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Determining the Electron-Donating Properties of Bidentate Ligands by ^{13}C NMR Spectroscopy

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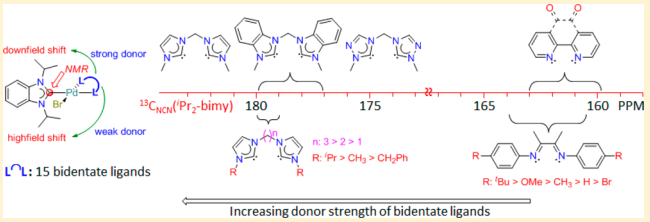
Supporting Information

ABSTRACT: A series of 15 mononuclear complexes [PdBr(^{i}Pr$_2$-bimy)(L$_2$)]PF$_6$ (**1**–**15**) (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene, L$_2$ = aromatic 1,2-diimines, diazabutadienes, or methylene-, ethylene- and propylene-bridged di-N-heterocyclic carbenes) and two dicarbene-bridged, dinuclear complexes [Pd$_2$Br$_4$(^{i}Pr$_2$-bimy)$_2$(diNHC)] (**16** and **17**) were synthesized and characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, and in some cases X-ray diffraction analysis. The influence of the 15 bidentate ligands L$_2$ on the $^{13}C_{carbene}$ signals of the ^{i}Pr$_2$-bimy reporter ligand in the chelate complexes was studied, on the basis of which a facile methodology for the donor strength determination of bidentate ligands was developed.



INTRODUCTION

Knowledge of the electron-donating ability of ligands is of utmost importance in coordination chemistry, since it is one of the key factors affecting the complexes' properties and reactivities.[1] For decades, a flurry of innovative research endeavors has been initiated with the intention to evaluate a ligand's relative electronic properties experimentally,[2] mostly considering monodentate ligands. In summary, there are two widely used methods. The dominating one in organometallic chemistry is Tolman's electronic parameter (TEP), which is the A$_1$ IR stretching frequency of the carbonyl ligands in complexes of the type [Ni(CO)$_3$L], where L is the ligand being studied.[2a,3] The second method, more widely used in classical coordination chemistry and introduced by Lever, is based on assessment of electrochemical E_0 values of a redox couple, for example, $Ru^{II/III}$, in analogous complexes differing solely in the ligand of interest to be compared. From these values, individual ligand electrochemical parameters (LEP) were derived.[4] Although LEP values are not a direct measure for the donating ability, they can be used to predict redox potentials of metal complexes, which are related to the donor strength of their ligands. Apart from these, NMR spectroscopy has been shown to be a useful technique for determining ligand donor strengths in metal complexes.[5] For example, studies with alkene complexes have shown that a more electron-rich metal center resulting from the donation of a stronger donor would lead to a higher-field chemical shift of the olefinic protons and carbon atoms.[6] More recently, we reported a new electronic parameter that is based on the evaluation and comparison of $^{13}C_{carbene}$ signals in complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(L)], where ^{i}Pr$_2$-bimy (1,3-diisopropylbenzimidazolin-2-ylidene) is the reporter carbene ligand, and L denotes the trans-standing, monodentate ligand of interest.[7] We observed that a more electron-donating coligand L would always lead to a more downfield ^{13}C signal of the carbene carbon in the ^{i}Pr$_2$-bimy ligand. Compared to TEP and LEP, our method can place both organometallic and classical Werner-type ligands on a unified scale, and the enhanced sensitivity allows for the detection of small differences within the same class of ligands, which are primarily due to subtle differences in inductive (I) and mesomeric (M) effects of substituents. Moreover, preparation of the generally air- and moisture-stable complex probes is much safer and more convenient. The nondestructive analysis by solution NMR for the determination of ligands' donating power also allows for further derivatizations or applications, for example, in catalysis, of the complex probes.[7b,d,8]

Compared to monodentate donors, bidentate ligands (L$_2$) can impart greater stabilities in their complexes due to the chelate effect, which is highly beneficial and desirable in transition metal chemistry. However, the electronic properties of bidentate ligands have been far less studied. Notably, Crabtree and co-workers evaluated carbonyl stretching frequencies of [*cis*-Mo(CO)$_4$L$_2$]-type complexes. These were converted to TEP using a conversion equation, which was based on the correlation of bis(monodentate) complexes [*cis*-Mo(CO)$_4$(L)$_2$] with [Ni(CO)$_3$L]. For ligands, which complexes could not be prepared, density functional theory calculations were conducted, and scaling factors had to be applied.[9−11] The necessity for scaling factors and conversion equations based on monodentate ligands in this indirect methodology complicates donor strength evaluation and may limit reliability. Apart from these, several groups have compared the relative donor strengths of L$_2$ ligands by simple comparisons of carbonyl stretching frequencies in metal carbonyl complexes. However, different transition metals, for

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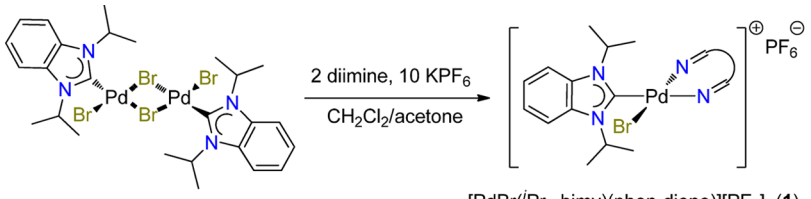
Scheme 1. Synthesis of [PdBr(^{i}Pr$_2$-Bimy)(diimine)]PF$_6$ Complexes 1−8



I

[PdBr(^{i}Pr$_2$-bimy)(phen-dione)][PF$_6$] (**1**)
[PdBr(^{i}Pr$_2$-bimy)(phen)][PF$_6$] (**2**)
[PdBr(^{i}Pr$_2$-bimy)(bipy)][PF$_6$] (**3**)
[PdBr(^{i}Pr$_2$-bimy)(R-DAB)][PF$_6$] (**4-8**)

example, Rh, W, Mn, and Cr, with different oxidation states, were used in these studies.[12−17] To the best of our knowledge, there is no general and unified system for the determination of electron-donating abilities of bidentate ligands.

As our contribution to a more accurate experimental detection of ligand donor strengths, we herein report an extension of our electronic parameter to bidentate ligands. For this purpose, the synthesis and characterizations of a new series of *trans*-[PdBr(^{i}Pr$_2$-bimy)(L$_2$)]PF$_6$ complexes bearing selected popular organometallic and classical Werner-type ligands is presented. On the basis of the ^{13}C NMR spectroscopic analyses of these complexes, the donor strengths of the 15 bidentate ligands L$_2$ were ranked on a unified scale.

RESULTS AND DISCUSSION

Diimines. 1,2-Bidentate nitrogen ligands such as aromatic and aliphatic α-diimines have acquired immense importance in coordination chemistry due to the diverse photochemical properties and catalytic activities of their complexes. Their versatile coordination behavior is further highlighted by the fact that they probably can bind to all transition metals. Ruthenium and platinum complexes of highly conjugated aromatic diimine ligands, such as phenanthroline (phen) and 2,2′-bipyridines (bipy), exhibit intense luminescence, which may find applications in optoelectronic devices.[18] In addition, metal-diimine complexes are well-known to mediate olefin polymerizations[1e,19] and C−C cross-coupling reactions (e.g., Suzuki−Miyaura).[20] Importantly, it has been reported that the electron-donating potential of these ligands has a prominent influence on the optical and catalytic properties of their complexes. Thus, in extension of our electronic parameter to bidentate ligands, we wish to probe the electron-donating abilities of aromatic and aliphatic diimine ligands.

