Dalton Transactions

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c8dt01618f

A palladacyclic N-heterocyclic carbene system used to probe the donating abilities of monoanionic chelators†

Xuechao Yan,[a] Rui Feng,[a] Chunhui Yan,[a] Peng Lei,[a] Shuai Guo *[a] and Han Vinh Huynh *[b]

Received 23rd April 2018,
Accepted 16th May 2018

DOI: 10.1039/c8dt01618f

rsc.li/dalton

A series of NHC-containing [C^N]- or [C^C']-type palladacyclic complexes of the general formula [PdBr(^{i}Pr$_2$-bimy)(L^X)] (**5–8**, **11**, **12**, ^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) have been synthesized and fully characterized. Using these complexes, the donating abilities of monoanionic chelators were probed for the first time. The [C^N]-type palladacycles **5–8** were prepared from acetato-bridged dipalladium complexes [Pd(μ-CH$_3$COO)(C^N)]$_2$ (**1–4**) and ^{i}Pr$_2$-bimy·H$^+$Br$^-$as precursors. In the case of the [C^C']-type NHC palladacycles (**11**, **12**), the hetero-bis(NHC) complexes *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(trz)] (**8**, **9**, trz = 1,2,3-triazolin-5-ylidene) containing the ^{i}Pr$_2$-bimy probe were first prepared followed by acetate-assisted cyclopalladations. The $^{13}C_{carbene}$ NMR signals of the ^{i}Pr$_2$-bimy ligands in all complexes (*i.e.* HEP and HEP2 values) are found to rationally reflect the donating abilities of the incorporated trz or [L^X]-type chelators with the exception of the Bzpy ligand (Bzpy = 2-(2-pyridinylmethyl)phenyl-*C*,*N*). This has been attributed to its larger bite angle, the resulting varied coordination geometry and the lack of electronic delocalization between the two donor units. The donicities of [L^X]-type chelators studied in this work were found to surpass those of all other bidentate ligands evaluated by HEP2 thus far.

Introduction

The properties of transition metal complexes are highly dependent on the electronic nature of their ligands. During the past few decades, various methods to measure the electron-donating abilities of ligands have been developed.[1] In this regard, the best known metric is undoubtedly the Tolman electronic parameter (TEP),[2] in which the A_1 carbonyl bands of [Ni(CO)$_3$(PR$_3$)] complexes serve as an indicator for the net-donor strength of the phosphine of interest. Along with the rapid development of NHC chemistry[3] (NHC = N-heterocyclic carbene), the TEP and related methods based on iridium and rhodium have also been used to evaluate NHCs.[1a–c,4] However, it is noteworthy that in certain cases, competing backdonation to the ligand of interest becomes non-negligible, complicating the interpretation of data.[1b]

In 2009, Huynh and co-workers reported a ^{13}C NMR-based electronic parameter (HEP), which makes use of the fact that a stronger donating ligand L in complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(L)] (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) leads to a more downfield $^{13}C_{carbene}$ NMR signal of the ^{i}Pr$_2$-bimy ligand (Chart 1, system **I**).[5] In contrast to carbonyl-based methods, the HEP utilizes a more Lewis-acidic palladium(II) center, which is known to be a weaker π-donor. Moreover, planar ligands, *e.g.* NHCs or pyridines, bind perpendicularly to the coordination plane in the HEP system, thus making the delocalization of d-electrons into their π-cloud less efficient. As such, the donor–acceptor ability of a ligand can be better separated, and it is primarily the σ-donating ability that is being evaluated. By using the HEP, the electron-donating abilities of various monodentate Werner-type and organometallic donors have been gauged and compared.[1d,6]

More recently, the HEP has been extended to the so-called HEP2, which probes the donor strengths of charge-neutral and symmetrical L^L bidentate ligands using cationic complexes of the formula [PdBr(^{i}Pr$_2$-bimy)(L^L)]PF$_6$ (Chart 1, System **II**).[7] Crowley *et al.* have also used HEP2 to study a few neutral unsymmetrical L$_1^L_2$ chelators with two different N-donors (HEP2, Chart 1, System **III**).[8] A point to note is that the HEP for monodentate ligands and HEP2 for bidentate ligands are structurally and electronically different systems, but rooted on the same concept. For example, cyclic ligands in the HEP probes usually coordinate in a perpendicular fashion with respect to the coordination plane. In HEP2 probes, however, a

[a]Department of Chemistry, Capital Normal University, Beijing, People's Republic of China. E-mail: guoshuai@cnu.edu.cn
[b]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

† Electronic supplementary information (ESI) available: Selected crystallographic data and NMR spectra. CCDC 1824536–1824539. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt01618f

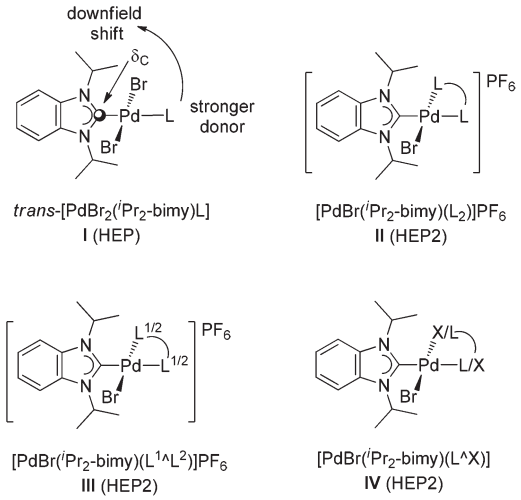


Chart 1 Previously reported HEP-based systems used to determine the donor strengths of monodentate ligands (I), neutral symmetric (II) and asymmetric bidentate ligands (III), and the target system (IV) in this work.

coplanar coordination mode is enforced by chelation. The different orientations will result in different electronic contributions to the reporter ligand, and thus the comparison of ligands can only be made within a given system. Moreover, coplanar attachment of a π-system *via* chelation potentially allows the metal to mesomerically act as a donor.[9] For such ligands, HEP2 therefore detects the net donor strengths.

