13C NMR Spectroscopic Determination of Ligand Donor Strengths Using N-Heterocyclic Carbene Complexes of Palladium(II)

ARTICLE *in* ORGANOMETALLICS · SEPTEMBER 2009

Impact Factor: 4.13 · DOI: 10.1021/om900667d

4 AUTHORS, INCLUDING:

Han Vinh Huynh
National University of Singapore
93 PUBLICATIONS **2,271** CITATIONS

SEE PROFILE

Jothibasu Ramasamy
King Abdullah University of Science and Tec…
12 PUBLICATIONS **331** CITATIONS

SEE PROFILE

ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 5395–5404 5395
DOI: 10.1021/om900667d

^{13}C NMR Spectroscopic Determination of Ligand Donor Strengths Using N-Heterocyclic Carbene Complexes of Palladium(II)

Han Vinh Huynh,* Yuan Han, Ramasamy Jothibasu, and Jie An Yang

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

Received July 28, 2009

The electronic parameters of 25 Werner-type and organometallic ligands have been experimentally determined and ranked on a unprecedented unified ^{13}C NMR scale using safe and easily obtainable complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)L]$^{n-}$ (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; L = ligand in question) as spectroscopic probes. The methodology is based on the sensitivity of the constant ^{i}Pr$_2$-bimy carbene signal to the donor strengths of the varying co-ligands, which even allows detection of backbone and substituent effects more accurately than previous carbonyl-based systems. For the evaluation of N-heterocyclic carbenes (NHCs), a one-pot approach to novel hetero-bis(carbene) complexes bearing two different NHCs is introduced. Furthermore, the first complex of a strongly donating indazolin-3-ylidene ligand is presented. The molecular structures of 10 complex probes have been characterized by single-crystal X-ray diffraction analyses.

Introduction

The properties and chemical reactivities of transition metal complexes are mainly determined by the electronic and steric effects imposed by the ligands. It is thus not surprising that much effort has been made to determine their donor capabilities. The most impactful experimental method is undoubtedly Tolman's electronic parameter (TEP), which compares the A_1 CO vibrational modes observed in the IR spectra of [Ni(CO)$_3$PR$_3$] complexes to determine the relative donor strengths of many phosphines contributing to their major impact as ligands in catalysis and organometallic chemistry.[1] The second major electronic parameter, developed by Lever, is based on electrochemical E_0 values of a redox couple (e.g., Ru$^{II/III}$) of complexes bearing the ligands of interest (LEP).[2] Using this method, the donor strengths of a wide range of common Werner-type ligands have been evaluated, which were not accessible by TEP. Although both methods have provided valuable insights for the characterization of ligands, they are encumbered by complicated synthetic or relatively uncommon analytical routes. For example, TEP determination requires utmost caution in the handling of the extremely toxic gas [Ni(CO)$_4$]. The limitations of LEP, on the other hand, are the requirement for less common electrochemical apparatus and the destructive nature of this analytical method (e.g., irreversible redox chemistry). It has also been noted that only few ligands appear in both TEP and LEP series, making a direct comparison difficult.[3] In analogy to phosphines, the electronic properties of N-heterocyclic carbenes (NHCs), which have gained immense popularity as highly nucleophilic organocatalysts[4] and ligands in organometallic chemistry,[5,6] are generally[7] determined by measuring the CO vibrational frequencies in low-valent mixed NHC-carbonyl complexes such as [Ni(CO)$_3$NHC][8] or [MX(CO)$_2$(NHC)] (M = Ir(I)[9] or Rh(I),[10] X = halide) as a modification of TEP. In these systems, it is assumed that the amount of π-back-donation to CO is directly related to the donor strength of the NHC. On the other hand, non-negligible π-back-donation from the electron-rich low-valent metal center to the NHC competing with that to the CO has not been accounted for,[11] although this contributes to inconsistent results. Furthermore, some authors rely on the *trans*-CO stretching frequencies, whereas others base their

*Corresponding author. E-mail: chmhhv@nus.edu.sg.

(1) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(2) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.
(3) Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806.
(4) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.
(5) (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
(6) (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (b) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
(7) Alternative less common experimental methods for characterizing the donor strengths of NHCs include calorimetric (see Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322) and cyclic voltammetric studies (see ref 9b and (a) Süssner, M.; Plenio, H. *Chem. Commun.* **2005**, 5417. (b) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648.
(8) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.
(9) (a) 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. (b) Leuthäusser, S.; Schwarz, D.; Plenio, H. *Chem. Eur. J.* **2007**, *13*, 7195. (c) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461.
(10) (a) Bittermann, A.; Härter, P.; Herdtweck, E.; Hoffmann, S. D.; Herrmann, W. A. *J. Organomet. Chem.* **2008**, *693*, 2079. (b) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.
(11) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755.

Published on Web 09/03/2009

parameters on the average CO stretching frequency of the *cis*- and the *trans*-disposed CO ligands. Other major drawbacks are associated with the preparation of the respective complexes, which requires either the handling of highly air/moisture-sensitive compounds such as free NHCs and, as mentioned above, extremely toxic [$Ni(CO)_4$], or the use of expensive Rh and Ir precursors as well as highly toxic CO gas.

As our contribution to overcome these limitations, we herein introduce a convenient, safe, and nondestructive new electronic parameter for the unified evaluation and comparison of Werner-type and organometallic ligands such as phosphines and NHCs, which is based on a ^{13}C NMR spectroscopic evaluation of a carbonyl-free mixed NHC/co-ligand Pd(II) system.

Results and Discussion

Previously, others[12] and we[13] have observed that the ^{13}C NMR chemical shift of the carbene carbon in NHC complexes is sensitive to the Lewis acidity of the metal center, which in turn is obviously influenced by the donor abilities of the co-ligands. Such a trend is apparent in complexes of the type *trans*-[$PdBr_2(^iPr_2$-bimy)L]$^{n-}$ [$^iPr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; L = $NCCH_3$ ($n = 0$), pyridine ($n = 0$), Br^- ($n = 1$), $^iPr_2$-bimy ($n = 0$)], in which the carbene resonance of the constant $^iPr_2$-bimy ligand shifts downfield with increasing donor strength of the *transoid* ligand L (here: $CH_3CN < Br^- < Py < {}^iPr_2$-bimy; Table 1, entries 1−4).[13−15] A detailed comparison of the respective chemical shifts in recently reported derivatives bearing isocyanides and primary amines as co-ligands further substantiates this claim (Table 1, entries 5−7).[16] It is anticipated that an extension to mixed-ligand complexes of the type *trans*-[$PdBr_2(^iPr_2$-bimy)L] bearing various imidazoles, phosphines, and NHC co-ligands should enable the direct comparison of these Werner-type and organometallic ligands on the same scale by determining the $^iPr_2$-bimy carbene shift. The *trans*-standing $^iPr_2$-bimy probe is hereby chosen, because it is least influenced by any steric effects and hence enables the most rigorous assessment of the electronic properties of the ligand in question.

Imidazoles. The synthesis of the respective $^iPr_2$-bimy/imidazole mixed-ligand complexes is straightforward and involves a common bridge-cleavage reaction of the easily available dimeric complex [$PdBr_2(^iPr_2$-bimy)]$_2$ (**1**) with 2 equiv of imidazole, *N*-methylimidazole, and *N*-phenylimidazole (Scheme 1). These three Werner-type ligands differing only in their N-substituents three bonds away from the N-donor have been chosen to test if our proposed electronic parameter can resolve possible remote substituent effects on the donor ability.

The desired complexes *trans*-[$PdBr_2(^iPr_2$-bimy)(Ph-imd)] (**2**), *trans*-[$PdBr_2(^iPr_2$-bimy)(Imd)] (**3**), and *trans*-[$PdBr_2$-($^iPr_2$-bimy)(Me-Imd)] (**4**) were all obtained as yellow solids in yields of > 89%. With the exception of nonpolar solvents such as alkanes, diethyl ether, and toluene, all complexes are well soluble in common organic solvents. Their formation is confirmed by ESI mass spectrometry and ^1H and ^{13}C NMR spectroscopies, which show the presence of the respective co-ligand. More important, the ^{13}C NMR shifts of the carbene carbon atoms are observed at 161.1 (**2**), 161.4 (**3**), and 161.6 ppm (**4**), respectively, indicating increasing donor strength in the order N-phenylimidazole < imidazole < *N*-methylimidazole, which is in agreement with the increasing positive inductive effects (+*I* effects) of the respective N-substituents (Table 1, entries 9, 10). These encouraging results demonstrate that the carbene shift is even sensitive enough to detect small electronic differences brought about remote modifications of the co-ligands.