The synthesis of the respective ^{i}Pr$_2$-bimy/diimine mixed-ligand complexes involves a standard bridge-cleavage reaction of the easily available and known dimeric complex **I**[7a] and concurrent chelate formation by ligand displacement of one bromido ligand with suitable 1,2-diimines[21], for example, 1,10-phenanthroline-5,6-dione (phen-dione), phen, bipy, and 1,4-di(4-R-phenyl)-2,3-dimethyl-1,4-diazabutadienes (R-DAB: R = Br, H, Me, OMe, ^{t}Bu). Subsequent anion metathesis reaction with KPF$_6$ affords the desired [PdBr(^{i}Pr$_2$-bimy)(diimine)]PF$_6$ complexes **1**−**8** (Scheme 1). With the exception of [PdBr(^{i}Pr$_2$-bimy)(Br-DAB)]PF$_6$ (**4**), all complexes were obtained in spectroscopically pure form in high yields (>80%) by simply washing with a nonpolar solvent such as hexane or diethyl ether. Complex **4** had to be purified by column chromatography and was isolated in a moderate yield of 40%. All complexes are pale-yellow solids and stable to air and moisture. Most complexes have fairly good solubilities in common polar organic solvents, such as CH_2Cl_2, $CHCl_3$, CH_3CN, dimethylformamide, and dimethyl sulfoxide (DMSO). Two exceptions are compounds [PdBr(^{i}Pr$_2$-bimy)(phen-dione)]PF$_6$ (**1**) and [PdBr(^{i}Pr$_2$-bimy)(bipy)]PF$_6$ (**3**), which sparingly dissolve in $CHCl_3$, hampering full NMR spectroscopic characterization in $CDCl_3$ (vide infra).

Formation of these complexes is indicated by positive-mode electrospray ionization mass spectrometry (ESI-MS), which shows base peaks owing to the [M − PF$_6$]$^+$ fragments. In their ^{1}H and ^{13}C NMR spectra, signals of the respective diimine ligands are observed. As expected, a doubling of ligand signals was observed after coordination, which led to inequivalent "transoid" and "cisoid" parts of the diimine ligands with respect to the NHC. The aromatic signals of the ^{i}Pr$_2$-bimy ligand remain largely unchanged upon cleavage of complex **I** and subsequent coordination of the diimine ligands. In the ^{1}H NMR spectra, the isopropyl C−H resonances are shifted upfield by 0.4−0.7 ppm as compared to that in the precursor complex **I**, and the isopropyl CH_3 resonances split into two doublets, indicating a restricted rotation of the ^{i}Pr$_2$-bimy ligands about the Pd−C bond in complexes **1**−**8**. This is also observed in their ^{13}C NMR spectra, where two singlets were detected for the isopropyl CH_3 groups. With exception of complexes **1** and **3**, the carbene carbon signals of all complexes were successfully obtained in a short time due to their good solubilities in $CDCl_3$ (Table 1). The poor solubility of the phen-dione and bipy complexes **1** and **3**, however, hampers the data collection. This problem was finally resolved by ^{13}C labeling their carbene donors via cleavage reaction using the $^{13}C_{carbene}$-labeled analogue of complex **I**.[7a] By doing so, detection of the carbene signals of **1** and **3** in $CDCl_3$ was accomplished in a short time (Table 1).

Table 1. Summary of ^{i}Pr$_2$-Bimy Carbenoid Resonances in Complexes Bearing Diimines

complex	L$_2$	δ C$_{carbene}$[a]
1	phen-dione	160.0[b]
2	phen	161.4
3	bipy	162.7[b]
4	Br-DAB	160.5
5	H-DAB	162.2
6	Me-DAB	162.6
7	OMe-DAB	162.8
8	^{t}Bu-DAB	163.4

[a]Measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to tetramethylsilane (TMS). [b]Carbene signal obtained from the $^{13}C_{carbene}$-labeled analogue.

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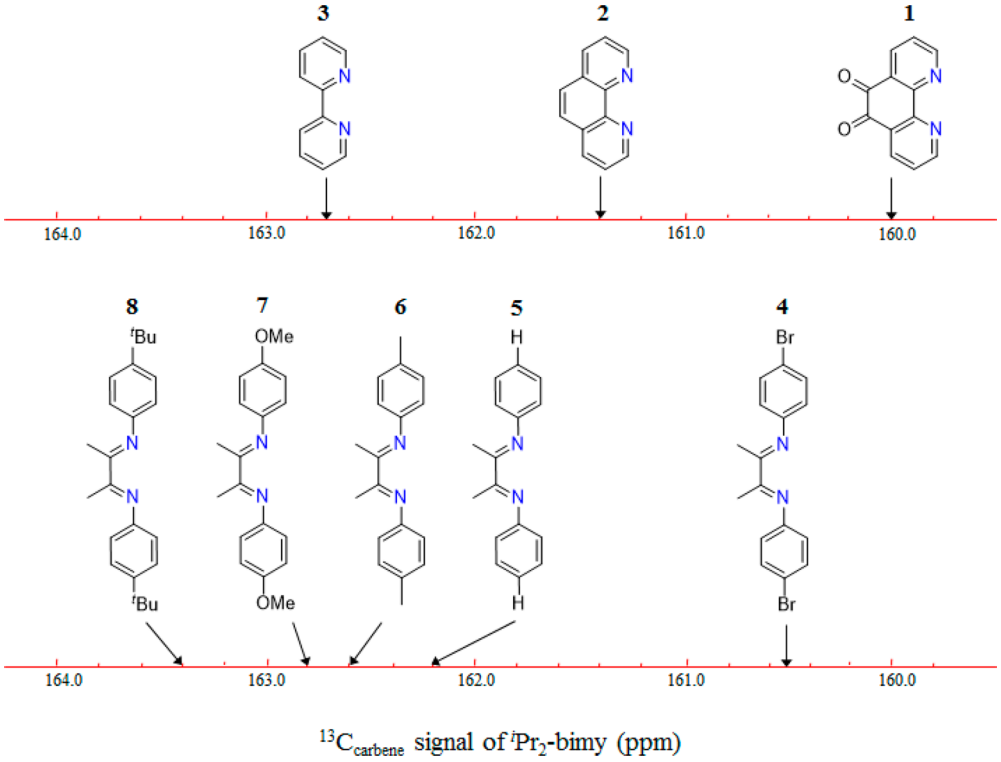

Figure 1. Donor abilities of aromatic and aliphatic diimines on the ^{13}C NMR scale.

The $^{13}C_{carbene}$ resonances of aromatic diimine complexes **1**–**3** are observed at 160.0, 161.4, and 162.7 ppm, respectively, indicating increasing donor strength from phen-dione to phen followed by bipy ligand, which is in agreement with negative inductive (−*I*) effects originating from the two electron-withdrawing carbonyl groups in the phen-dione or the additional benzannulation in the phen ligand compared to the bipy parent. The $^{13}C_{carbene}$ shifts of DAB complexes **4**–**6** range from 160.5 to 162.6 ppm, showing the intermediate donating ability of the R-DAB chelators (R = Br, H, Me) compared to phen-dione and bipy. The OMe-DAB and ^{t}Bu-DAB ligands possess stronger donating power than the bipy ligand with their complexes' carbene signals found at 162.8 and 163.4 ppm. It is important to highlight at this point that routine ^{13}C NMR spectroscopy, with an estimated standard deviation of ∼0.02 ppm, is much more sensitive than routine IR spectroscopy.[7a] This means that the differences observed here are significant. Notably, our method can discern differences within the five R-DAB ligands, which only differ in their para substituents five bonds away from the N-donor and seven bonds away from the reporter nuclei. On the basis of the $^{13}C_{carbene}$ resonances, we can rank the five DAB ligands according to their decreasing donor abilities in the order ^{t}Bu-DAB > OMe-DAB > Me-DAB > H-DAB > Br-DAB. This order is reasonable and consistent with the decreasing positive inductive (+*I*) effect of the *para*-substituent in the order ^{t}Bu > Me > H > Br (Figure 1).