Although monoanionic [L^X]-type bidentate ligands, especially those containing aryl-derived carbanions, have been extensively employed in organometallic chemistry and transition metal mediated catalysis,[10] the donating abilities of such chelators have not been systematically probed due to the lack of suitable and straightforward methodologies.

Herein, we report the syntheses and structural elucidations of various neutral palladacycles of type **IV** incorporating $^{i}Pr_2$-bimy as the reporter ligand and different aryl-based, monoanionic [L^X]-type (L = N, C; X = C′) chelators. Additionally, it should be noted that the synthesis of HEP2-based complex probes of the type [PdBr($^{i}Pr_2$-bimy)(L_1^L_2)]PF_6 (**III**) or [PdBr($^{i}Pr_2$-bimy)(L^X)] (**IV**) bearing asymmetric bidentate ligands is less straightforward compared to that of type **II** due to the potential formation of two geometric isomers (Chart 1). The latter are expected to give two different HEP2 values, and thus the knowledge of the exact binding modes is crucial for the donor strength evaluations using these systems. Using complexes of system **IV**, the donating abilities of asymmetric and monoanionic bidentate ligands are evaluated and compared for the first time.

Results and discussion

Syntheses of [C^N]-type palladacycles bearing pyridine-based asymmetric chelators

Pyridine-derived [C^N]-type chelators are commonly used as monoanionic bidentate ligands in coordination chemistry.[10] Thus, a series of [PdBr(C^N)($^{i}Pr_2$-bimy)] complexes bearing these types of chelators were initially targeted.

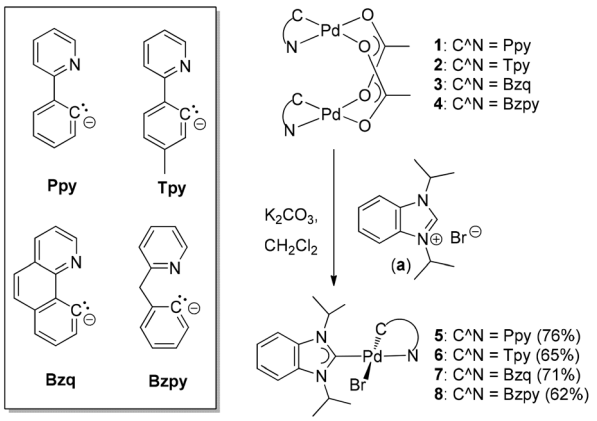
Acetato-bridged dinuclear complexes **1–4** can be conveniently accessed *via* reported procedures starting from their corresponding pyridine derivatives with $Pd(OAc)_2$ (Scheme 1).[11] These acetato complexes can serve as potential basic precursors for further metalation reactions. Hence, complexes **1–4** were treated with two equivalents of $^{i}Pr_2$-bimy·$H^{+}Br^{-}$ (**a**) in CH_2Cl_2, affording the desired NHC-incorporated palladacycles **5–8** in decent yields. Moreover, it was found that improved yields can be achieved in the presence of K_2CO_3 as an additional and external base, which was therefore included in the optimized procedures.

In the ^{1}H NMR spectra of all complexes **5–8**, the signals assigned to the NCHN protons of salt **a** are absent suggesting the successful carbene coordination. The isopropyl C–H protons give signals at 6.11 ppm (for **5** and **6**) and 6.19 ppm (for **7** and **8**) respectively, owing to which these resonances are not diagnostic for the distinction of the incorporated [C^N]-type chelators. In the ^{13}C NMR spectra of complexes **5–8**, the $^{13}C_{carbene}$ signals are observed at 184.6 ppm (**5**), 184.7 ppm (**6**), 183.7 ppm (**7**) and 183.6 ppm (**8**). These $^{13}C_{carbene}$ signals are found to correlate to the expected donating abilities of the corresponding bidentate ligands with the exception of complex **8** (*vide infra*).

The solid-state structures of complexes **5–7** were elucidated by X-ray crystallographic studies of single crystals obtained from slow evaporation of their solutions in a mixture of CH_2Cl_2 and *n*-hexane. As a representative, the molecular structure of **5** is depicted in Fig. 1. The molecular structures of **6–7**, selected crystallographic data and bond parameters are given in the ESI.† In all three cases, the aryl moieties of [C^N]-type chelators are *cis* to the carbene ligand. Moreover, chelation enforces a coplanar arrangement between the chelator and the square-planar coordination plane. A similar coordination behavior was also observed in the known analogues.[12]

Syntheses of [C^C′]-type palladacycles bearing carbene-based asymmetric chelators

Various NHCs with *N*-aryl wingtips can undergo cyclopalladations leading to the formation of [C^C′]-type chelators.[13] To



Scheme 1 Syntheses of NHC-containing [C^N]-type palladacycles **5–8**.