Table 1. Summary of All $^iPr_2$-bimy Carbenoid Resonances in *trans*-[$PdBr_2(^iPr_2$-bimy)L] Complexes

entry	ligand L (complex no.)	$\delta C_{carbene}$ ($^iPr_2$-bimy)[a]	Pd−$C_{carbene}$ ($^iPr_2$-bimy) [Å]
1	CH_3CN[13]	158.4	1.9359(19)
2	Py[13]	160.0	1.953(4)
3	Br^-[13]	165.6	1.951(5)
4	$^iPr_2$-bimy[15]	180.6	2.017(2)
5	H_2N-Xyl[16]	160.1	
6	CN-Xyl[16]	168.8	1.992(2)
7	CN-Cy12[16]	169.1	1.984(9)
8	Ph-Imd (**2**)	161.1	
9	Imd (**3**)	161.4	1.943(2)
10	Me-Imd (**4**)	161.6	1.952(3)
11	PPh_3 (**5**)	173.1[b]	
12	P*m*Tol_3 (**6**)	173.6[b]	
13	PCy_3 (**7**)	176.4[b]	
14	**A** (**8**)	180.1	2.022(6)
15	**B** (**9**)	179.0	2.020(3)
16	**C** (**10**)	178.3[c]	2.014(3)
17	**D** (**11**)	176.6[b,c]	
18	**E** (**12**)	178.3[b]	2.018(4)
19	**IMes** (**13**)	177.2[c]	2.001(3)
20	**SIMes** (**14**)	177.6	2.008(2)
21	**IPr** (**15**)	177.5[c]	1.998(7)
22	**SIPr** (**16**)	177.6	
23	**Indy** (**17**)	181.6[c]	2.019(6)
24	***a*NHC** (**18**)	181.9	
25	**Pyry** (**19**)	182.4	

[a] Measured in $CDCl_3$ and internally referenced to the solvent residual signal at 77.7 ppm relative to TMS. [b] Confirmed by ^{13}C-labeled $^iPr_2$-bimy. [c] Confirmed by HMBC NMR spectroscopy.

Phosphines. Phosphines are a special class of ligands, in which the σ-donor strength is approximately inverse to the π-acceptor ability. Thus strongly donating trialkylphosphines are usually weak and negligible π-acceptors incapable of competing with CO ligands for π-back-donation from low-valent metal centers. This also explains the success of the TEP method in determining their donor abilities. In order to probe the electronic properties of phosphines using our electronic parameter, mixed NHC/phosphine complexes with a *trans*-configuration are required. However, it has been reported that such complexes slowly isomerize to the more preferred *cis* form due to the transphobia effect,[17] which would hamper data collection. To circumvent this problem, we have explored the feasibility of ^{13}C labeling the carbene donor in the $^iPr_2$-bimy ligand. For this purpose, $H^{13}COOH$ can be condensed with 1,2-phenylenediamine to give ^{13}C-labeled benzimidazole. Dialkylation of the latter with

(12) (a) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2005**, 37. (b) Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, 501, Cl.

(13) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 6447.

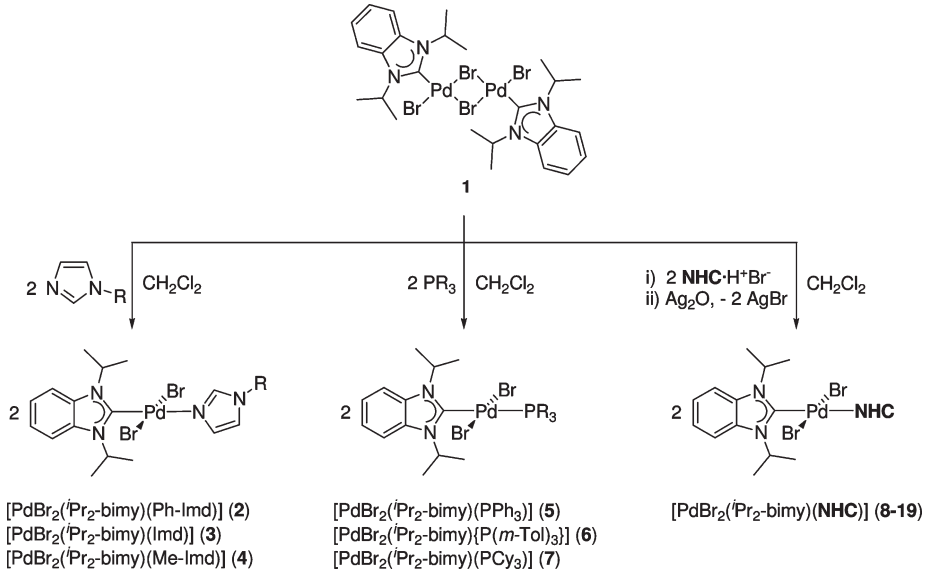
(14) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267.

(15) Han, Y.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2007**, *692*, 3606.

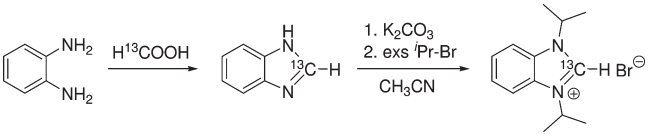
(16) Han, Y.; Huynh, H. V. *Dalton Trans.* **2009**, 2201.

(17) (a) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (b) Han, Y.; Lee, L. J.; Huynh, H. V. *Organometallics* **2009**, *28*, 2778. (c) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267.

Scheme 1. Synthesis of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)L] Complexes, Where L = Imidazoles, Phosphines, and N-Heterocyclic Carbenes



Scheme 2. Synthesis of ^{13}C-Labeled 1,3-Diisopropylbenzimidazolium Bromide



an excess of isopropyl bromide afforded 1,3-diisopropylbenzimidazolium bromide (Scheme 2) as a precursor to ^{13}C-labeled complex **1**, which in turn offered easy access to the ^{13}C-labeled mixed NHC/phosphine complexes *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(PPh_3)] (**5**), *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(P{*m*-Tol}$_3$)] (**6**), and *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(PCy_3)] (**7**).

The NMR spectroscopic detection of the ^{i}Pr_2-bimy $^{13}C_{carbene}$ signal in these complexes can even be accomplished by a single scan (Table 1, entries 11−13). The ^{i}Pr_2-bimy $^{13}C_{carbene}$ signals of all three phosphine complexes were found more downfield than those with isocyanide ligands, corroborating the superior donor abilities of the former. Among the selected phosphines, PCy_3 is stronger than PPh_3 and P(*m*-Tol)$_3$, which is in line with the greater $+I$ effect of cyclohexyl compared to aryl groups. Although P(*m*-Tol)$_3$ differs from PPh_3 merely by *meta*-methyl substituents located four bonds away from the P-donor atom, its slightly increased donating power is evidenced by the more downfield shift, again highlighting the sensitivity of this method in detecting subtle electronic differences.

N-Heterocyclic Carbenes. The evaluation and comparison of NHCs' donor strengths requires *trans*-hetero-bis(carbene) complexes, i.e., complexes that contain two different NHC ligands. It must be noted that currently no synthetic protocol is known for their preparation. In analogy with other mixed NHC/co-ligand complexes, it should be possible to cleave dimeric **1** with various free NHCs. However, this would require the careful handling of air- and moisture-sensitive free carbenes, not to mention that certain types of NHCs are prone to dimerization and therefore not available for this route.[18] Thus a more straightforward and facile methodology was developed, which involves a combined bridge-cleavage and Ag-carbene transmetalation protocol. This was accomplished by a simple one-pot reaction of the dimeric **1** with Ag-carbene species obtained from the reaction of Ag_2O and various azolium bromides in order to avoid halide scrambling (Scheme 1).[19] These reactions afforded *trans*-complexes, which beautifully serves the purpose of this work. Our initial focus was to compare common five-membered NHCs derived from different types of heterocycles with different backbones. To eliminate any additional sterical or electronical interferences of the N-substituents, four identically *N*,*N*′-dibenzyl-substituted carbene precursors derived from imidazoline (**A**·H^+Br^-), imidazole (**B**·H^+Br^-), benzimidazole (**C**·H^+Br^-), and triazole (**D**·H^+Br^-) were chosen (Chart 1). The desired hetero-bis(carbene) complexes *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(NHC)] (**8**−**11**) bearing NHCs **A**−**D** were obtained as air- and moisture-stable yellow solids in moderate to excellent nonoptimized yields of 60−95%. In general, the complexes are very well soluble in common organic solvents with the exception of nonpolar hexane and toluene. Complex **8** shows the best solubility and is even well soluble in diethyl ether.

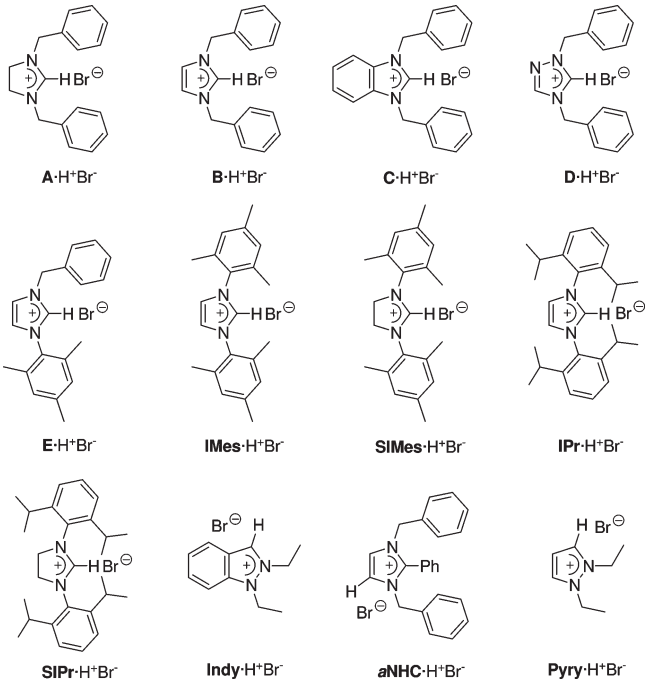
Their formation was confirmed by positive mode ESI mass spectrometry, which shows $[M - Br]^+$ cations due to loss of one bromo ligand. Their ^{1}H NMR spectra show the absence of the NCHN protons indicative of the respective precursor salts. While the benzylic protons in complexes **8**−**10** all gave rise to one singlet pointing to a *trans*-arrangement, two benzylic singlets are observed for **11** at 5.98 and 5.85 ppm, respectively, due to the asymmetrical nature of the triazolin-5-ylidene ligand **D**. Consequently, two closely spaced doublets at 1.68 and 1.65 ppm are assigned to the isopropyl CH_3 protons, indicating restricted rotation of both carbene ligands in **11**. The good solubility of the complexes also gave rise to well-resolved ^{13}C NMR spectra. As mentioned earlier, a stronger donating co-ligand should lead to a more downfield shift of the $^{13}C_{carbene}$ resonance of the constant ^{i}Pr_2-bimy ligand. Moreover, it is commonly agreed that π-back-donation to NHCs in Pd(II) complexes is minimal due to the more Lewis acidic metal center,[20] certainly so compared to the

(18) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896.

