g cm^{-3})	2.253	2.074	1.837
radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	4.609	3.937	3.232
θ range (deg)	2.04−27.50	2.39−27.50	2.24−27.49
no. of unique data	4446	4676	5698
max, min transmn	0.6557, 0.1407	0.6942, 0.3162	0.7820, 0.2742
final R indices ($I > 2\sigma(I)$)	R1 = 0.0467, wR2 = 0.1265	R1 = 0.0437, wR2 = 0.0986	R1 = 0.0320, wR2 = 0.0805
R indices (all data)	R1 = 0.0610, wR2 = 0.1362	R1 = 0.0560, wR2 = 0.1037	R1 = 0.0368, wR2 = 0.0829
goodness of fit on F^2	1.038	1.058	1.015
peak/hole (e Å^{-3})	1.335/−0.951	2.113/−1.051	1.704/−0.568

NCH_3), 2.94 (s, 3 H, $NCCH_3$), 2.93 (s, 3 H, $NCCH_3$), 2.05−2.02 (m, 2 H, CH_2), 1.75−1.64 (m, 3 H, CH_2), 1.45−1.39 (m, 4 H, CH_2), 1.34−1.29 (m, 4 H, CH_2 and CH_2CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): 145.0, 143.9 ($NCCH_3$), 125.5 ($CC{=}N{-}Cy$), 69.8 (CH), 42.7 (CH_2CH_3), 34.2 (NCH_3), 33.2, 27.0, 25.3 (CH_2), 14.7, 14.4, 14.3 (CH_3), $C{=}N{-}Cy$ not detected. IR (KBr pellet): 1617 (s, C=N−Cy) cm^{-1}. Anal. Calcd for $C_{30}H_{50}I_4N_6Pd_2$: C, 29.65; H, 4.15; N, 6.92. Found: C, 29.07; H, 4.21; N, 6.65. MS (ESI): m/z 649 [1/2 M + CH_3CN + H]$^+$.

Diiodo(2,6-dimethylphenyl-*C*-imino)(2,6-dimethylphenyl isocyanide)palladium(II) (10). 2,6-Dimethylphenyl isocyanide (21 mg, 0.16 mmol) was added to a suspension of **1a** (40 mg, 0.04 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at ambient temperature for 24 h. The orange precipitate was filtered off, and the solvent of the filtrate was removed under reduced pressure to afford a yellow solid. Slow evaporation of a concentrated dichloromethane/toluene solution afforded the analytically pure product as yellow crystals (43 mg, 0.056 mmol, 70%). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.21 (t, ^3J(H,H) = 7.6 Hz, 1 H, Ar H), 7.07 (d, ^3J(H,H) = 7.6 Hz, 2 H, Ar H), 6.86−6.82 (m, 3 H, Ar H), 4.38 (m, ^3J(H,H) = 7.6 Hz, 2 H, CH_2), 3.96 (s, 3 H, NCH_3), 2.92 (s, 3 H, $NCCH_3$), 2.91 (s, 3 H, $NCCH_3$), 2.19 (s, 12 H, CH_3), 1.49 (t, ^3J(H,H) = 7.6 Hz, 3 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2): 151.3 ($C{=}N{-}Xy$), 143.8, 143.0 ($NCCH_3$), 135.0, 129.1, 128.3, 127.87, 127.83, 126.7, 123.3 (Ar C), 42.3 (CH_2), 33.7 (NCH_3), 19.8, 18.7, 14.4, 12.6, 12.4 (CH_3), $C{\equiv}N{-}Xy$ and C4-pyr not detected. IR (KBr pellet): 2170 (s, C≡N−Xy) cm^{-1}, 1623 (s, C=N−Xy) cm^{-1}. Anal. Calcd for $C_{26}H_{32}I_2N_4Pd$: C, 41.05; H, 4.24; N, 7.36. Found: C, 41.23; H, 4.22; N, 7.21. MS (ESI): m/z 633 [M − I]$^+$.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K (**4** and **9**·4CH_3CN) or 223(2) K (**1a**·4CH_2Cl_2, **5**, and **6**), with the SMART suite of programs.[20] Data were processed and corrected for Lorentz and polarization effects with SAINT[21] and for absorption effect with SADABS.[22] Structure solution and refinement were carried out with the SHELXTL suite of programs.[23] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Table 1.

Acknowledgment. We thank the National University of Singapore for financial support (Grant No. R 143-000-410-112) and the CMMAC staff of our department for technical assistance.

Supporting Information Available: Text, figures, and a table giving a detailed discussion, selected crystallographic data, and molecular structures of **4** and **5** and CIF files giving crystallographic data for **1a**·4CH_2Cl_2, **4**−**6**, and **9**·4CH_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

(20) *SMART version 5.628*; Bruker AXS Inc., Madison, WI, 2001.
(21) *SAINT+ version 6.22a*; Bruker AXS Inc., Madison, WI, 2001.
(22) Sheldrick, G. W. *SADABS version 2.10*; University of Göttingen, Göttingen, Germany, 2001.
(23) *SHELXTL version 6.14*; Bruker AXS Inc., Madison, WI, 2000.