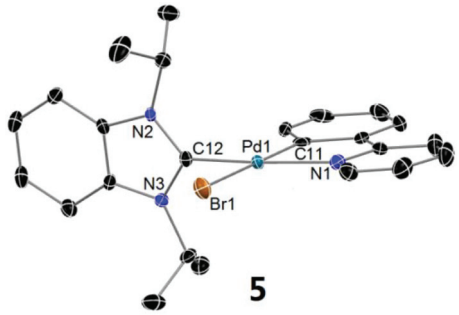
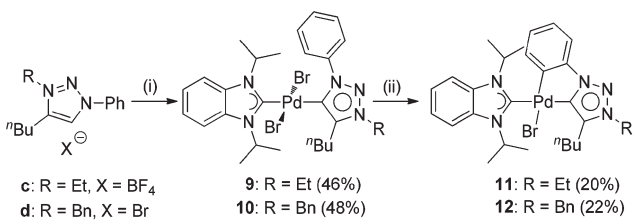


Fig. 1 Molecular structures of complexes **5** showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

assess the electron-donating abilities of such bidentate ligands, two new monocationic 1,2,3-triazole-derived salts **c** and **d** were synthesized as the precursors *via* a two-step procedure (Scheme SI-1, see the ESI†). In the ^{1}H NMR spectra of **c** and **d**, two downfield singlets at 8.64 ppm (**c**) and 10.23 ppm (**d**) characteristic of the triazolium C–H protons are observed.

With the two precursor salts **c** and **d** in hand, and in analogy to the syntheses of **1–4**, the preparation of acetato-bridged dinuclear [C^C′]-type palladacycles was initially attempted. Such complexes could be potentially applied as basic precursors in further metallations to synthesize NHC-containing [C^C′]-type palladacycles. Notably, some analogues have been previously reported by Sankararaman *et al.*[14] However, in our hands, several attempts either using the silver-NHC transfer method or by direct deprotonation with $Pd(OAc)_2$ were to no avail, and mixtures of inseparable products were always obtained.

Thus, a different synthetic strategy was employed (Scheme 2). First, salts **c** and **d** were treated with Ag_2O to yield silver–carbene species, and subsequent transmetalation to the known dimeric complex $[PdBr_2(^{i}Pr_2\text{-bimy})]_2$ [15] led to the formation of hetero-bis(carbene) complexes **9** and **10** in moderate yields. Subsequently, C–H activations assisted by NaOAc as an external base in DMSO successfully afforded the cyclopalladated complexes **11** and **12** as off-white solids, although in low yields. Notably, similar NHC-containing palladacycles were typically obtained through cyclopalladations followed by carbene ligations.[12a–f] To the best of our knowledge, the "cyclopalladation at the final step" synthetic strategy presented herein is employed for the first time to access such complexes.



Scheme 2 Syntheses of bis(carbene) complexes **9**/**10** and NHC-palladacycles **11**/**12**. Conditions for step (i): (a) Ag_2O, TBAB (only for **c**); (b) $[PdBr_2(^{i}Pr_2\text{-bimy})]_2$. Conditions for step (ii): NaOAc, DMSO.

In the ^{1}H NMR spectrum of **9**, two characteristic multiplets at 6.22 and 5.96 ppm for the isopropyl C–H protons are observed suggesting the loss of 2-fold rotational symmetry of the $^{i}Pr_2$-bimy ligand. Similar signals (6.20 and 5.98 ppm) are also found in the case of **10**. In the ^{13}C NMR spectra of **9** and **10**, the $^{i}Pr_2$-bimy ligands show the carbene resonances at 181.1 and 180.8 ppm, and the two $^{13}C_{carbene}$ signals at 158.5 and 159.1 ppm are assigned to 1,2,3-triazole-derived mesoionic carbene ligands.

Single crystals of complex **10** suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of **10** in a mixture of CH_2Cl_2 and *n*-hexane. The molecular structure is depicted in Fig. SI-2,† and the selected crystallographic data and bond parameters are summarized in Tables SI-1 and SI-2 (see the ESI†). The triazolin-5-ylidene ligand is found to be *trans* to the reporter carbene and perpendicular to the coordination plane, which is in line with earlier observations.[6f]

Previously, complexes of the general type *trans*-$[PdBr_2(^{i}Pr_2\text{-bimy})(trz)]$ (trz = 1,2,3-triazolin-5-ylidene) have been employed to determine the donating abilities of 1,2,3-triazole-derived mesoionic carbenes (*vide supra*).[6f] The syntheses of **9** and **10** further broaden the scope of the HEP for these ligands, and the $^{i}Pr_2$-bimy $^{13}C_{carbene}$ NMR signals of a series of *trans*-$[PdBr_2(^{i}Pr_2\text{-bimy})(trz)]$ complexes including **9** and **10** are compared on a Pd^{II} ^{13}C NMR spectroscopic scale (Fig. 2). Based on the comparison of the HEP values, a decreasing donor strength of trz ligands in the order of **i** > **v** > **ii**/**iii**/**vi** > **iv** can be inferred. This trend clearly underlines the presence of substituent effects in this series of trz ligands. For example, the fact that ligand **vi** is stronger donating than **iv** can be rationalized by the increased +*I* effect of the *n*-butyl *versus* phenyl group.