(19) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(20) Ray, L.; Shaikh, M. M.; Ghosh, P. *Dalton Trans.* **2007**, 4546.

Chart 1. Azolium Salts Used for the Preparation of Hetero-bis(carbene) Pd(II) Complexes



more electron-rich carbonyl-based Ni(0), Ir(I), or Rh(I) systems mentioned above. Even when an extremely strong co-donor would enable such back-donation to $^{i}Pr_2$-bimy, the resulting paramagnetic shielding term would nevertheless contribute to a downfield shift of the respective carbene signal in line with our concept. Obviously, two carbene signals are expected for each hetero-bis(carbene) complex, and a differentiation may be difficult in cases where their chemical shifts fall in a narrow range (e.g., in complex **11**). This problem, however, can be elegantly solved by conducting HMBC NMR experiments, in which cross-peaks correlating the carbene carbon with protons in the respective N-substituent or ligand backbone allow for an unambiguous assignment of the correct carbene donors. Furthermore, ^{13}C-labeled hetero-bis(carbene) complexes are also accessible via ^{13}C-labeled dimeric **1**, as described for the phosphine analogues (*vide supra*). A comparison of these signals in complexes **8**−**11** indeed shows decreasing donor ability for the NHC co-ligands in the order **A** > **B** > **C** > **D** (Table 1, entries 14−17). This correlation is remarkable considering the simplicity of this system, and the resulting trend is reasonable when the inductive effects of the varying backbones adjacent to the NCN moiety are considered. Clearly, the greater $+I$ effect of two sp^3 carbon atoms in saturated **A** over two sp^2 carbon atoms in unsaturated **B** should translate into a stronger carbene donor of the former. Benzannulation in **C** further weakens the $+I$ effect, and introduction of an electronegative nitrogen atom in **D** even results in an $-I$ effect giving rise to the weakest donor. Notably, carbonyl-based systems have not been useful for differentiating the donor abilities of saturated imidazolidin-2-ylidenes versus the unsaturated imidazolin-2-ylidenes. In some cases, unsaturated NHCs were unexpectedly determined to be even stronger donors than saturated NHCs.[8,9] Previously, it was also reported that N-substituents do not affect the donor abilities in NHCs.[2,21] In order to verify this statement, we tested the sensitivity of our method for the determination of substituent effects in saturated and unsaturated NHCs. For this purpose, the four currently most popular carbenes, **IMes**, **SIMes**, **IPr**, and **SIPr**, bearing aromatic N-substituents were chosen. In addition, we included carbene **E**, which has one *N*-benzyl and one *N*-mesityl substituent in order to close the gap between **IMes** and carbene **B**. The corresponding hetero-bis(carbene) complexes **12**−**16** were synthesized in the same way as **8**−**11** and also obtained as stable yellow solids in nonoptimized yields of 43−98%. Similarly, their identities have been confirmed by ESI or FAB mass spectrometry, which shows isotopic patterns corresponding to $[M - Br]^+$ or $[M + Na]^+$ cations. As expected, signals for two different carbene ligands were observed in all their ^{1}H and ^{13}C NMR spectra. More important, a comparison of the $^{13}C_{carbene}$ signals for the constant $^{i}Pr_2$-bimy ligand in complexes **12** and **13** compared to **9** indeed revealed a surprising and measurable influence of the N-substituents on the donor ability of NHC ligands in Pd(II) complexes (Table 1, entries 18−22). The stepwise substitution of benzyl with mesityl groups going from **B** (179.0 ppm) to **E** (178.3 ppm) and finally to **IMes** (177.2 ppm) leads to a stepwise high-field shift corroborating decreasing donor ability of the carbenes in the order **B** > **E** > **IMes**. Again this observation is reasonable and can be explained by the greater $+I$ effect of alkyl versus aryl substituents. It is also interesting to note that carbene **E** and **C** have supposedly the same donor strength. Thus, the change of one substituent from benzyl to mesityl in imidazolin-2-ylidenes has a comparable effect to that of benzannulation. Finally, comparison of the relevant signals in complexes **13**−**16** again confirms that saturated NHCs are in general stronger donors than their unsaturated analogues, which is also in line with the calculated relative basicity of related NHCs.[22] For the more popular carbenes the order of decreasing donor strength has been established as **SIPr** ≈ **SIMes** > **IPr** > **IMes**. Notably, the change from saturated to unsaturated NHCs bearing N-aryl groups has a smaller impact on the electronic properties than for those with N-alkyl substituents. A likely reason is the presence of two opposing effects in **SIMes**/**SIPr** (i.e., donating effect of the backbone and withdrawing effect from the aryl groups). Finally, a comparison of the relevant signals in the previously reported homo-bis(carbene) complex *trans*-[$PdBr_2$-($^{i}Pr_2$-bimy)$_2$][15] with complex **4** corroborates strong substituent effects also in benzimidazolin-2-ylidenes. Replacement of both benzyl groups in **C** with isopropyl substituents results in an increased donor strength even superior to that of saturated carbene **A** (Figure 1).

Having investigated backbone and substituent effects in common NHCs we focused on nonclassical NHCs, in which the carbene center is adjacent to only one nitrogen atom. For this purpose an indazole-derived carbene (**Indy**), a so-called *abnormal* or C4-bound NHC (***a*NHC**), and a pyrazole-based carbene (**Pyry**) have been chosen. To the best of our knowledge, the coordination chemistry of indazolin-3-ylidenes has not been reported yet. The corresponding *trans*-hetero-bis(carbene) complexes **17**, **18**, and **19** show similar properties to their classical counterparts and were obtained as yellow solids in the same manner as described above employing the indazolium salt **Indy**·H^+Br^-, the C-2 protected imidazolium salt ***a*NHC**·H^+Br^-, and the pyrazolium salt **Pyry**·H^+Br^-, respectively. Evaluation of the $^{i}Pr_2$-bimy

(21) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676.

(22) Magill, A. M.; Cavell, K. J.; Yates, B. *J. Am. Chem. Soc.* **2004**, *126*, 8717.

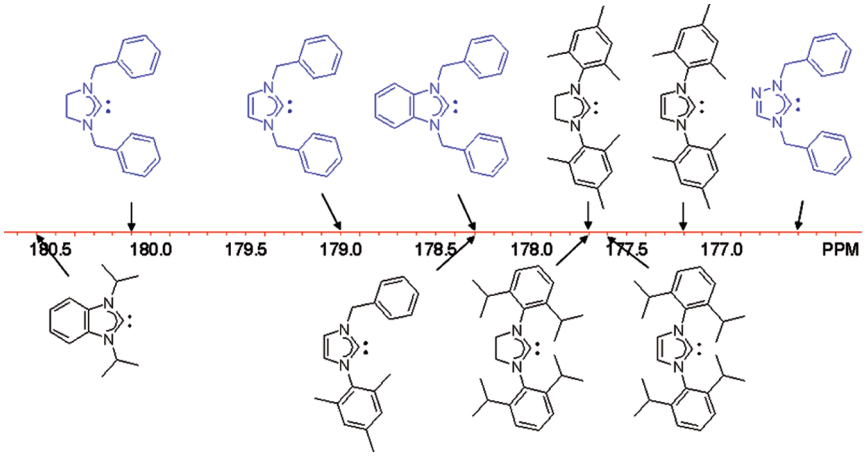


Figure 1. Donor abilities of common NHCs on the ^{13}C NMR scale.

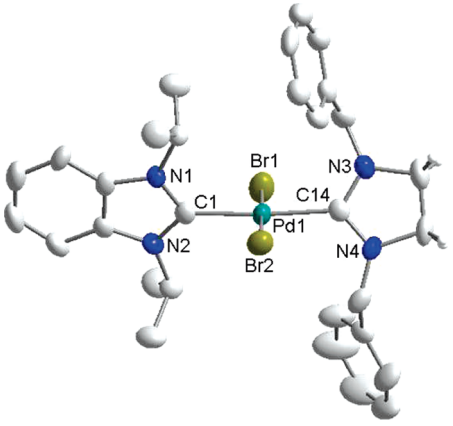


Figure 2. Molecular structure of **8** in the solid state (with the exception of the imidazoline-CH2 groups, hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.022(6), Pd1−C14 2.041(6), Pd1−Br1 2.4348(8), Pd1−Br2 2.4383(8), N1−C1 1.360(8), N2−C1 1.360(7), N3−C14 1.332(8), N4−C14 1.332(8); N2−C1−N1 106.7(5), N4−C14−N3 109.2(6).