The positioning of the OMe-DAB ligand can be explained by the positive mesomeric (+*M*) effect of the methoxy group, which not only compensates its negative inductive (−*I*) effect, but even increases electron density via p−π conjugation of its lone pairs with the aromatic rings. These results demonstrate that our ^{13}C-based electronic parameter can be extended to the evaluation of bidentate ligands. It appears that the method is sufficiently sensitive for detecting small electronic differences within the same ligand class brought about remote ligand modifications. The relative contributions of such influences to the chemical shift, which is also affected by polarity, and the solvation and sterical differences of the complexes will be subject to further studies.

Slow evaporation of concentrated solutions of complexes **2** and **7** in $CHCl_3$/hexane afforded single crystals, which were analyzed by X-ray diffraction. Figure 2 depicts their molecular structures, in which both palladium centers are coordinated by one NHC, one bromido, and one chelating diimine ligand. The NHC planes in both complexes are perpendicular to the $PdCN_2Br$ coordination plane with dihedral angles of 89° and 81° in complexes **2** and **7**, respectively. In complex **7**, the two N-aryl rings tilt toward different directions about the chelating plane with dihedral angles of 63° and 67°. The N3−Pd1−N4 bite angles in complex **2** (81°) and **7** (79°) are very similar, which is also observed for their Pd−$C_{carbene}$ bond lengths of 1.977(7) and 1.976(3) Å.

Dicarbenes. In addition to the evaluation of the ubiquitous bidentate diimine ligands, we are particularly interested in the donor strength determination of chelating dicarbenes due to their increasing importance as ligands in catalytic reactions and organometallic chemistry in general.

Simple dicarbenes formed by bridging two classical NHCs can differ in their heterocyclic backbones, their external N-substituents (R groups), and finally in the nature of their linkers (Chart 1). Changes in any of these three parameters may affect their electron-donating abilities. To study whether all these effects can be determined by our electronic parameter, seven diNHCs were targeted (Chart 1, **A**–**G**), the precursors of which were prepared according to literature procedures.[22] Overall, these salts, and consequently their diNHCs, form three comparable groups, each differing in only one parameter: (i)

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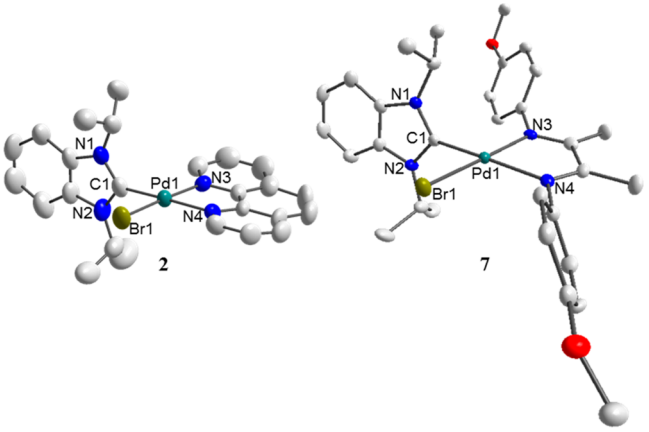


Figure 2. Molecular structures of **2** and **7** in the solid state (hydrogen and counterion atoms are omitted for clarity; ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [deg] of **2**: Pd1–C1 1.977(7), Pd1–N3 2.044(5), Pd1–N4 2.071(5), Pd1–Br1 2.3925(10), N1–C1 1.356(9), N2–C1 1.329(10); C1–Pd1–Br1 85.7(2), C1–Pd1–N3 96.9(3), N4–Pd1–N3 81.0(2), N4–Pd1–Br1 96.31(16), N2–C1–N1 109.7(6). **7**: Pd1–C1 1.976(3), Pd1–N3 2.035(3), Pd1–N4 2.087(3), Pd1–Br1 2.4119(5), N1–C1 1.349(4), N2–C1 1.353(4); C1–Pd1–Br1 84.01(10), C1–Pd1–N3 99.30(12), N4–Pd1–N3 78.56(11), N4–Pd1–Br1 98.32(8), N2–C1–N1 108.0(3).

heterocyclic backbone (**A**·2HBr, **B**·2HBr, **C**·2HBr), (ii) N3 substituent (**C**·2HBr, **D**·2HBr, **E**·2HBr), and (iii) linker length (**D**·2HBr, **F**·2HBr, **G**·2HBr).

Generally, the carbene precursors were first reacted with Ag_2O to obtain the intermediate Ag-NHC species, which subsequently transfers the diNHC to the Pd center in *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(CH_3CN)] (**II**)[23] under displacement of the CH_3CN and one bromido ligand. Anion exchange using KPF_6 gave the [PdBr(^{i}Pr_2-bimy)(diNHC)]PF_6 complexes **9**–**13** bearing diNHCs **A**–**E**, respectively, in moderate to decent yields of over 60% (Scheme 2, Method 1). Complexes **14** and **15** with ethylene- and propylene-bridged diNHCs **F** and **G**, however, were only isolated as minor byproducts in low yields of 8% (**14**) and 18% (**15**) through this route. The major products isolated were the dipalladium species **16** and **17** (Scheme 2, Method 1), in which the diNHCs are bridging two palladium(II) centers, instead of chelating to one palladium(II) Lewis acid as required for the formation of complexes **14** and **15**. We attribute the low yields of the latter to the difficult formation of the less stable seven- and eight-membered palladacycles during the transmetalation step as opposed to the more stable six-membered cycles in complexes **9**–**13**.

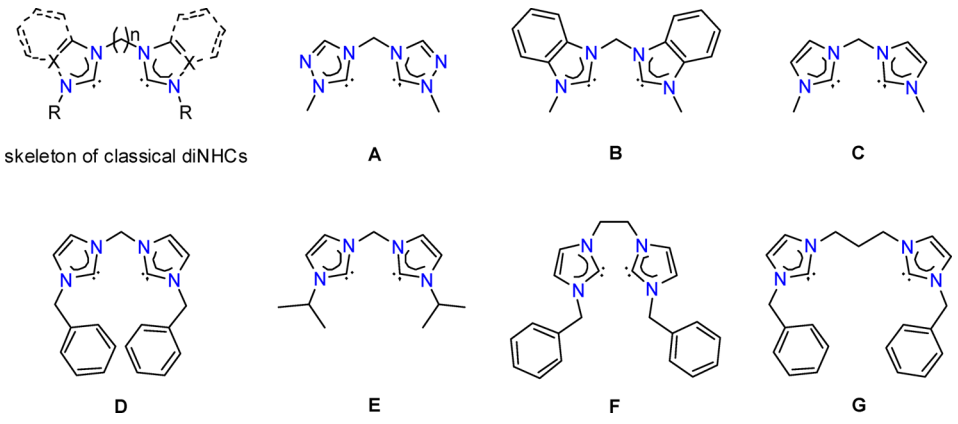
To circumvent this, a reversed protocol was attempted for the preparation of **14** and **15**, whereby the known diNHC complexes **III** and **IV** were preformed[24] and then subjected to attack by the ^{i}Pr_2-bimy ligand generated in situ by deprotonation of the 1,3-diisopropylbenzimidazolium salt with K_2CO_3. KPF_6 was again added to replace the bromide anion, affording complexes **14** and **15** in higher yields of 56% and 85%, respectively (Scheme 2, Method 2). To the best of our knowledge, these heterotris(NHC) palladium(II) complexes are the first of their kind to contain a metal center that is simultaneously coordinated by both a monodentate NHC and a bidentate diNHC.[25]