In the ^{1}H NMR spectra of **11** and **12**, the isopropyl C–H protons show only one multiplet at 5.98 ppm indicating greater symmetry upon cyclometalation. Characteristic doublets at 6.40 ppm (**11**) and 6.42 ppm (**12**) were observed, which are assigned to the Ar–H_b protons (Fig. SI-3, see the ESI†)

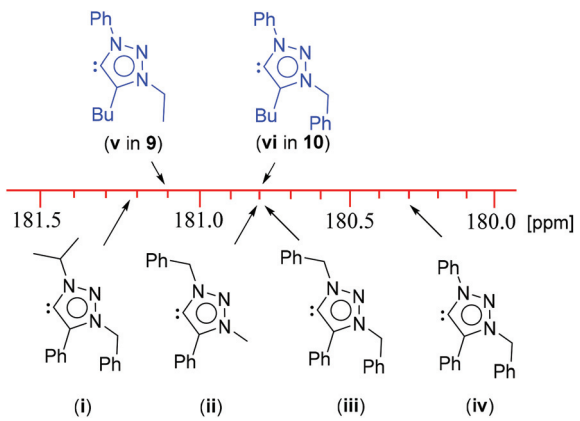


Fig. 2 Relative donor abilities of trz ligands on a HEP scale. ^{13}C NMR spectra were recorded in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm.

ortho to the aryl carbon donors. Similar signals were also found for the [C^N]-type analogues **5–8**.

In principle, HEP2 complex probes of the general formula [PdBr(^{i}Pr$_2$-bimy)(L^X)] can have two geometric isomers (*vide supra*). The fact that only one set of signals is observed in the NMR spectra of **11**/**12** clearly implicates the presence of a single isomer in both cases. Notably, the precursor complexes **9**/**10** bear two mutually *trans*-standing carbenes, which expectedly retain such coordination fashions after C–H activations of aryl wingtips. These ligand orientations of **11**/**12** are unambiguously determined by 1D NOESY NMR spectroscopic analyses (Fig. SI-3, SI-4, see the ESI†). Several attempts to grow single crystals of **11**/**12** were to no avail. However, an in-plane coordination enforced by chelation can be expected for the C^C′ bidentate ligands.

Two $^{13}C_{carbene}$ signals were detected in the ^{13}C NMR spectra of **11** and **12**. The resonances at 162.0 ppm (**11**) and 162.7 ppm (**12**) assigned to 1,2,3-triazole-derived carbenes are found to be comparable to those in earlier reported palladium triazolin-5-ylidene complexes.[13] The much more downfield signals at 193.0 ppm (**11**) and 192.9 ppm (**12**) are assigned to the $C_{carbene}$ atoms of ^{i}Pr$_2$-bimy ligands, which allows direct comparison of the donor strengths for the [C^C′]-type chelators incorporated into **11** and **12** *versus* the [C^N]-type bidentate ligands of **5–8** on a unified ^{13}C NMR spectroscopic scale (*vide infra*).

Donor strength comparisons of pyridine-based [L^X]-type chelators

The $^{13}C_{carbene}$ NMR resonances of the ^{i}Pr$_2$-bimy reporter ligand (*i.e.* HEP2 values) in complexes **5–8**, **11** and **12** allow for the donor strength determinations and comparisons of [L^X]-type monoanionic bidentate ligands. Complexes **5–8** all bear pyridine-based bidentate ligands, which are first internally ranked and then further compared with previously reported symmetric or asymmetric pyridine-based chelators. A summary of all these structurally related complexes is given in Table 1, and their HEP2 values are shown on a ^{13}C NMR spectroscopic scale (Fig. 3 and 4).

In the [C^N]-type series synthesized here, a stepwise upfield shift going from 184.7 ppm (Tpy) to 184.6 ppm (Ppy) and further to 183.7 ppm (Bzq) was observed (Fig. 3). This is rational since (i) the attachment of a methyl group to Ppy supposedly enhances the donating ability through a +*I* effect (*cf.* Tpy and Ppy); and (ii) a phenyl ring fused to Ppy is expected to reduce the donor strength (*cf.* Bzq and Ppy).

Interestingly, the bidentate ligand Bzpy leads to a slightly more upfield HEP2 compared to Ppy, although the former is assumed to be a stronger bidentate donor on grounds of the +*I* effect of the additional CH_2 spacer. Nevertheless, electronic communication between the two donor-containing rings is less feasible, which diminishes mesomeric contributions. Moreover, it is reasonable to assume that the structural changes induced by an increased bite-angle of Bzpy and the resulting 6-membered palladacycle lead to sterically induced dilution of the electronic effects. A similar observation was previously made by Herrmann and Kühn *et al.*, who reported a series of complexes *fac*-[ReBr(CO)$_3$(L^L)] (L^L = chelating diNHC) with variations in alkylene bridges between the two carbenes.[16] They did not find any clear influence of the alkylene bridges on the carbonyl IR vibrations and NMR resonances and attributed this to the variations in ligand bite angles and the resulting change in molecular geometries.

Table 1 Summary of the ^{i}Pr2-bimy $^{13}C_{carbene}$ signals (HEP2) in complexes bearing pyridine-containing chelators

Complex	L	HEP2[a]
[PdBr(^{i}Pr$_2$-bimy)(Ppy)] (**5**)	Ppy	184.6
[PdBr(^{i}Pr$_2$-bimy)(Tpy)] (**6**)	Tpy	184.7
[PdBr(^{i}Pr$_2$-bimy)(Bzq)] (**7**)	Bzq	183.7
[PdBr(^{i}Pr$_2$-bimy)(Bzpy)] (**8**)	Bzpy	183.6
[PdBr(^{i}Pr$_2$-bimy)(Bipy)]PF$_6$	Bipy	162.7[b]
[PdBr(^{i}Pr$_2$-bimy)(Phen)]PF$_6$	Phen	161.4[b]
[PdBr(^{i}Pr$_2$-bimy)(Phen-dione)]PF$_6$	Phen-dione	160.0[b]
[PdBr(^{i}Pr$_2$-bimy)(*reg*-Pytri-Ph)]PF$_6$	*reg*-Pytri-Ph	156.7[c]
[PdBr(^{i}Pr$_2$-bimy)(*reg*-Pytri-Bn)]PF$_6$	*reg*-Pytri-Bn	156.7[c]
[PdBr(^{i}Pr$_2$-bimy)(*inv*-Pytri-Ph)]PF$_6$	*inv*-Pytri-Ph	158.3[c]
[PdBr(^{i}Pr$_2$-bimy)(*inv*-Pytri-Bn)]PF$_6$	*inv*-Pytri-Bn	158.2[c]