$^{13}C_{carbene}$ resonances in **17**, **18**, and **19** revealed that these unusual carbenes are the strongest donors reported in this series in the order **Indy** < ***a*NHC** < **Pyry**. The inferior donor strength of the newly introduced indazolin-3-ylidene ligand compared to that of the abnormal imidazolin-4-ylidene and the strongest donating pyrazolin-3-ylidene is reasonable and due to benzannulation.

Molecular Structures. Having determined the donor strengths of various imidazoles, phosphines, and NHCs, it was of interest to investigate any possible correlation of the donor strength to the Pd−carbene bond distances. The molecular structures of 10 complexes (**3**, **4**, **8**−**10**, **12**−**15**, **17**) have been determined by single-crystal X-ray diffraction. As found by NMR spectroscopy in solution, all complexes adopt a square-planar geometry with the co-ligands in question *trans* to the constant $^{i}Pr_2$-bimy ligand. As representatives, only the molecular structures of the hetero-bis(carbene) complexes **8** and **17** bearing the strongly donating NHC **A** and the newly introduced **Indy** ligand are depicted in Figures 2 and 3.

With inclusion of previously reported mixed $^{i}Pr_2$-bimy-co-ligand Pd(II) complexes, it can be noted that the relevant Pd−$C_{carbene}$ ($^{i}Pr_2$-bimy) bond lengths can cover the wide

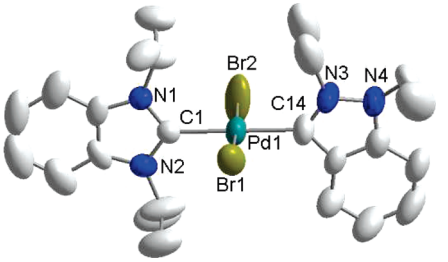


Figure 3. Molecular structure of **17** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.019(6), Pd1−C14 2.017(7), Pd1−Br1 2.430(12), Pd1−Br2 2.4302(10), N1−C1 1.342(8), N2−C1 1.330(8), N3−C14 1.304(11); N2−C1−N1 107.4(6), C14−N3−N4 113.8(7).

range of 1.9359(19) Å (for CH_3CN) to 2.022(6) Å (for **A**) dependent on the nature of the co-ligand (Table 1). A detailed comparison of these bond lengths reveals that they are often longer for complexes with stronger donors. In general this bond elongation is in line with a less Lewis-acidic metal center. However, this trend is not strictly followed by all complexes, and thus a significant correlation can be excluded. This is understandable, since bond parameters are generally affected by a complicated interplay of various factors including crystal packing, solvation, and counteranion effects.

Comparison with TEP. The introduction of a general ^{13}C NMR spectroscopic electronic parameter for ligands requires some additional comments on (i) the availability of the methodology, (ii) the ease of probe preparation, and (iii) the significance of observed chemical shift differences in comparison to TEP and related carbonyl-based methods. It must be noted that both IR and NMR spectroscopies are nowadays standard methods and commonly available in synthetic laboratories. Although data collection for IR spectra requires less time than for ^{13}C NMR spectra, it is generally accepted that the latter is more accurate and provides more valuable information for the structural elucidation of a compound and the determination of its purity. One advantage of our approach is the combination of these necessary steps with the evaluation of the ligand electronic parameter, and thus no additional measurements are

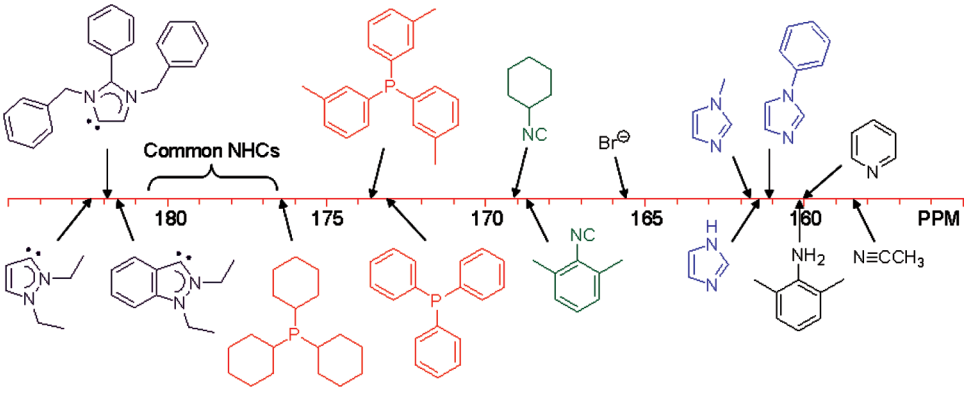


Figure 4. Donor abilities of Werner-type and organometallic ligands on a unified ^{13}C NMR scale.

required. In contrast to the difficulties associated with the probe preparation for TEP and related systems highlighted earlier (*vide supra*), the synthetic pathway to our complex probes is straightforward and does not involve any highly toxic and air- or moisture-sensitive compounds. From a health and chemical safety point of view this is certainly an improvement. Finally, our method puts both Werner-type and organometallic ligands on a unified scale, which previously has not been possible using TEP. The donor strengths of different ligand types are reflected correctly on this scale with carbene chemical shifts of the constant ^{i}Pr-bimy probe ranging from 158.4 to 182.4 ppm (Figure 4).

In addition, this method also allows differentiation on a finer level as shown for the common five-membered ring NHCs **A**−**D**, which are all primarily strong σ-donors. The relevant ^{13}C NMR data in this series differ by 3.5 ppm as compared to a difference of 6−7 cm^{-1} on an IR scale determined of a similar series using a Rh-CO system in CH_2Cl_2.[10b] In this respect, it is worth noting that ^{13}C NMR shifts are commonly given with one decimal place (e.g., 186.3 ppm) on a scale of 0−240 ppm, whereas IR data are reported in wavenumbers without decimal places on a scale of 400−4000 cm^{-1}. From a very simplistic point of view this may imply error margins of 0.1 ppm versus 1 cm^{-1}, which already points to the superior sensitivity of the ^{13}C NMR probe. However, it is probably more accurate to compare the broadness of the respective signals. In general, solution spectra are broadened by various factors apart from the spectrometer resolution. Therefore, the best estimate for the error margin is the peak width at half-height ($w_{1/2}$). For a typical solution IR, this is probably at least a few cm^{-1}, explaining why reporting decimals of wavenumbers is meaningless. Furthermore, the broadness of IR bands is also strongly dependent on the functional group in question. For example, we have determined the $w_{1/2}$ value of a strong and sharp CO absorption band commonly used for the determination of donor strengths to be >20 cm^{-1}. On the other hand, $w_{1/2}$ for ^{13}C NMR chemical shifts amounts only to ~0.02 ppm, and thus 0.1 ppm is an overestimate.[23] Taking this into account, a difference of 3.5 ppm is very significant, as the error is expected to be less than 0.1 ppm, whereas that of 6−7 cm^{-1} is not statistically significant (within 3σ) even at an optimistic resolution of 2 cm^{-1} for solution IR data.

(23) For NMR spectroscopy, the natural line width due to relaxation is supposed to be ~0.02 Hz. But the theoretical digital resolution of the spectrometer is the reciprocal of the acquisition time. A typical acquisition time (roughly the time between pulses) for a ^{13}C spectrum of probably ~1 s will give 1 Hz resolution, which in turn corresponds to better than 0.0025 ppm on a 400 MHz spectrometer under optimal conditions (proper shimming, etc.). The determination of the peak width at half height as the observed estimated standard deviation is probably more practical and realistic.

Conclusion

The results reported herein demonstrate that the donor abilities of various Werner-type and organometallic ligands can be efficiently determined by ^{13}C NMR spectroscopy on complexes of the type *trans*-[$PdBr_2$(^{i}Pr-bimy)(L)], in which ^{i}Pr-bimy denotes the carbene probe and L the ligand in question. The advantages of this methodology include (1) the preparation of the spectroscopic probes is safe, straightforward, and does not involve highly toxic or sensitive materials and thus inert atmosphere is not required; (2) this method is nondestructive and the complexes can be quantitatively reisolated for further reactivity or catalytic studies; (3) NMR spectrometers are standard analytical tools and commonly available in most laboratories. The data obtained using this Pd-^{i}Pr-bimy system can be concluded as (i) remote substituent effects (up to four bonds away) do influence the electronic properties of ligands in general including NHCs; (ii) the backbone of NHCs (saturated, unsaturated, benzannulated, or heteroatom) does influence their donor strength significantly; and (iii) Werner-type and organometallic ligands can be compared on a unified scale for the first time. These findings, although in some cases contrasting previous results obtained from carbonyl-based systems, are reasonable and reflect the influence of inductive effects more correctly. Overall, we believe that our electronic parameter is more suitable for the determination of ligand donor strengths in general, especially on a finer level, which in turn helps in the development of new ligands with fine-tuned electronic properties. We are currently expanding this investigation to include more unusual carbenes and other Werner-type ligands on this unified scale.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed without taking precautions to exclude air and moisture. All solvents were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 or AMX 500 spectrometer, and the chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. To account for possible influences of concentration, temperature, and purity, all NMR spectra have been determined by measuring saturated or nearly saturated solutions of crystalline and pure materials using the same deuterated solvent and at the same

temperature. Mass spectra were measured using a Finnigan MAT LCQ (ESI) and a Finnigan MAT 95XL-T (FAB) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore. Di-μ-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II) (**1**),[14] dibenzylimidazolium bromide (**B**), and dibenzylbenzimidazolium bromide (**C**) were prepared according to literature procedures.[24]