Monopalladium complexes **9**–**15** are off-white solids, while the two bridged dipalladium species **16** and **17** are yellow powders. These two neutral complexes also have very good solubilities in common organic solvents such as diethyl ether, ethyl acetate, $CHCl_3$, CH_2Cl_2, CH_3CN, DMSO, etc. On the other hand, the cationic complexes **9**–**13** are insoluble in ethers and only well-soluble in polar organic solvents. Surprisingly, the solubilities of **14** and **15** bearing the longer ethylene- and propylene-linked diNHCs are significantly poorer in $CHCl_3$ and CH_2Cl_2, but remain good in CH_3CN and DMSO. ESI-MS revealed base peaks from m/z 565 to 745 for the molecular [M – PF_6]$^+$ cations of complexes **9**–**15**, while strong isotopic envelopes centered at m/z 1199 and 1213 were recorded for the [M – Br]$^+$ fragments of the dinuclear species **16** and **17**.

NMR spectra of the complexes were recorded in $CDCl_3$ (**9**–**13**, **16**, **17**) or CD_3CN (**14**, **15**) at 298 K. Most complexes give rise to well-resolved spectra at this temperature with the exception of the [PdBr(^{i}Pr_2-bimy)(**A**)]PF_6 complex (**9**), where only broad signals are observed in its ^{1}H NMR spectrum. At room temperature, the ^{i}Pr_2-bimy NCH and bridging NCH_2N protons are not resolved due to a fast fluxional behavior. Cooling the sample to 273 K improves the resolution, and a well-resolved spectrum was finally obtained when the temperature was further decreased to 243 K (Figure 3).

When sufficiently resolved, complexes **9**–**15** share very similar ^{1}H and ^{13}C NMR spectra. Besides the doubling of the diNHC signals upon coordination as observed for the diimine complexes, further splitting due to diastereotopy of N3-substituents is noted for complexes with benzyl and isopropyl groups. For example, complex **13** shows four doublets in its ^{1}H

Chart 1. Lewis Structures of 7 Classical diNHCs



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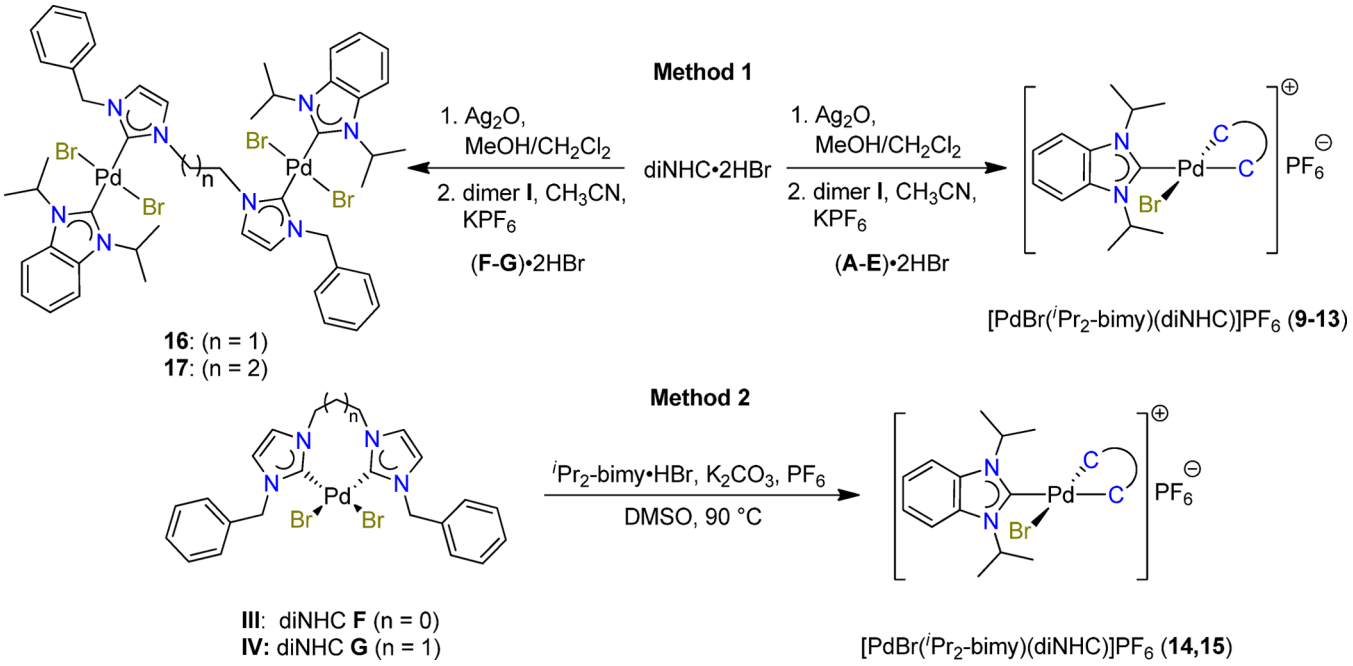
Scheme 2. Syntheses of [PdBr(^{i}Pr$_2$-Bimy)(diimine)]PF$_6$ Complexes 9−15 and [Pd$_2$Br$_4$(^{i}Pr$_2$-Bimy)$_2$(diNHC)] Complexes 16−17



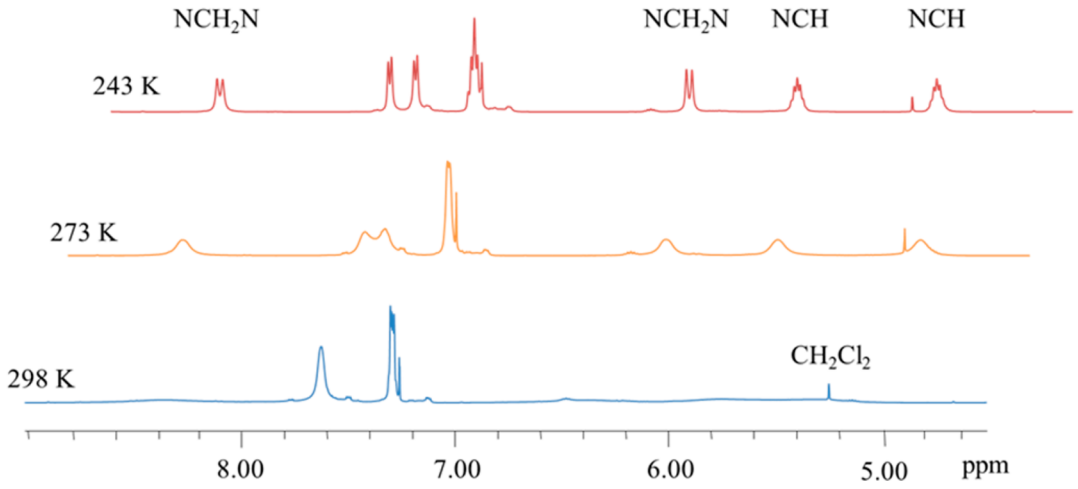


Figure 3. Variable-temperature ^{1}H NMR spectra of complex **9** in the region of 4.5−9.0 ppm.