[a] Measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to tetramethylsilane (TMS). [b] Data from ref. 7. Bipy = 2,2′-bipyridine, Phen = 1,10-phenanthroline, Phen-dione = 1,10-phenanthroline-5,6-dione. [c] Data from ref. 8 were referenced to 77.16 instead. The HEP2 values shown here were obtained by adding 0.54 ppm to the reported data for proper comparison. *reg*-Pytri-Ph = 1-(2-pyridyl)-4-phenyl-1,2,3-triazole, *reg*-Pytri-Bn = 1-(2-pyridyl)-4-benzyl-1,2,3-triazole, *inv*-Pytri-Ph = 1-phenyl-4-(2-pyridyl)-1,2,3-triazole, *inv*-Pytri-Bn = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole.

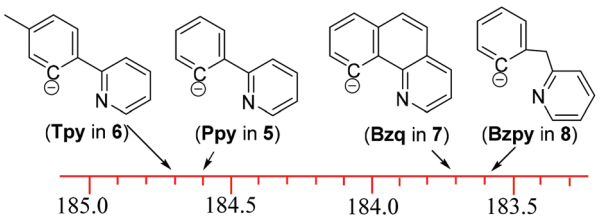


Fig. 3 Donor strength comparison of selected pyridine-based chelators on a HEP2 scale.

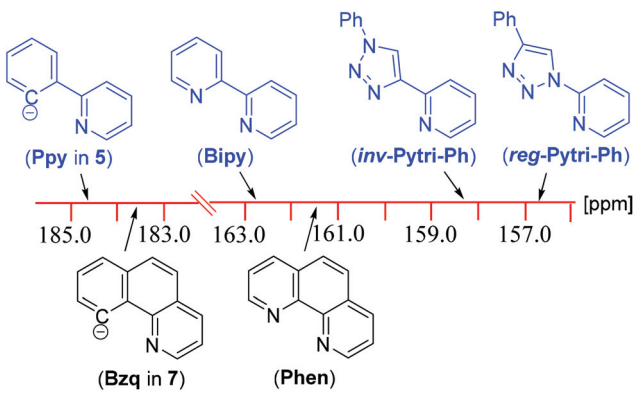


Fig. 4 Donor strength comparison of selected charge-neutral and monoanionic pyridine-based chelators on a HEP2 scale.

Such steric interferences on HEP-related methods remain to be addressed in the near future with greater detail.

The HEP2 value of Ppy in **5** was further compared to selected counterparts bearing pyridine-based symmetric or asymmetric [N^N]-type chelators (Fig. 4). Note that in all cases the pyridine moieties are exclusively *trans* to the $^{i}Pr_2$-bimy probe leading to the formation of 5-membered metallacycles. By comparison of the HEP2 values, a decreasing donating ability in the order of Ppy > Bipy > *inv*-Pytri-Ph > *reg*-Pytri-Ph can be deduced. The fact that Ppy is by far the strongest chelator is reasonable, since the anionic carbon donor in Ppy is more electron releasing compared to neutral N-donors in all the other cases. Additionally, it should be noted that steric interferences on the HEP2 values of Ppy and Bipy can be essentially excluded, because they are structurally very similar. The same statement can be made for the case of Bzq *versus* Phen (Fig. 4).

Donor strength comparisons of carbene-based [L^X]-type chelators

Previously, Huynh *et al.* determined the HEP2 values of symmetric and classical dicarbene ligands with simple alkyl linkers (system **II**, *vide supra*), which allow donor strength comparison with the carbene-containing [C^C′]-type chelators in the newly synthesized complexes **11**/**12**. The HEP2 values of these ligands are shown on a ^{13}C NMR spectroscopic scale (Fig. 5), and a more detailed summary is given in Table 2.

The HEP2 values of Et-pty and Bn-pty in **11** and **12** are 193.0 ppm and 192.9 ppm, respectively. They are significantly larger than those of all previously studied dicarbene ligands (177.1–180.3 ppm), which implies that their donicities surpass those of all dicarbenes evaluated by HEP2 thus far. This result is well in line with intuition, since (i) mesoionic 1,2,3-triazole-derived carbenes are known to be stronger donors compared to classical Arduengo-type NHCs;[6f,17] and (ii) the aryl carbanion is expected to be a stronger donor than neutral carbon donors. In addition to these reasonable arguments, one must also note that electronic communication between the two donors in the dicarbene ligands is interrupted by the alkyl bridge. The lack of mesomeric interactions between the two donor units may additionally contribute to a weaker donicity compared to that of the monoanionic [C^C′] chelators. Again, more detailed future studies are required to address this specific issue.