1,3-Dibenzylimidazolinium bromide ($\mathbf{A\cdot H^+Br^-}$). A mixture of ethylenediamine (1.0 mL, 14.8 mmol) and benzaldehyde (3.32 mL, 32.5 mmol) was stirred in toluene (10 mL) at ambient temperature for 6 h. The solvent was then removed *in vacuo* to give the diimine as a yellow liquid. $NaBH_4$ (3.4 g, 77.3 mmol) was dissolved in methanol (10 mL) and slowly added to the diimine in methanol (10 mL) at 0 °C. The mixture was allowed to stir overnight at ambient temperature. Methanol was then removed *in vacuo*, and the residue was dissolved in diethyl ether (30 mL) and extracted with H_2O (2 × 20 mL) and brine (20 mL). Drying of the ether layer gave the diamine as a yellow liquid. To the diamine, triethyl orthoformate (7.4 mL, 44.4 mmol) and NH_4Br (1.45 g, 14.8 mmol) were added and stirred for 4 h at 100 °C. The reaction mixture was cooled to ambient temperature, and excess triethyl orthoformate was removed *in vacuo* at 60 °C for 2 h. The resultant liquid was dissolved in a minimal amount of CH_2Cl_2, and the solution was added dropwise into diethyl ether (150 mL) and stirred overnight at room temperature. The resultant ether layer was decanted to give an oily residue, which was washed with tetrahydrofuran to give the product as a white solid. Yield: 3.04 g, 9.18 mmol, 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.07 (s, 1 H, NCHN), 7.37−7.26 (m, 10 H, Ar-H), 4.81 (s, 4 H, CH_2Ph), 3.75 (s, 4 H, N$(CH_2)_2$N). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 158.7 (s, NCHN), 133.1, 129.8, 129.6, 129.5 (s, Ar-C), 52.9 (s, CH_2Ph), 48.5 (s, N(CH_2)$_2$N). MS (ESI): m/z = 251 [M − Br]$^+$.

1,4-Dibenzyl-1,2,4-triazolium bromide ($\mathbf{D\cdot H^+Br^-}$). A mixture of 1,2,4-triazole (346 mg, 5.0 mmol) and NaOH (0.8 mL, 6.25 M, 5.0 mmol) was suspended in acetonitrile (10 mL) and stirred for 1 h at ambient temperature. Benzyl bromide (1.42 mL, 12 mmol) was added, and the mixture was stirred under reflux for 12 h. After cooling the reaction mixture to ambient temperature, the solvent was removed *in vacuo*. To the residue was added dichloromethane (10 mL), and the resulting suspension was filtered through Celite. Removing the solvent of the filtrate *in vacuo* followed by washing the residue with diethyl ether afforded the product as a pale orange solid. Yield: 1.50 g, 4.53 mmol, 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.68 (s, 1 H, $NC_{(5)}$HN), 8.64 (s, 1 H, $NC_{(3)}$HN), 7.57−7.51 (m, 4 H, Ar-H), 7.37−7.32 (m, 6 H, Ar-H), 5.76 (s, 2 H, CH_2Ph), 5.66 (s, 2 H, CH_2Ph). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 144.0 (s, $NC_{(5)}$N), 143.5 (s, $NC_{(3)}$N), 132.38, 132.36, 130.6, 130.4, 130.3, 130.2, 130.1, 129.9 (s, Ar-C), 57.1 (s, CH_2Ph), 53.0 (s, CH_2Ph). MS (ESI): m/z = 250 [M − Br]$^+$.

1,2-Diethylindazolium Bromide ($\mathbf{Indy\cdot H^+Br^-}$). NaOH (160 mg, 4 mmol) was added to the solution of indazole (354 mg, 3 mmol) in CH_3CN (10 mL), and the suspension was stirred at ambient temperature for 1 h. Ethyl bromide (0.89 mL, 12 mmol) was added to the suspension, and the resulting mixture was further stirred under reflux conditions for 24 h. The solvent from the reaction mixture was removed under reduced pressure, and CH_2Cl_2 was added to the residue. The resulting suspension was filtered, and the solvent of the filtrate was removed under vacuum. Upon washing the residue with ethyl acetate, a white solid was obtained (252 mg, 0.99 mmol, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.80 (s, 1 H, NCHN), 7.98 (d, 1 H, Ar-H), 7.71 (m, 2 H, Ar-H), 7.37 (m, 1 H, Ar-H), 5.10 (q, 2 H, ^3J(H,H) = 7.26 Hz, NCH_2CH$_3$), 4.91 (q, 2 H, ^3J(H,H) = 7.23 Hz, NCH_2-CH$_3$), 1.68 (t, 3 H, ^3J(H,H) = 7.26 Hz, NCH$_2$CH_3), 1.42 (t, 3 H, ^3J(H,H) = 7.23 Hz, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 140.6 (s, NCHN), 134.3, 134.2, 125.9, 124.1, 120.5, 111.1 (s, Ar-H), 47.8 (s, NCH$_2$CH$_3$), 43.6 (s, NCH$_2$CH$_3$), 16.0 (s, NCH$_2$CH$_3$), 15.3 (s, NCH$_2$CH$_3$). ESI (MS): m/z = 175 [M − Br]$^+$.

1,3-Dibenzyl-2-phenylimidazolium Bromide ($\mathbf{\textit{a}NHC\cdot H^+Br^-}$). $\mathbf{\textit{a}NHC\cdot H^+Br^-}$ was prepared in analogy with $\mathbf{D\cdot H^+Br^-}$ from 2-phenylimidazole (721 mg, 5.0 mmol), NaOH (0.8 mL, 6.25 M, 5.0 mmol), and benzyl bromide (1.42 mL, 12 mmol). Yield: 1.925 g, 4.75 mmol, 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, N$(CH)_2$N, 2 H), 7.65−7.63 (m, Ar-H, 1 H), 7.57−7.52 (m, Ar-H, 4 H), 7.24−7.23 (m, Ar-H, 6 H), 7.10−7.08 (m, Ar-H, 4 H), 5.32 (s, CH_2Ph, 4 H). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 145.2 (s, NCN), 133.7, 133.5, 131.3, 130.5, 129.8, 129.7, 128.9, 123.5, 121.5 (s, Ar-C and N(CH)$_2$N), 53.3 (s, CH_2Ph). MS (ESI): m/z = 325 [M − Br]$^+$.

1,2-Diethylpyrazolium Bromide ($\mathbf{Pyry\cdot H^+Br^-}$). A mixture of pyrazole (225 mg, 3.3 mmol) and NaOH (200 mg, 5 mmol) was suspended in CH_3CN (7 mL) and stirred at ambient temperature for 1 h. To the suspension was added ethyl bromide (0.94 mL, 13 mmol). The reaction mixture was stirred under reflux conditions for 24 h. After removing the volatiles under reduced pressure, CH_2Cl_2 was added to the residue and the resulting suspension was filtered. The solvent of the filtrate was removed under vacuum, and the resulting residue was subsequently washed with ethyl acetate to give a white solid (176 mg, 0.86 mmol, 26%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, 2 H, ^3J(H,H) = 2.94 Hz, Ar-H), 6.51 (t, 1 H, ^3J(H,H) = 2.97 Hz, Ar-H), 4.57 (q, 4 H, ^3J(H,H) = 7.23 Hz, NCH_2CH$_3$), 1.38 (t, 6 H, ^3J(H,H) = 7.23 Hz, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 137.0, 108.0 (s, CH), 46.1 (s, NCH$_2$CH$_3$), 15.0 (s, NCH$_2$CH$_3$). ESI (MS): m/z = 125 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1-phenylimidazole)palladium(II) (2).** A mixture of complex **1** (94 mg, 0.1 mmol) was suspended in CH_2Cl_2 (10 mL). To this suspension was added a solution of 1-phenylimidazole (26 uL, 0.2 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at ambient temperature for 2 h. The solvent was removed under reduced pressure, and the residue was washed with hexane. Crystallization from a concentrated CH_2Cl_2/toluene solution afforded the product as yellow crystals (110 mg, 0.18 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (s, NCHN), 7.85 (s, 1 H, CH), 7.59−7.56 (dd, 2 H, Ar-H), 7.49−34 (m, 5 H, Ar-H), 7.21−7.18 (m, 3 H, Ar-H and CH), 6.36 (m, 2 H, ^3J(H,H) = 7.1 Hz, CH(CH$_3$)$_2$), 1.77 (d, 12 H, ^3J(H,H) = 7.1 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 161.1 (s, NCN), 139.1 (s, NCHN), 137.1, 134.0, 131.5, 130.6, 129.0, 122.8, 122.3, 118.8, 113.1 (s, Ar-C and CH), 55.0 (s, CH(CH$_3$)$_2$), 21.1 (s, CH(CH_3)$_2$). Anal. Calcd for $C_{22}H_{26}Br_2N_4Pd$: C, 43.13; H, 4.28; N, 9.14. Found: C, 43.65; H, 4.20; N, 8.91. MS (ESI): m/z = 677 [M − Br + (1-phenylimidazole)]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(imidazole)palladium(II) (3). 3** was prepared in analogy with **2** from **1** (47 mg, 0.05 mmol) and imidazole (7 mg, 0.1 mmol). Slow evaporation of a concentrated EtOH/chloroform solution afforded the product as yellow crystals (48 mg, 0.09 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (br, 1 H, NH), 8.30 (s, NCHN), 7.70 (s, 1 H, CH), 7.60−7.56 (dd, 2 H, Ar-H), 7.23−7.19 (dd, 2 H, Ar-H), 6.93 (s, 1 H, CH), 6.33 (m, 2 H, ^3J(H,H) = 6.9 Hz, CH(CH$_3$)$_2$), 1.77 (d, 12 H, ^3J(H,H) = 6.9 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 161.4 (s, NCN), 138.9 (s, NCHN), 134.2, 130.0, 122.8, 116.3, 113.3 (s, Ar-C and CH), 55.0 (s, CH(CH$_3$)$_2$), 21.3 (s, CH(CH_3)$_2$). Anal. Calcd for $C_{16}H_{22}Br_2N_4Pd$: C, 35.81; H, 4.13; N, 10.44. Found: C, 36.17; H, 4.07; N, 10.41. MS (ESI): m/z = 525 [M − Br + imidazole]$^+$, 535 [M − H]$^-$, 617 [M + Br]$^-$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1-methylimidazole)palladium(II) (4). 4** was prepared in analogy with **2** from **1** (47 mg, 0.05 mmol) and 1-methylimidazole (8 uL, 0.1 mmol). Slow evaporation of a concentrated CH_2Cl_2/toluene