NMR spectrum, which are attributed to the inequivalent isopropyl CH$_3$ signals of the diNHC ligand. Similarly, four AM patterned doublets are observed in the ^{1}H NMR spectra of complexes **12**, **14**, and **15**, assignable to the benzylic protons. In most cases, the linker protons become diastereotopic upon complexation as well. For example, two doublets at 8.48 and 6.29 ppm are observed for the methylene spacer in the spectrum of complex **9** (Figure 3). The coupling pattern for the ^{i}Pr$_2$-bimy ^{1}H NMR signals in these complexes are more complicated than those found in the diimine derivatives, showing two septets at 5.25 and 6.02 ppm for the NCH protons. This indicates a restricted rotation of the N-substituents in the ^{i}Pr$_2$-bimy probe after diNHC coordination.

The reduced symmetry also leads to a doubling of the ^{13}C NMR signals for the diNHC ligands and the ^{i}Pr$_2$-bimy probe. As expected, three downfield carbene signals are detected in these seven complexes, most of which are sufficiently different to be properly assigned in accordance with literature values for related complexes.[7a,24] Complex **10**, bearing the dibenzimidazolin-2-ylidene chelator, on the other hand, shows three carbene resonances in a very narrow range. Here, heteronuclear multiple-bond correlation NMR experiments were conducted to assist the correct assignment. Two-dimensional cross-peak correlations between the carbene carbon atoms with the protons in the respective N-substituents allow for an unambiguous assignment to the correct carbene atom. The detection of the ^{i}Pr$_2$-bimy carbene signals in CDCl$_3$ of the poorly soluble complexes **14** and **15** was accomplished by using the ^{13}C-labeled 1,3-diisopropylbenzimidazolium salt[7a] in their syntheses.

The NMR spectra of the dipalladium complexes **16** and **17** are much simpler, with the benzylic protons resonating as one singlet at 5.80 and 5.76 ppm, respectively. The equivalent ethylene protons in **16** show one singlet, and the propylene protons in **17** gave rise to a triplet and a multiplet in a 4:2 integral ratio. Restricted rotation of the ^{i}Pr$_2$-bimy ligand about

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the Pd−C bond in both complexes is evidenced by two septets and doublets assignable to the isopropyl substituents. Each complex exhibits only two carbene signals in its ^{13}C NMR spectrum, and the more downfield signal at 178.8 ppm (**16**) or 179.1 ppm (**17**) is assigned to the $^{i}Pr_2$-bimy ligand.

Table 2 summarizes the diagnostic $^{13}C_{carbene}$ resonances of the $^{i}Pr_2$-bimy probe in complexes **9**−**15**. Generally, they are much more downfield than those in the diimine counterparts, confirming stronger donating abilities of the diNHC ligands. The group (i) diNHCs **A**−**C** (ditriazolin-5-ylidenes (ditazy), dibenzimidazolin-2-ylidene (dibimy), and diimidazolin-2-ylidene (diimi)) in complexes **9**−**11** differ only in their heterocyclic backbone, and by comparison of the $^{i}Pr_2$-bimy reporter signals, we can deduce an increasing electron-donating ability in the order of **A** (ditazy) < **B** (dibimy) < **C** (diimi). This backbone influence is consistent with that reported for monodentate NHCs; that is, benzannulation in **B** and introduction of an electronegative nitrogen atom in **C** result in a successive increase of $-I$ effect and weakening of the respective donors. This trend also agrees with that obtained from the CO stretches calculated by Crabtree and co-workers based on a [Mo(CO)$_4$(diNHC)] (diNHC = diimi, ditazy) system[11] and the CO stretches measured by Veige et al. from a [Rh(CO)$_2$(diNHC)]OTf (diNHC = diimi, dibimy) system.[15] In addition, comparison among group (ii) ligands (i.e., **C**−**E**) in complexes **11**−**13** reveals that our electronic parameter can also detect N3-substituent effects of diNHCs in the order of **D** (Bn) < **C** (Me) < **E** (^{i}Pr) in line with their increasing $+I$ effects. Effects induced by the linkers as a special type of N-substituent effect in diNHCs of group (iii), however, have rarely been investigated. From increasing downfield shifts of the $^{i}Pr_2$-bimy $^{13}C_{carbene}$ resonances in complexes **12** < **14** < **15**, we can conclude that simple lengthening of the linkers by a CH_2 group leads to a detectable increase of donor strength in the order of **D** (methylene) < **F** (ethylene) < **G** (propylene). The very small difference between **D** and **F** is understandable, since all carbon atoms in the bridges experience $-I$ effects of at least one electron-withdrawing nitrogen atom. In ligand **G** the situation is different, as the central CH_2 group in the bridge exerts a $+I$ effect, which can effectively increase electron density. Generally, this result is in line with the fact that the $+I$ effect of an alkyl group increases with the chain length, which has also been testified by Ito's group via comparing the CO stretches of [Mo(CO)$_4$(diNHC)] (diNHC = methylene- and ethylene-bridged imidazolin-2-ylidenes).[16] However, no clear trend was detected when similar carbonyl-based methods using *fac*-[(CO)$_3$ReBr(diNHC)]-type complexes were employed.[17] This highlights the better sensitivity and broader applicability of this ^{13}C NMR-based electronic parameter compared to carbonyl-based methods. Although these results are in line with chemical intuition, there is no doubt that changes in the ligand bite angles and the resulting changes in the geometry of the complexes may influence the ^{13}C NMR shifts more strongly

Table 2. Summary of $^{i}Pr_2$-Bimy Carbenoid Resonances in Complexes 9−15 Bearing diNHC Chelators

complex	L_2	δ $C_{carbene\text{-}probe}$ [a]
9	**A**	177.1
10	**B**	178.7
11	**C**	179.9
12	**D**	179.51[b]
13	**E**	180.0
14	**F**	179.54[b,c]
15	**G**	180.3[c]

[a]Measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to TMS. [b]two decimal placings are given to highlight the small, but discernible differences. [c]Carbene signal obtained from the carbene ^{13}C-labeled analogue.