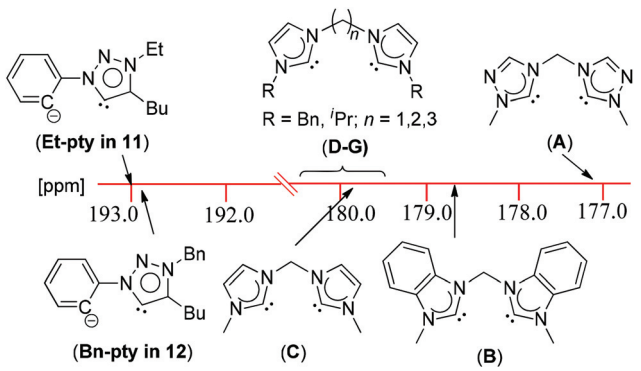


Fig. 5 Donor strength comparison of selected carbene-based chelators on a HEP2 scale.

Table 2 Summary of $^{iPr2\text{-}bimy}$ $^{13}C_{carbene}$ signals (HEP2) in complexes bearing carbene-containing chelators

Complex	L	HEP2[a]
[PdBr($^{i}Pr_2$-bimy)(Et-pty)] (**11**)	Et-pty	193.0
[PdBr($^{i}Pr_2$-bimy)(Bn-pty)] (**12**)	Bn-pty	192.9
[PdBr($^{i}Pr_2$-bimy)(**A**)]PF_6	**A**	177.1[b]
[PdBr($^{i}Pr_2$-bimy)(**B**)]PF_6	**B**	178.7[b]
[PdBr($^{i}Pr_2$-bimy)(**C**)]PF_6	**C**	179.9[b]
[PdBr($^{i}Pr_2$-bimy)(**D**)]PF_6	**D** (R = Bn, n = 1)	179.51[b]
[PdBr($^{i}Pr_2$-bimy)(**E**)]PF_6	**E** (R = ^{i}Pr, n = 1)	180.0[b]
[PdBr($^{i}Pr_2$-bimy)(**F**)]PF_6	**F** (R = Bn, n = 2)	179.54[b]
[PdBr($^{i}Pr_2$-bimy)(**G**)]PF_6	**G** (R = Bn, n = 3)	180.3[b]

[a] Measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to tetramethylsilane (TMS). [b] Data from ref. 7.

A comparison among the [C^C′] chelators in complexes **11** *versus* **12** reveals that a change of the *N*-benzyl substituent to a more electron-releasing ethyl group brings a small, but yet detectable shift of the HEP2 value, although this variation is considerably far away from that of the $^{i}Pr_2$-bimy probe.[18] This observation also highlights that HEP2 is sufficiently sensitive to detect subtle electronic differences of monoanionic chelators.

Finally, the HEP2 results obtained also demonstrate that monoanionic [C^C′]-type chelators are significantly more donating than all [C^N]-type chelators studied herein. Again, this observation is in line with the fact that mesoionic 1,2,3-triazolin-5-ylidenes are much stronger donors compared to pyridines.[5,6f]

The reasonability of all results discussed above collectively and clearly indicates that palladacyclic NHC complexes of the general formula [PdBr($^{i}Pr_2$-bimy)(L^X)] accessed in this work can serve as a suitable system to probe the donating abilities of monoanionic chelators.

Conclusion

We have reported the syntheses of a series of new palladacycles bearing various monoanionic and asymmetric [L^X]-type chelators (L = C, N; X = C) and 1,3-diisopropylbenzimidazolin-2-ylidene as the constant reporter ligand. The specific coordination mode and arrangement of the incorporated non-symmetric bidentate ligands were verified by either X-ray diffraction analyses or 1D NOESY NMR spectroscopy.

These complexes have allowed for the systematic determination and comparison of the donating abilities of [L^X]-type chelators for the first time using the HEP2 method. The rational results obtained provide useful knowledge for the design of the cyclometallated complexes. More importantly, they can facilitate the understanding of structure–activity relationships observed in applications of related metallacycles

in the areas such as homogeneous catalysis or photoluminescence. The fact that Bzpy (Bzpy = 2-(2-pyridinylmethyl) phenyl-*C*,*N*) does not follow the expected order on grounds of inductive effects has been tentatively attributed to a larger bite angle, the severely varied coordination geometry and the lack of electronic delocalization brought about by a different structure of this ligand. Research addressing this issue and other limitations to the method rooted in steric interferences as well as further broadening the scope of bidentate ligands is currently underway in our laboratories.

Experimental section

General considerations

Unless otherwise stated, all the manipulations were carried out without taking precautions to exclude air and moisture. All chemicals and solvents were used as received without further purification if not mentioned otherwise. ^{1}H, ^{13}C and NOESY NMR spectra were recorded on a Varian 600 MHz spectrometer and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to $(CH_3)_4Si$ (^{1}H,^{13}C). ESI mass spectra were recorded using an Agilent 6540 Q-TOF mass spectrometer. X-ray single crystal diffractions of complexes **5** and **7** were carried out using an Agilent Xcalibur Eos Gemini diffractometer at the Beijing University of Chemical Technology. X-ray single crystal diffractions of complexes **6** and **10** were carried out using a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer (for complex **6**) at Beijing Normal University and a Rigaku XtaLAB P200 MM003 diffractometer (for complex **10**) at Capital Normal University. Elemental analyses were carried out on a vario EL cube elemental analyzer at the Beijing University of Chemical Technology.

General synthetic procedure for complexes 5–8

The acetato-bridged dipalladium complex [Pd(μ-CH_3COO)(C^N)]$_2$ (0.1 mmol) and salt **a** (56.6 mg, 0.2 mmol) were dissolved in CH_2Cl_2 (15 mL). To the resulting solution, K_2CO_3 (28 mg, 0.2 mmol) was added. The reaction mixture was stirred and heated under reflux for 24 h. The resulting suspension was cooled to ambient temperature, and deionized water (10 mL) was added. The organic phase was collected and dried over Na_2SO_4. All the volatiles were removed under vacuum. An analytically pure compound was obtained by crystallization from the solution of the crude product in a mixture of CH_2Cl_2 and *n*-hexane.