(24) Huynh, H. V.; Wong, L. R.; Ng, P. S. *Organometallics* **2008**, *27*, 2231.

solution afforded the product as yellow crystals (49 mg, 0.089 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1 H, NCHN), 7.93 (s, 1 H, CH), 7.58−7.55 (dd, 2 H, Ar-H), 7.20−7.17 (dd, 2 H, Ar-H), 6.80 (s, 1 H, CH), 6.33 (m, 2 H, ^3J(H,H) = 7.1 Hz, C*H*(CH_3)$_2$), 3.67 (s, 3 H, NCH_3), 1.75 (d, 12 H, ^3J(H,H) = 7.1 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 161.6 (s, NCN), 141.0 (s, NCHN), 134.1, 130.9, 122.7, 120.5, 113.2 (s, Ar-C), 55.0 (s, *C*H(CH_3)$_2$), 34.8 (s, NCH_3), 21.2, (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{17}H_{24}Br_2N_4Pd$: C, 37.08; H, 4.39; N, 10.18. Found: C, 37.28; H, 4.23; N, 10.28. MS (ESI): m/z = 573 [M + Na]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(triphenylphosphine)palladium(II) (5).** The ^{13}C-labeled complex **1** (9.4 mg, 0.01 mmol) and triphenylphosphine (0.02 mmol, 5.2 mg) were dissolved in $CDCl_3$ (0.6 mL) for direct NMR measurement. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78−7.71 (m, 6 H, Ar-H), 7.59−7.55 (dd, 2 H, Ar-H), 7.46−7.39 (m, 9 H, Ar-H), 7.22−7.19 (dd, 2 H, Ar-H), 6.00 (m, ^3J(H,H) = 6.9 Hz, ^3J(C,H) = 4.4 Hz, 2 H, NC*H*(CH_3)$_2$), 1.77 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 173.1 (d, ^2J(P,C) = 192.1 Hz, NCN-^{i}Pr$_2$-bimy). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ 18.6 (d, ^2J(P,C) = 192.1 Hz, PPh_3).

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(tri-*m*-tolylphosphine)palladium(II) (6).** The ^{13}C-labeled complex **1** (9.4 mg, 0.01 mmol) and tri-*m*-tolylphosphine (0.02 mmol, 6.1 mg) were dissolved in $CDCl_3$ (0.6 mL) for direct NMR measurement. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, ^2J(P,C) = 11.4 Hz, 3 H, Ar-C), 7.59−7.56 (dd, 2 H, Ar-C), 7.45 (t, 3 H, Ar-C), 7.34−7.24 (m, 8 H, Ar-C), 7.21−7.19 (dd, 2 H, Ar-C), 6.05 (m, ^3J(H,H) = 7.0 Hz, ^3J(C,H) = 4.4 Hz, 2 H, NC*H*(CH_3)$_2$), 2.36 (s, 9 H, CH_3), 1.78 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 173.6 (d, ^2J(P,C) = 190.6 Hz, NCN-^{i}Pr$_2$-bimy). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ 18.8 (d, ^2J(P,C) = 190.6 Hz, P(*m*-Tol)$_3$).

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(tricyclohexylphosphine)palladium(II) (7).** The ^{13}C-labeled complex **1** (56 mg, 0.06 mmol) and tricyclohexylphosphine (0.18 mmol, 50 mg) were dissolved in DCM (10 mL) and stirred for 1 h at ambient temperature. The solvent was removed under reduced pressure. Crystallization of the residue by slow evaporation of a concentrated $CHCl_3$/toluene solution afforded yellow crystals, which were washed with a small amount of diethyl ether and dried *in vacuo*. Yield: 43 mg, 0.057 mmol, 48%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7.53 (dd, 2 H, Ar-H), 7.21−7.18 (dd, 2 H, Ar-H), 6.00 (m, ^3J(H,H) = 7.1 Hz, ^3J(C,H) = 4.3 Hz, 2 H, NC*H*(CH_3)$_2$), 2.51 (m, 3 H, PCH), 2.06−2.02 (m, 6 H, CH_2), 1.83−1.63 (m, 15 H, CH_2), 1.77 (d, ^3J(H,H) = 7.1 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.34−1.28 (m, 9 H, CH_2). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 176.4 (d, ^2J(P,C) = 177.8 Hz, NCN-^{i}Pr$_2$-bimy), 134.4 (d, ^2J(C,C) = 5.5 Hz, Ar-C), 122.7, 113.3 (s, Ar-C), 54.3 (d, ^2J(C,C) = 8.2 Hz, N*C*H(CH_3)$_2$), 32.7 (d, ^1J(P,C) = 19.2 Hz, PCH), 30.8 (s, CH_2), 28.4 (d, ^2J(P,C) = 11.0 Hz, CH_2), 27.5 (s, CH_2), 21.5 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ 23.3 (d, ^2J(P,C) = 177.8 Hz, PCy_3). Anal. Calcd for $C_{31}H_{51}Br_2N_2PdP$: C, 49.78; H, 6.87; N, 3.74. Found: C, 50.13; H, 6.36; N, 3.53. MS (FAB): m/z = 670 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dibenzylimidazolidin-2-ylidene)palladium(II) (8).** **A**·H$^+$Br$^-$ (66 mg, 0.2 mmol), Ag_2O (28 mg, 0.12 mmol), and **1** (93 mg, 0.1 mmol) were suspended in DCM (10 mL) and stirred at ambient temperature overnight shielded from light. The resultant suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give a yellow solid. Diethyl ether (30 mL) was added to the residue, and the mixture was stirred overnight at ambient temperature. The ether layer was collected by filtration and dried *in vacuo* to give the crude product as a yellow solid. Slow evaporation at ambient temperature of a concentrated acetonitrile solution yielded colorless needle crystals suitable for X-ray diffraction studies. Yield: 87 mg, 0.12 mmol, 60%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67−7.66 (d, 4 H, Ar-H), 7.53−7.50 (m, 2 H, Ar-H), 7.42−7.39 (m, 4 H, Ar-H), 7.35−7.32 (m, 2 H, Ar-H), 7.18−7.16 (m, 2 H, Ar-H), 6.05 (m, ^3J(H,H) = 6.95 Hz, 2 H, C*H*(CH_3)$_2$), 5.33 (s, 4 H, C*H*$_2$Ph), 3.42 (s, 4 H, N(C*H*$_2$)$_2$N), 1.69 (d, ^3J(H,H) = 6.95 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 199.2 (s, NCN-**A**), 180.1 (s, NCN-^{i}Pr$_2$-bimy), 136.8, 134.2, 129.5, 129.4, 128.5, 122.6, 113.2 (s, Ar-C), 55.3 (s, *C*H(CH_3)$_2$), 54.4 (s, *C*H$_2$Ph), 48.9 (s, N(*C*H$_2$)$_2$N), 21.8 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{30}H_{36}Br_2N_4Pd$: C, 50.12; H, 5.05; N, 7.79. Found: C, 50.03; H, 5.04; N, 7.74. MS (ESI): m/z = 639 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dibenzylimidazolin-2-ylidene)palladium(II) (9).** **B**·H$^+$Br$^-$ (66 mg, 0.2 mmol), Ag_2O (28 mg, 0.12 mmol), and **1** (93 mg, 0.1 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo*. Slow evaporation at ambient temperature of a concentrated chloroform solution yielded yellow needle crystals suitable for X-ray diffraction studies. Yield: 91 mg, 0.13 mmol, 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58−7.50 (m, 6 H, Ar-H), 7.45−7.35 (m, 6 H, Ar-H), 7.18−7.15 (dd, 2 H, Ar-H), 6.75 (s, 2 H, CH), 6.01 (m, ^3J(H,H) = 6.95 Hz, 2 H, C*H*(CH_3)$_2$), 5.84 (s, 4 H, C*H*$_2$Ph), 1.67 (d, ^3J(H,H) = 6.95 Hz, 12 H, C*H*$_3$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 179.0 (s, NCN-^{i}Pr$_2$-bimy), 172.0 (s, NCN-**B**), 137.0, 134.3, 129.5, 129.1, 128.8, 122.5, 122.0, 113.2 (s, Ar-C and CH), 55.4 (s, *C*H(CH_3)$_2$), 54.4 (s, *C*H$_2$Ph), 21.6 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{30}H_{34}Br_2N_4Pd$: C, 50.12; H, 5.05; N, 7.79. Found: C, 50.45; H, 4.78; N, 7.72. MS (ESI): m/z = 637 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dibenzylbenzimidazolin-2-ylidene)palladium(II) (10).** **C**·H$^+$Br$^-$ (76 mg, 0.2 mmol), Ag_2O (28 mg, 0.12 mmol), and **1** (93 mg, 0.1 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo*. Slow evaporation at ambient temperature of a concentrated acetone solution yielded yellow needle crystals suitable for X-ray diffraction studies. Yield: 146 mg, 0.19 mmol, 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71−7.67 (d, 4 H, Ar-H), 7.52−7.50 (dd, 2 H, Ar-H), 7.44−7.31 (m, 6 H, Ar-H), 7.25−7,10 (m, 6 H, Ar-H), 6.21 (s, 4 H, C*H*$_2$Ph), 5.96 (m, ^3J(H,H) = 7.1 Hz, 2 H, C*H*(CH_3)$_2$), 1.64 (d, ^3J(H,H) = 7.1 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 185.1 (s, NCN-**C**), 178.3 (s, NCN-^{i}Pr$_2$-bimy), 136.5, 135.5, 134.3, 129.5, 128.6, 128.5, 123.7, 122.6, 113.2, 111.8 (s, Ar-C), 54.5 (s, *C*H(CH_3)$_2$), 53.3 (s, *C*H$_2$Ph), 21.5 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{34}H_{36}Br_2N_4Pd$: C, 53.25; H, 4.73; N, 7.31. Found: C, 53.14; H, 4.63; N, 7.16. MS (ESI): m/z = 687 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,4-dibenzyl-1,2,4-triazolin-5-ylidene)palladium(II) (11).** **D**·H$^+$Br$^-$ (66 mg, 0.2 mmol), Ag_2O (28 mg, 0.12 mmol), and **1** (93 mg, 0.1 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give the product as a yellow solid. Yield: 119 mg, 0.17 mmol, 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (s, 1 H, NCHN), 7.64−7.61 (d, 2 H, Ar-H), 7.54−7.35 (m, 10 H, Ar-H), 7.20−7.17 (dd, 2 H, Ar-H), 5.98 (m, 3 H, C*H*$_2$Ph and C*H*(CH_3)$_2$), 5.85 (m, 3 H, C*H*$_2$Ph and C*H*(CH_3)$_2$), 1.67 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.65 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 176.6 (s, NCN-^{i}Pr$_2$-bimy), 176.3 (s, NCN-**D**), 143.1, 136.2, 135.4, 134.2, 129.8, 129.4, 129.3, 129.1, 129.0, 128.8, 122.7, 113.32, 113.29 (s, Ar-C), 57.4, 54.6, 54.5, 53.2 (s, *C*H$_2$Ph and *C*H(CH_3)$_2$), 21.54, 21.51 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{29}H_{33}Br_2N_5Pd$: C, 48.52; H, 4.63; N, 9.76. Found: C, 48.89; H, 4.66; N, 9.72. MS (ESI): m/z = 638 [M − Br]$^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(3-benzyl-1-mesitylimidazolin-2-ylidene)palladium(II) (12).** **E**·H$^+$Br$^-$ (71 mg, 0.20 mmol), Ag_2O (24 mg, 0.10 mmol), and **1**