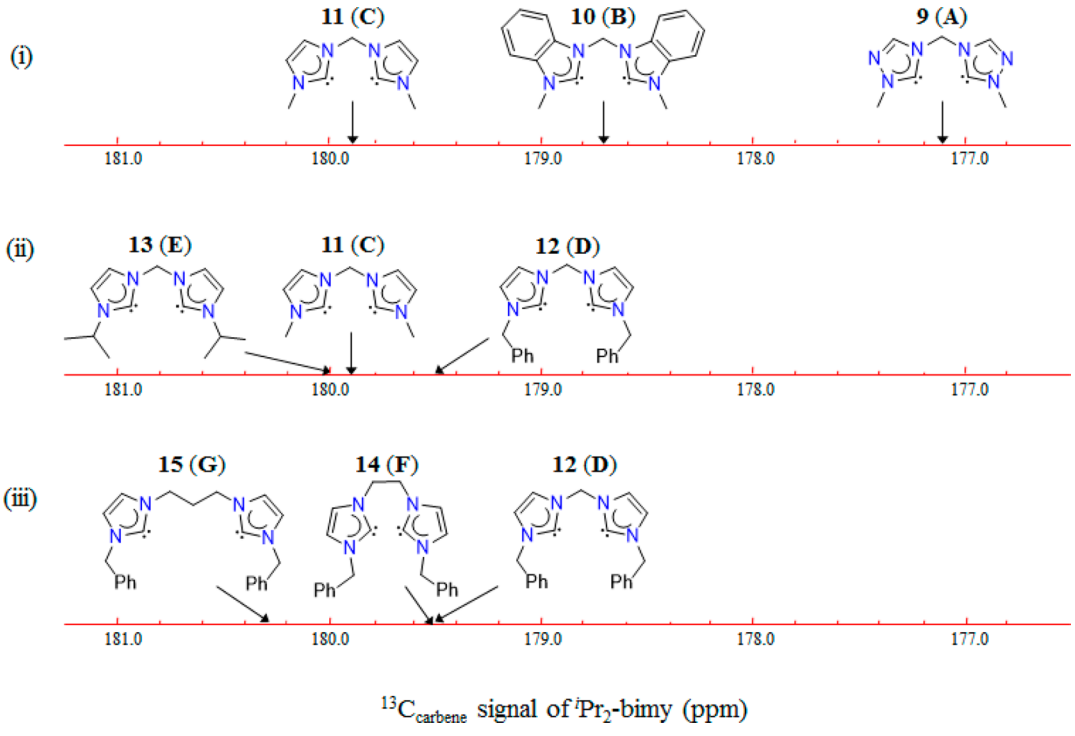

Figure 4. Donor abilities of dicarbenes on the ^{13}C NMR scale.

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than their donor strengths. This potential limitation of the methodology must be addressed in additional studies.

Overall, we can see from Figure 4 that the NHC backbone has the most significant influence among the three parameters studied with chemical shift differences >1.0 ppm. Different N3 substituents and linkers within the imidazole-derived system give rise to diNHCs (**C**−**G**) with varying donating potentials in the order of **G** (propylene, Bn) > **E** (methylene, ^{i}Pr) > **C** (methylene, Me) > **F** (ethylene, Bn) > **D** (methylene, Bn). The results obtained provide useful information for the electronic fine-tuning of ligands, which is one of the key factors for complex stability and their applications.

Single crystals of **9**, **11**, **14**, and **15** can easily be grown upon standing of concentrated solutions (DMSO for **9**, CH_2Cl_2/hexane for **11**, $CHCl_3$/hexane for **15**) or from diffusion of diethyl ether into a solution of **14** in CH_3CN. The molecular structures are shown in Figure 5 along with selected bond

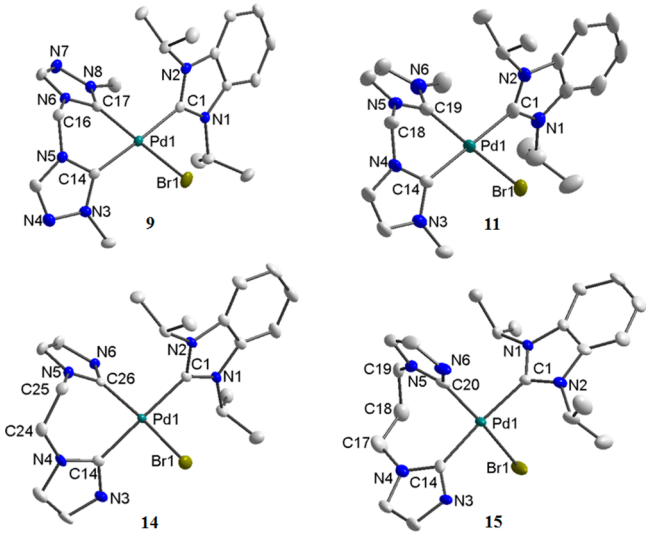

Figure 5. Molecular structures of **9**, **11**, **14**, and **15** in the solid state (hydrogen atoms, counterions, solvent molecules, and N-benzyl substituents in complexes **14** and **15** are omitted for clarity; ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [deg]: **9**, Pd1−C1 2.0251(19), Pd1−C17 1.9977(18), Pd1−C14 2.0190(19), Pd1−Br1 2.4576(3); C1−Pd1−C17 92.30(7), C14−Pd1−C17 84.14(7), C14−Pd1−Br1 93.01(5), C1−Pd1−Br1 90.77(5). **11**, Pd1−C1 2.038(4), Pd1−C19 2.003(4), Pd1−C14 2.033(4), Pd1−Br1 2.4556(16); C1−Pd1−C19 94.52(17), C14−Pd1−C19 85.89(16), C14−Pd1−Br1 91.63(12), C1−Pd1−Br1 87.83(13). **14**, Pd1−C1 2.044(2), Pd1−C14 1.995(2), Pd1−C26 2.026 (2), Pd1−Br1 2.4646(3); C1−Pd1−C14 94.24(9), C14−Pd1−C26 84.88(10), C26−Pd1−Br1 91.31(7), C1−Pd1−Br1 90.56(7). **15**, Pd1−C1 2.055(4), Pd1−C20 1.998(4), Pd1−C14 2.036(4), Pd1−Br1 2.4623(6); C1−Pd1−C20 93.88(15), C14−Pd1−C20 87.69(15), C14−Pd1−Br1 89.91(10), C1−Pd1−Br1 89.79(11).

parameters. The asymmetric unit of complex **11** contains two independent molecules. The two molecules in this complex have essentially the same structure except for several bond parameter differences slightly over 3σ, and only one of them is shown as a representative.

The cationic complexes **9**, **11**, **14**, and **15** crystallize as mononuclear species, in which one $^{i}Pr_2$-bimy, the diNHC, and one bromido ligand coordinate the palladium center in a distorted square−planar geometry. Complex **11** bearing the methylene-bridged diNHC ligand **C** and complex **14** with ethylene-bridged diNHC ligand **F** have very similar bite angles (85.9° vs 84.9°). The bite angle in complex **15** with a propylene-bridged diNHC is only slightly bigger with 87.7°. The six- to eight-membered palladacycles all adopt boat-like conformations similar to those reported for simple dihalido−diNHC complexes.[24,22,26−28] Among the three carbene donors in each complex, the $^{i}Pr_2$-bimy ring plane always has the largest dihedral angle with respect to the PdC_3Br coordination plane (**9**, 70.2°; **11**, 74.3°; **14**, 78.6°; **15**, 76.2°). The short methylene bridge of the diNHC ligands prevents an otherwise preferred perpendicular orientation, which results in small dihedral angles ranging from 39.2° to 52.7° in complexes **9** and **11**. Elongation of the spacer in the diNHCs of complexes **14** and **15** increases the flexibility leading to larger dihedral angles of 62.9° to 74.3°. The Pd−C ($^{i}Pr_2$-bimy) distances in these four complexes fall in a narrow range of about 2.0 Å, which are generally longer than those found in the diimine analogues. This is due to less Lewis-acidic metal centers resulting from the coordination of the stronger donating diNHC ligands, although no clear correlation between these distances and the electron-donating powers among diNHCs was found.