Complex **5** was obtained in a yield of 76% following the general procedure with complex **1** as the metal precursor. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.55–9.54 (m, 1H, Ar–H), 7.84–7.81 (m, 1H, Ar–H), 7.75–7.74 (m, 1H, Ar–H), 7.68–7.65 (m, 2H, Ar–H), 7.60–7.58 (m, 1H, Ar–H), 7.29–7.27 (m, 2H, Ar–H), 7.23–7.22 (m, 1H, Ar–H), 7.08–7.06 (m, 1H, Ar–H), 6.87–6.84 (m, 1H, Ar–H), 6.24–6.23 (m, 1H, Ar–H), 6.11 (septet, 2H, C*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 1.77 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 1.61 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 184.6 (NCN), 164.9, 156.1, 152.0, 147.1, 139.1, 137.9, 134.4, 130.1, 124.9, 124.5, 123.1, 122.9, 118.8, 113.5 (Ar–C), 55.3 (*C*H$(CH_3)_2$), 21.5, 21.4 (CH(*C*H$_3)_2$). ESI-MS (positive) *m*/*z* 462 [M − Br]$^{+}$. Anal. Calcd for $C_{24}H_{26}BrN_3Pd$: C, 53.10; H, 4.83; N, 7.74%; found: C, 53.16; H, 4.51; N, 7.68%.

Complex **6** was obtained in a yield of 65% following the general procedure with complex **2** as the metal precursor. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.52–9.51 (m, 1H, Ar–H), 7.79–7.78 (m, 1H, Ar–H), 7.68–7.66 (m, 3H, Ar–H), 7.48–7.47 (m, 1H, Ar–H), 7.29–7.28 (m, 2H, Ar–H), 7.19–7.17 (m, 1H, Ar–H), 6.90–6.88 (m, 1H, Ar–H), 6.11 (septet, 2H, C*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 6.09–6.08 (m, 1H, Ar–H), 2.07 (s, 3H, Tpy-CH_3), 1.77 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 1.61 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 184.7 (NCN), 165.0, 156.0, 151.8, 144.4, 140.1, 139.0, 138.6, 134.4, 125.7, 124.3, 122.8, 122.6, 118.5, 113.5 (Ar–C), 55.3 (*C*H$(CH_3)_2$), 22.3 (Tpy-CH_3), 21.6, 21.4 (CH(*C*H$_3)_2$). ESI-MS (positive) *m*/*z* 476 [M − Br]$^{+}$. Anal. Calcd for $C_{25}H_{28}BrN_3Pd$: C, 53.92; H, 5.07; N, 7.55%; found: C, 54.16; H, 5.45; N, 7.36%.

Complex **7** was obtained in a yield of 71% following the general procedure with complex **3** as the metal precursor. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.73–9.72 (m, 1H, Pyr–H), 8.31–8.29 (m, 1H, Ar–H), 7.77–7.75 (m, 1H, Ar–H), 7.70–7.69 (m, 2H, Ar–H), 7.64–7.62 (m, 1H, Ar–H), 7.59–7.56 (m, 2H, Ar–H), 7.31–7.30 (m, 2H, Ar–H), 7.23–7.21 (m, 1H, Ar–H), 6.47–6.46 (m, 1H, Ar–H), 6.19 (heptet, 2H, C*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 1.79 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz), 1.62 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 7 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 183.7 (NCN), 155.0, 154.1, 150.7, 137.7, 134.6, 134.5, 134.4, 129.6, 129.3, 127.3, 124.2, 123.4, 122.9, 122.4, 113.5 (Ar–C), 55.4 (*C*H$(CH_3)_2$), 21.6, 21.4 (CH(*C*H$_3)_2$). ESI-MS (positive) *m*/*z* 486 [M − Br]$^{+}$. Anal. Calcd for $C_{26}H_{26}BrN_3Pd$: C, 55.09; H, 4.62; N, 7.41%; found: C, 55.06; H, 4.79; N, 7.27%.

Complex **8** was obtained in a yield of 62% following the general procedure with complex **4** as the metal precursor. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.38–9.37 (m, 1H, Ar–H), 7.67 (t, 1H, Ar–H, $^{3}J_{H,H}$ = 7 Hz), 7.60–7.59 (m, 2H, Ar–H), 7.40 (d, 1H, Ar–H, $^{3}J_{H,H}$ = 7 Hz), 7.23–7.22 (m, 2H, Ar–H), 7.18 (t, 1H, Ar–H, $^{3}J_{H,H}$ = 7 Hz), 7.12 (d, 1H, Ar–H, $^{3}J_{H,H}$ = 7 Hz), 6.87 (t, 1H, Ar–H, $^{3}J_{H,H}$ = 7 Hz), 6.68–6.63 (m, 2H, Ar–H), 6.19 (br s, 2 H, C*H*$(CH_3)_2$), 4.41 (br s, 2 H, Bzpy-CH_2), 1.80 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H,H}$ = 6 Hz), 1.47 (br s, 6H, CH(C*H*$_3)_2$). ^{13}C NMR ($CDCl_3$, 150 MHz): 183.6 (NCN), 159.2, 154.5, 149.3, 139.2, 138.7, 134.1, 127.6, 124.6, 122.7, 111.5, 113.3 (Ar–C), 55.3 (*C*H$(CH_3)_2$), 50.3 (CH_2), 21.7 (CH(*C*H$_3)_2$). ESI-MS (positive) *m*/*z* 476 [M − Br]$^{+}$. Anal. Calcd for $C_{25}H_{28}BrN_3Pd$: C, 53.92; H, 5.07; N, 7.55%; found: C, 53.80; H, 5.35; N, 7.19%.