(94 mg, 0.10 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give the product as a yellow solid. Yield: 146 mg, 0.19 mmol, 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, 2 H, Ar-H), 7.49−7.37 (m, 5 H, Ar-H), 7.12−7.11 (m, 2 H, Ar-H), 7.07 (s, 2 H, Ar-H), 6.87−6.86 (m, 2 H, CH), 5.88 (m, ^3J(H,H) = 6.95 Hz, 1 H, C*H*(CH_3)$_2$), 5.87 (s, 2 H, CH_2), 5.58 (m, ^3J(H,H) = 6.95 Hz, 1 H, C*H*(CH_3)$_2$), 2.43 (s, 3 H, *p*-CH_3), 2.34 (s, 6 H, *o*-CH_3), 1.70 (d, ^3J(H,H) = 6.95 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.45 (d, ^3J(H,H) = 6.95 Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 178.3 (s, NCN-^{i}Pr$_2$-bimy), 173.4 (s, NCN-**E**), 139.1, 137.4, 137.0, 136.5, 134.2, 134.1, 129.7, 129.6, 129.4, 128.9, 123.9, 122.33, 122.30, 121.2, 113.1, 112.9 (s, Ar-C and CH), 55.6 (s, CH_2), 54.3, 53.9 (s, *C*H(CH_3)$_2$), 21.8 (s, *p*-CH_3), 21.7, 21.1 (s, CH(*C*H$_3$)$_2$), 20.3 (s, *o*-CH_3). Anal. Calcd for $C_{32}H_{38}Br_2N_4Pd$: C, 51.60; H, 5.14; N, 7.52. Found: C, 51.58; H, 5.10; N, 7.52. MS (ESI): m/z = 767 $[M + Na]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dimesitylimidazolin-2-ylidene)palladium(II) (13). IMes·H$^+$Br$^-$** (193 mg, 0.50 mmol), Ag_2O (58 mg, 0.25 mmol), and **1** (234 mg, 0.25 mmol) were suspended in DCM (30 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give the product as a yellow solid. Yield: 382 mg, 0.49 mmol, 98%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.36 (dd, 2 H, Ar-H), 7.09−7.07 (m, 8 H, Ar-H and CH), 5.43 (m, ^3J(H,H) = 6.95 Hz, 2 H, C*H*(CH_3)$_2$), 2.44 (s, 6 H, *p*-CH_3), 2.42 (s, 12 H, *o*-CH_3), 1.47 (d, ^3J(H,H) = 6.95 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 177.2 (s, NCN-^{i}Pr$_2$-bimy), 175.5 (s, NCN-**IMes**), 139.1, 137.2, 136.5, 134.3, 129.3, 123.6, 122.1, 112.6 (s, Ar-C and CH), 53.8 (s, *C*H(CH_3)$_2$), 21.8 (s, *p*-CH_3), 21.3 (s, CH(*C*H$_3$)$_2$), 20.4 (s, *o*-CH_3). Anal. Calcd for $C_{34}H_{42}Br_2N_4Pd\cdot CH_2Cl_2$: C, 49.00; H, 5.17; N, 6.53. Found: C, 49.45; H, 5.04; N, 6.57. MS (FAB): m/z = 693 $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dimesitylimidazolidin-2-ylidene)palladium(II) (14). SIMes·H$^+$Br$^-$** (155 mg, 0.40 mmol), Ag_2O (46 mg, 0.20 mmol) and **1** (187 mg, 0.20 mmol) were suspended in DCM (20 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give the product as a yellow solid. Yield: 304 mg, 0.39 mmol, 98%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.33 (dd, 2 H, Ar-H), 7.07−7.06 (dd, 2 H, Ar-H), 7.04 (s, 4 H, Ar-H), 5.25 (m, ^3J(H,H) = 6.95 Hz, 2 H, C*H*(CH_3)$_2$), 4.02 (s, 4 H, CH_2), 2.62 (s, 12 H, *o*-CH_3), 2.39 (s, 6 H, *p*-CH_3), 1.40 (d, ^3J(H,H) = 6.95 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 204.0 (s, NCN-**SIMes**), 177.6 (s, NCN-^{i}Pr$_2$-bimy), 138.3, 136.4, 134.2, 129.5, 122.1, 112.6 (s, Ar-C), 53.7 (s, *C*H(CH_3)$_2$), 51.6 (s, CH_2), 21.7 (s, *p*-CH_3), 21.2 (s, CH(*C*H$_3$)$_2$), 20.6 (s, *o*-CH_3). Anal. Calcd for $C_{34}H_{44}Br_2N_4Pd$: C, 52.69; H, 5.72; N, 7.23. Found: C, 52.74; H, 5.73; N 6.94. MS (FAB): m/z = 695 $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene){1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene}palladium(II) (15). IPr·H$^+$Br$^-$** (94 mg, 0.20 mmol), Ag_2O (24 mg, 0.10 mmol), and **1** (94 mg, 0.10 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the solvent of the filtrate was removed *in vacuo*. The residue was subjected to column chromatography (SiO_2, diethyl ether/hexane, 4:1). The first band (R_f = 0.9) was collected and dried under vacuum to afford the product as a yellow solid. Yield: 127 mg, 0.15 mmol, 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (t, 2 H, Ar-H), 7.39 (d, 4 H, Ar-H), 7.35−7.33 (dd, 2 H, Ar-H), 7.16 (s, 2 H, CH), 7.05−7.03 (dd, 2 H, Ar-H), 5.34 (m, ^3J(H,H) = 6.90 Hz, 2 H, NC*H*(CH_3)$_2$), 3.30 (m, ^3J(H,H) = 6.90 Hz, 4 H, C*H*(CH_3)$_2$), 1.45 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.38 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.11 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 178.2 (s, NCN-**IPr**), 177.5 (s, NCN-^{i}Pr$_2$-bimy), 147.8, 136.7, 134.2, 130.3, 124.9, 124.1, 122.0, 112.8 (s, Ar-C and CH), 53.7 (s, N*C*H(CH_3)$_2$), 29.5 (s, *C*H(CH_3)$_2$), 27.3, 23.6, 21.2 (s, CH-(*C*H$_3$)$_2$). Anal. Calcd for $C_{40}H_{54}Br_2N_4Pd$: C, 56.05; H, 6.35; N, 6.54. Found: C, 56.19; H, 6.29; N, 6.22. MS (ESI): m/z = 777 $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene){1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene}palladium(II) (16). SIPr·H$^+$Br$^-$** (94 mg, 0.20 mmol), Ag_2O (24 mg, 0.10 mmol), and **1** (94 mg, 0.10 mmol) were suspended in DCM (15 mL) and stirred at ambient temperature for 3 days shielded from light. The resulting suspension was filtered over Celite, and the solvent of the filtrate was removed *in vacuo*. The residue was subjected to column chromatography (SiO_2, ethyl acetate/hexane, 3:7). The first band (R_f = 0.88) was collected and dried under vacuum to afford the product as a yellow solid. Yield: 73 mg, 0.085 mmol, 43%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (t, 2 H, Ar-H), 7.35−7.32 (m, 6 H, Ar-H), 7.04−7.01 (m, 2 H, Ar-H), 5.20 (m, ^3J(H,H) = 6.90 Hz, 2 H, NC*H*(CH_3)$_2$), 4.15 (s, 4 H, CH_2), 3.73 (m, ^3J(H,H) = 6.90 Hz, 4 H, C*H*(CH_3)$_2$), 1.53 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.33 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.24 (d, ^3J(H,H) = 6.90 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 206.3 (s, NCN-**SIPr**), 177.6 (s, NCN-^{i}Pr$_2$-bimy), 149.0, 136.9, 134.1, 129.5, 124.5, 121.9, 112.9 (s, Ar-C), 54.3 (s, CH_2), 53.6 (s, N*C*H(CH_3)$_2$), 29.6 (s, *C*H(CH_3)$_2$), 27.8, 24.4, 21.2 (s, CH-(*C*H$_3$)$_2$). Anal. Calcd for $C_{40}H_{56}Br_2N_4Pd$: C, 55.92; H, 6.57; N, 6.52. Found: C, 56.18; H, 6.56; N, 6.30. MS (ESI): m/z = 881 $[M + Na]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,2-diethylindazolin-3-ylidene)palladium(II) (17).** Ag_2O (0.18 mmol, 42 mg) was added to a suspension of **Indy·H$^+$Br$^-$** (0.353 mmol, 90 mg) and complex **1** (0.176 mmol, 165 mg) in dichloromethane (10 mL). The mixture was stirred for 12 h at ambient temperature shielded from light. The resulting suspension was filtered through Celite and subsequently passed through silica gel, giving a clear yellow solution. The solvent of the filtrate was removed under reduced pressure to afford the product as a yellow solid (198 mg, 0.31 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, 1 H, Ar-H), 7.57 (m, 3 H, Ar-H), 7.32 (t, 1 H, Ar-H), 7.21 (m, 3 H, Ar-H), 6.41 (br, m, 1 H, NC*H*(CH_3)$_2$), 6,27 (br, m, 1 H, NC*H*(CH_3)$_2$), 5.09 (q, 2 H, ^3J(H,H) = 6.9 Hz, NC*H*$_2$CH$_3$), 4.34 (q, 2 H, ^3J(H,H) = 7.55 Hz, NC*H*$_2$CH$_3$), 1.92 (br, d, 6 H, NCH(C*H*$_3$)$_2$), 1.87 (br, d, 6 H, NCH(C*H*$_3$)$_2$), 1.80 (t, 3 H, ^3J(H,H) = 6.9 Hz, NCH$_2$C*H*$_3$), 1.19 (t, 3 H, ^3J(H,H) = 7.55 Hz, NCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 181.6 (s, NCN-^{i}Pr$_2$-bimy), 180.6 (s, NCN-**Indy**), 141.5, 134.5, 134.2, 132.0, 131.9, 130.6, 122.9, 122.6, 122.5, 113.2, 113.1, 109.8 (s, Ar-C), 54.5, 54.3 (s, N*C*H(CH_3)$_2$), 47.7 (s, N*C*H$_2$CH$_3$), 43.0 (s, N*C*H$_2$CH$_3$), 22.0, 21.9 (s, NCH(*C*H$_3$)$_2$), 16.3 (s, NCH$_2$*C*H$_3$), 13.9 (s, NCH$_2$*C*H$_3$). Anal. Calcd for $C_{24}H_{32}Br_2N_4Pd$: C, 44.85; H, 5.02; N, 8.72. Found: C, 44.40; H, 4.71; N, 8.57. ESI (MS): m/z = 563 $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dibenzyl-2-phenylimidazolin-4-ylidene)palladium(II) (18). *a*N-HC·H$^+$Br$^-$** (81 mg, 0.20 mmol), Ag_2O (24 mg, 0.10 mmol), and **1** (94 mg, 0.10 mmol) were suspended in DCM (20 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was dried *in vacuo* to give the product as a yellow solid. Yield: 151 mg, 0.19 mmol, 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55−7.06 (m, 19 H, Ar-H), 7.04 (s, 1 H, NCH), 6.00 (m, ^3J(H,H) = 6.95 Hz, 2 H, NC*H*(CH_3)$_2$), 5.88 (s, 2 H, C*H*$_2$Ph), 4.94 (s, 2 H, C*H*$_2$Ph), 1.63 (d, ^3J(H,H) = 6.95 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 181.9 (s, NCN-^{i}Pr$_2$-bimy), 150.4 (s, N*C*CH-**F**), 144.0 (NCN), 137.8, 135.1, 134.3, 132.0, 130.7, 129.9, 129.8, 129.2, 129.1, 128.1, 127.8, 127.7, 126.0, 124.7, 122.1, 113.0 (s, Ar-C and NC*C*H), 54.4 (s, *C*H$_2$Ph), 54.0, (s, N*C*H(CH_3)$_2$), 52.0 (s, *C*H$_2$Ph), 21.5 (s, CH(*C*H$_3$)$_2$). Anal. Calcd