Single crystals of dipalladium complex **17** were grown by slow evaporation of a saturated solution in diethyl ether. As depicted in Figure 6, the complex features two neutral trans-

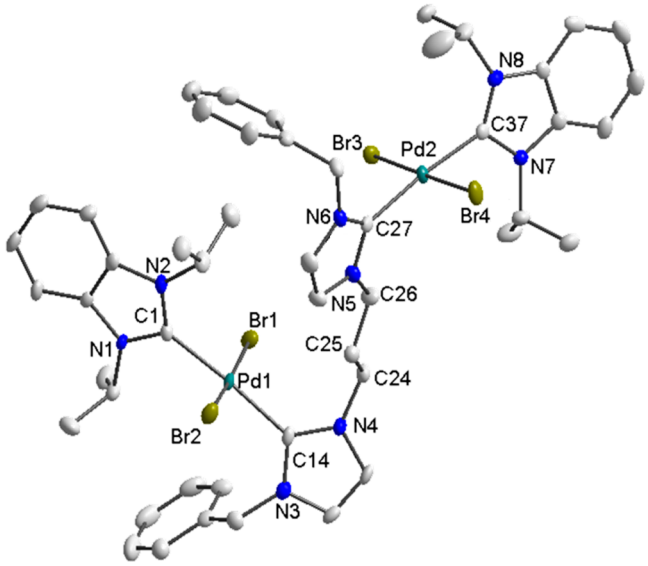

Figure 6. Molecular structures of **17** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.014(3), Pd1−Br1 2.4473(5), Pd1−C14 2.042(3), Pd1−Br2 2.4370(5), Pd2−C37 2.031(3), Pd2−Br3 2.4346(4), Pd2−C27 2.031(3), Pd2−Br4 2.4530(5); C1−Pd1−Br1 87.84(10), C14−Pd1−Br1 91.66(10), C14−Pd1−Br2 91.61(10), C1−Pd1−Br2 89.34(10), C37−Pd2−Br3 89.63(9), C27−Pd2−Br3 92.20(9), C27−Pd2−Br4 88.90(9), C37−Pd2−Br4 89.27(9).

configured palladium(II) centers. The propylene-linked diNHC coordinates in a bridging manner. The dihedral angles between the NHC and the PdC_2Br_2 coordination planes are generally larger for the $^{i}Pr_2$-bimy ligands (78.4°, 85.3°) compared to those of the bridging diNHC ligand (69.9° and 66.9°). The Pd−C ($^{i}Pr_2$-bimy) bond lengths do not differ significantly from those of the cationic chelates **9**, **11**, **14**, and **15**, indicating that the cis-positioned coligand (Br vs NHC) does not affect these distances much regardless of the overall charge of the complex.

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CONCLUSION

Mononuclear complexes of the general formula [PdBr(^{i}Pr$_2$-bimy)(L$_2$)]PF$_6$ (**1**−**15**) bearing 15 different bidentate ligands, including aromatic diimines, dizabutadienes, and di-N-heterocyclic carbenes, have been synthesized and fully characterized. In addition, two dicarbene-bridged dipalladium complexes were isolated and characterized as well. Using these monopalladium complex probes, we could evaluate and rank the net donating abilities of the 15 bidentate ligands based on their influences on the $^{13}C_{carbene}$ signal of the constant ^{i}Pr$_2$-bimy reporter ligand. The facile and nondestructive methodology is sufficiently sensitive for detecting subtle changes up to seven bonds away, which corroborates the successful extension of our ^{13}C NMR-based electronic parameter from monodentate to bidentate ligands. The satisfying results obtained for the three types of bidentate ligands are encouraging, and an expansion of this study to a greater diversity of bidentate ligands bearing other donors is currently ongoing in our laboratory with the intention of testing the scope and limitations of our electronic parameter.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out without precautions to exclude air and moisture unless otherwise stated. Solvents were used as received. ^{1}H and ^{13}C NMR chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane. Only the synthetic procedures and characterizations of four representative complexes, namely, **2**, **9**, **14**, and **16**, are presented here.

*Bromido(1,3-diisopropylbenzimidazolin-2-ylidene)-(phenanthroline)palladium(II) hexafluoro-phosphate (**2**).* Complex **I** (94 mg, 0.10 mmol) was suspended in CH_2Cl_2 (10 mL), and solutions of phenanthroline (36 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) and KPF_6 (200 mg, 1.00 mmol) in acetone (5 mL) were added stepwise. The reaction mixture was stirred overnight, and all volatiles were removed under reduced pressure. CH_2Cl_2 (30 mL) was added to the residue, and the suspension was filtered. The solvent of the filtrate was removed under vacuum, giving the crude product as a yellow solid. The product was further purified by recrystallization from $CHCl_3$/hexane. Yield: 138 mg, 0.19 mmol, 96%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (d, ^3J(H,H) = 3 Hz, 1 H, Ar−H), 8.85−8.83 (m, 1 H, Ar−H), 8.77−8.75 (m, 1 H, Ar−H), 8.18 (d, ^3J(H,H) = 5 Hz, 2 H, Ar−H), 8.02−7.97 (m, 3 H, Ar−H), 7.77 (dd, ^3J(H,H) = 3 Hz, 2 H, Ar−H), 7.43 (dd, ^3J(H,H) = 3 Hz, 2 H, Ar−H), 6.11 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 1.82 (d, ^3J(H,H) = 7 Hz, 6 H, CH_3), 1.72 (d, ^3J(H,H) = 7 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 161.4 ($C_{carbene}$), 151.9, 151.6, 147.8, 147.1, 141.9, 140.7, 134.3, 132.2, 131.4, 128.9 (2×), 127.7, 126.6, 124.7, 114.1 (Ar−C), 55.9 (NCH), 22.1, 21.6 (CH_3). ^{31}P{^{1}H} NMR (202.45 MHz, $CDCl_3$): −144.1 (m, ^1J(P,F) = 712 Hz, PF_6). ^{19}F{^{1}H} NMR (282.38 MHz, $CDCl_3$): 2.5 (d, ^1J(P,F) = 712 Hz, PF_6). Anal. Calcd for $C_{25}H_{28}BrF_6N_4PPd$: C, 41.95; H, 3.94; N, 7.83. Found: C, 41.81; H, 3.66; N, 7.73%. MS (ESI): m/z 569 [M − PF_6]$^+$.

*Bromido(A)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium-(II) Hexafluorophosphate (**9**).* The dicarbene precursor salt (68 mg, 0.20 mmol) and silver oxide (47 mg, 0.20 mmol) were stirred in MeOH (10 mL) and CH_2Cl_2 (5 mL) at ambient temperature for 3 h. To the resulting suspension was slowly dropped in the CH_3CN solution of complex **II**, which was in situ generated by stirring complex **I** in CH_3CN for 2 h. Compound KPF_6 (200 mg, 1.00 mmol) was then added to the suspension, and the mixture was stirred overnight. Solvent was removed under reduced pressure, CH_2Cl_2 (50 mL) was added to the residue, and the suspension was filtered. The filtrate was concentrated to 5 mL and added to diethyl ether (50 mL). The precipitate was collected and dried to give the product as an off-white solid. Yield: 93 mg, 0.13 mmol, 65%. ^{1}H NMR (500 MHz, $CDCl_3$, 243 K): δ 9.47 (s, 1 H, Ar−H), 9.07 (s, 1 H, Ar−H), 8.48 (d, ^2J(H,H) = 13 Hz, 1 H, NC*H*HN), 7.69 (d, ^3J(H,H) = 8 Hz, 1 H, Ar−H), 7.57 (d, ^3J(H,H) = 8 Hz, 1 H, Ar−H), 7.32−7.26 (m, 2 H, Ar−H), 6.29 (d, ^2J(H,H) = 13 Hz, 1 H, NCH*H*N), 5.79 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 5.14 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 4.24 (s, 3 H, NCH_3), 3.38 (s, 3 H, NCH_3), 1.83−1.81 (m, 6 H, $CH(CH_3)_2$), 1.57 (d, ^3J(H,H) = 7 Hz, 3 H, $CH(CH_3)_2$), 1.18 (d, ^3J(H,H) = 7 Hz, 3 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 177.1 ($C_{carbene\text{-}probe}$), 170.5 ($C_{carbene\text{-}trans}$), 163.8 ($C_{carbene\text{-}cis}$), 143.7, 142.1, 134.0, 124.0, 114.2 (Ar−C), 59.6 (NCH_2N), 55.7 (br−s, NCH), 41.9, 40.3 (NCH_3), 21.7 (br−s, $CH(CH_3)_2$). ^{31}P{^{1}H} NMR (202.45 MHz, $CDCl_3$): −143.7 (m, ^1J(P,F) = 714 Hz, PF_6). ^{19}F{^{1}H} NMR (282.38 MHz, $CDCl_3$): 4.5 (d, ^1J(F,P) = 714 Hz, PF_6). Anal. Calcd for $C_{20}H_{28}BrF_6N_8PPd$: C, 33.75; H, 3.97; N, 15.74. Found: C, 33.40; H, 3.78; N, 15.34%. MS (ESI): m/z 567 [M − PF_6]$^+$.