for $C_{36}H_{38}Br_2N_4Pd$: C, 54.53; H, 4.83; N, 7.07. Found: C, 54.11; H, 4.75; N, 6.93. MS (ESI): $m/z = 713$ $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(1,2-diethylpyrazolin-3-ylidene)palladium(II) (19).** Ag_2O (14 mg, 0.06 mmol) was added to a suspension of **Pyry**·H^+Br^- (21 mg, 0.10 mmol) and complex **1** (47 mg, 0.05 mmol) in dichloromethane (7 mL). The resulting mixture was stirred for 12 h at ambient temperature shielded from light and subsequently filtered through Celite. The solvent of the filtrate was removed under reduced pressure to yield a white solid (56 mg, 0.095 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, 2 H, Ar-H), 7.36 (d, 1 H, Ar-H), 7.17 (dd, 2 H, Ar-H), 6.60 (d, 1 H, Ar-H), 6.26 (m, 2 H, ^3J(H,H) = 6.95 Hz, NC*H*$(CH_3)_2$), 4.93 (q, 2 H, ^3J(H,H) = 6.95 Hz, NCH_2CH$_3$), 4.19 (q, 2 H, ^3J(H,H) = 6.90 Hz, NCH_2CH$_3$), 1.81 (d, 12 H, ^3J(H,H) = 6.90 Hz, NCH-(CH_3)$_2$), 1.73 (t, 3 H, ^3J(H,H) = 6.9 Hz, NCH$_2$CH_3), 1.49 (t, 3 H, ^3J(H,H) = 6.90 Hz, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 182.4 (s, NCN-^{i}Pr$_2$-bimy), 174.5 (s, NCN-**Pyry**), 134.3, 132.0, 122.4, 116.5, 113.1 (s, Ar-C), 54.3 (s, N*C*H$(CH_3)_2$), 46.6 (s, N*C*H$_2$CH$_3$), 44.5 (s, N*C*H$_2$CH$_3$), 21.8 (s, NCH$(CH_3)_2$), 16.2 (s, NCH$_2$*C*H$_3$), 15.3 (s, NCH$_2$*C*H$_3$). Anal. Calcd for $C_{20}H_{30}Br_2N_4Pd$: C, 40.53; H, 5.10; N, 9.45. Found: C, 40.28; H, 4.93; N, 9.46. ESI (MS): $m/z = 513$ $[M - Br]^+$.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs.[25] Data were processed and corrected for Lorentz and polarization effects with SAINT,[26] and for absorption effect with SADABS.[27] Structural solution and refinement were carried out with the SHELXTL suite of programs.[28] 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 put 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 for complexes **3**, **4**, **8**−**10**, **12**−**15**, and **17** is given in the Supporting Information.

Acknowledgment. We thank the National University of Singapore for financial support (Grant No. R 143-000-327-133) and the CMMAC staff of our department for technical assistance. Prof. W. K. Leong is acknowledged for the fruitful discussion.

Supporting Information Available: ^{13}C NMR and HMBC spectra, crystallographic data, CIF files for complexes **3**, **4**, **8**−**10**, **12**−**15**, and **17**, and ORTEP plots with selected bond lengths and angles for complexes **3**, **4**, **9**−**10**, and **12**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

(25) *SMART version 5.628*; Bruker AXS Inc.: Madison, WI, 2001.

(26) *SAINT+ version 6.22a*; Bruker AXS Inc.: Madison, WI, 2001.

(27) Sheldrick, G. W. *SADABS version 2.10*; University of Göttingen, 2001.

(28) *SHELXTL version 6.14*; Bruker AXS Inc.: Madison, WI, 2000.