*Bromido(F)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium-(II) Hexafluorophosphate (**14**).* This complex could be obtained analogously to the complex **9** (Method 1) with further purification using colum chromatography (CH_2Cl_2/MeOH: 40/1) in low yield (14 mg, 0.02 mmol, 8%). The yield was increased by using a different protocol (Method 2): complex **III** (121 mg, 0.20 mmol), 1,3-diisopropylbenzimidazolium salt (57 mg, 0.20 mmol), K_2CO_3 (34 mg, 0.24 mmol), and KPF_6 (200 mg, 1.00 mmol) were mixed in DMSO (10 mL) and heated at 90 °C overnight. The solvent was removed by vacum distillation. The resulting residue was suspended in CH_2Cl_2 (30 mL) and then extracted with H_2O (4 × 20 mL). Drying of the organic phase over Na_2SO_4 followed by removal of the solvent in vacuo afforded an orange solid. The solid was washed with $CHCl_3$ (20 mL) to give the off white product. Yield: 98 mg, 0.11 mmol, 56%. ^{1}H NMR (500 MHz, CD_3CN): δ 7.73 (d, ^3J(H,H) = 8 Hz, 1 H, Ar−H), 7.51 (d, ^3J(H,H) = 8 Hz, 1 H, Ar−H), 7.44 (t, ^3J(H,H) = 7 Hz, 2 H, Ar−H), 7.39 (d, ^3J(H,H) = 7 Hz, 1 H, Ar−H), 7.35 (d, ^3J(H,H) = 2 Hz, 1 H, Ar−H), 7.30 (t, ^3J(H,H) = 8 Hz, 1 H, Ar−H), 7.27 (ps−d, ^3J(H,H) = 2 Hz, 1 H, Ar−H), 7.24−7.20 (m, 2 H, Ar−H), 7.07 (d, ^3J(H,H) = 7 Hz, 2 H, Ar−H), 7.01 (t, ^3J(H,H) = 7 Hz, 1 H, Ar−H), 6.80 (t, ^3J(H,H) = 8 Hz, 2 H, Ar−H), 6.76 (d, ^3J(H,H) = 2 Hz, 1 H, Ar−H), 6.33 (d, ^2J(H,H) = 16 Hz, 1 H, NC*H*HPh), 6.27 (d, ^3J(H,H) = 8 Hz, 2 H, Ar−H), 6.05−5.98 (m, 1 H, NC*H*HCH_2), 5.58 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 5.45 (d, ^2J(H,H) = 16 Hz, 1 H, NCH*H*Ph), 5.41 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 4.82−4.76 (m, 2 H, NC*H*HPh and NCH*H*CH_2), 4.54−4.48 (m, 3 H, NCH*H*Ph and NCH_2CH_2), 1.69−1.66 (m, 6 H, CH_3), 1.29 (d, ^3J(H,H) = 7 Hz, 3 H, CH_3), 1.13 (d, ^3J(H,H) = 7 Hz, 3 H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, CD_3CN): 180.4 ($C_{carbene\text{-}probe}$), 166.1 ($C_{carbene\text{-}trans}$), 161.4 ($C_{carbene\text{-}cis}$), 138.9, 135.6, 134.3, 133.6, 130.2, 129.4, 129.1, 128.8, 127.6, 127.3, 125.1, 124.6, 124.5, 124.01, 123.96, 123.0, 114.32, 114.28 (Ar−C), 55.5, 55.4, 55.3, 54.1 (NCH and NCH_2Ph), 49.7, 47.8 (NCH_2), 21.8, 21.0, 20.3, 20.2 (CH_3). ^{31}P{^{1}H} NMR (202.45 MHz, CD_3CN): −144.0 (m, ^1J(F,P) = 708 Hz, PF_6). ^{19}F{^{1}H} NMR (282.38 MHz, CDCl3): 3.4 (d, ^1J(F,P) = 708 Hz, PF_6). Anal. Calcd for $C_{35}H_{40}BrF_6N_6PPd$: C, 47.99; H, 4.60; N, 9.59. Found: C, 47.91; H, 4.31; N, 9.78%. MS (ESI): m/z 731 [M − PF_6]$^+$. The ^{13}C-labeled complex was obtained though the same procedure starting from the C2 ^{13}C-labeled 1,3-diisopropylbenzimidazolium salt. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 179.54 ($C_{carbene\text{-}probe}$). MS (ESI): m/z 732 [M − PF_6]$^+$.

*Ethylene-Bridged Dipalladium Complex (**16**).* Yield: 44 mg, 0.03 mmol, 34%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.58 (m, 2 H, Ar−H), 7.55−7.53 (m, 2 H, Ar−H), 7.50 (ps−d, ^3J(H,H) = 7 Hz, 4 H, Ar−H), 7.40 (t, ^3J(H,H) = 8 Hz, 4 H, Ar−H), 7.34 (t, ^3J(H,H) = 8 Hz, 2 H, Ar−H), 7.22−7.20 (m, 4 H, Ar−H), 7.19 (d, ^3J(H,H) = 2 Hz, 2 H, Ar−H), 6.56 (d, ^3J(H,H) = 2 Hz, 2 H, Ar−H), 6.19 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 6.06 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 5.80 (s, 4 H, NCH_2Ph), 5.48 (s, 4 H, NCH_2), 1.89 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3), 1.67 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 178.8 ($C_{carbene\text{-}benz}$), 170.7 ($C_{carbene\text{-}imi}$), 136.8, 134.3, 134.2, 129.5, 128.9, 128.8, 124.8, 122.7 (2 ×), 120.8, 113.32, 113.30 (Ar−C), 55.3, 54.7, 54.5 (NCH, NCH_2Ph), 51.4 (NCH_2), 21.9, 21.6 (CH_3). Anal. Calcd for $C_{48}H_{58}Br_4N_8Pd_2$: C, 45.06; H, 4.57; N, 8.76. Found: C, 44.79; H, 4.48; N, 8.64%. MS (ESI): m/z 1199 [M − Br]$^+$.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental details for complexes **1**, **3**−**8**, **10**−**13**, **15**, and **17**, selected crystallographic data and CIF files for **2**·$CHCl_3$, **7**·$0.25H_2O$, **9**·$0.25H_2O$, **11**·$0.5CH_2Cl_2$, **14**·CH_3CN, **15**·$CHCl_3$, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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