Synthesis of compound c

4-Butyl-1-phenyl-1,2,3-triazole (201.2 mg, 1 mmol) and triethyloxonium tetrafluoroborate (380.0 mg, 2 mmol) were mixed in a 25 mL Schlenk tube. To this mixture, dry 1,2-dichloroethane (1 mL) was added. The tube was sealed and the reaction mixture was stirred at 90 °C for 24 h. All the volatiles were removed *in vacuo*. To the residue, 2 mL of CH_3OH was added and the resulting suspension was stirred at ambient temperature for 0.5 h exposed to air to remove excess oxonium salt. All

the volatiles were removed *in vacuo*, and then the residue was washed with ethyl acetate (3 × 10 mL) and dried under vacuum affording the product as an off-white powder (132.5 mg, 0.42 mmol, 42%). ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 8.64 (s, 1H, NCH), 7.78–7.75 (m, 2H, Ar–H), 7.46–7.43 (m, 3H, Ar–H), 4.51 (q, 2H, NC$\underline{H}_2$CH$_3$, $^3J_{H,H}$ = 12 Hz), 2.79 (t, 2H, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$, $^3J_{H,H}$ = 12 Hz), 1.70–1.63 (m, 2H, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.56 (t, 3H, NCH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 12 Hz), 1.37–1.28 (m, 2H, CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 0.81 (t, 3H, CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 12 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 145.8, 135.2, 132.0, 130.5, 126.2, 121.6 (Ar–C), 47.3 (N$\underline{C}$H$_2$CH$_3$), 29.1 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 23.0 (CH$_2\underline{C}$H$_2$CH$_2$CH$_3$), 22.4 (NCH$_2\underline{C}$H$_3$), 14.0 (CH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 13.7 (CH$_2$CH$_2$CH$_2\underline{C}$H$_3$). ESI-MS (positive) *m*/*z* 230 $[M - BF_4]^+$.

Synthesis of compound d

A mixture of 4-butyl-1-phenyl-1,2,3-triazole (201.2 mg, 1 mmol) and benzyl bromide (1 mL) was stirred in a 25 mL Schlenk tube and heated at 120 °C for 72 h. After the mixture was cooled to ambient temperature, diethyl ether (10 mL) was added and the resulting suspension was stirred overnight. Then the precipitate was washed with a copious amount of diethyl ether and dried under vacuum to give the desired compound as an off-white powder (294.2 mg, 0.79 mmol, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.23 (s, 1H, C^5$_{triazole}$–H), 8.21–8.20 (m, 2H, Ar–H), 7.60–7.58 (m, 3H, Ar–H), 7.42–7.41 (m, 3H, Ar–H), 7.38–7.36 (m, 2H, Ar–H), 5.99 (s, 2H, NCH$_2$), 3.01 (t, 2H, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$, $^3J_{H,H}$ = 6 Hz), 1.71 (br s, 2H, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.37–1.31 (m, 2H, CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 0.83 (t, 3H, CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 146.7 (C^5$_{triazole}$), 135.4, 132.5, 131.7, 131.1, 130.5, 130.2, 129.1, 128.9, 122.0 (Ar–C), 56.6 (NCH$_2$), 30.0 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 24.6 (CH$_2\underline{C}$H$_2$CH$_2$CH$_3$), 22.9 (CH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 14.1 (CH$_2$CH$_2$CH$_2\underline{C}$H$_3$). ESI-MS (positive) *m*/*z* 292 $[M - Br]^+$.

Synthesis of complex 9

A mixture of dimeric complex $[PdBr_2(^iPr_2\text{-bimy})]_2$ (187.4 mg, 0.2 mmol) and tetra-butyl ammonium bromide (128.9 mg, 0.4 mmol) was stirred in CH_2Cl_2 (10 mL) at ambient temperature for 2 h. Then salt **c** (126.8 mg, 0.4 mmol) and Ag_2O (55.6 mg, 0.24 mmol) were added, and the reaction mixture was stirred at ambient temperature for 18 h in the dark. Then the suspension was filtered over Celite. Then the filtrate was washed with deionized H_2O (3 × 10 mL). Drying of the organic phase over Na_2SO_4 followed by the removal of the solvent *in vacuo* afforded the crude product as an yellow powder. Then the crude product was purified using column chromatography (SiO_2, CH_2Cl_2/petroleum ether (v : v) = 3 : 1). The eluent contains 3‰ triethyl amine. The product was afforded as a yellow solid (128 mg, 0.18 mmol, 46%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.33 (d, 2H, Ar–H, $^3J_{H,H}$ = 6 Hz), 7.61–7.49 (m, 5H, Ar–H), 7.16–7.15 (m, 2H, Ar–H), 6.22 (heptet, 1H, NCH, $^3J_{H,H}$ = 7.2 Hz), 5.96 (heptet, 1H, NCH, $^3J_{H,H}$ = 7 Hz), 4.37 (q, 2H, NCH$_2$, $^3J_{H,H}$ = 6 Hz), 3.12 (t, 2H, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$, $^3J_{H,H}$ = 6 Hz), 2.23 (m, 2H, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.79 (d, 6H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6 Hz), 1.66–1.61 (m, 11H, CH(C$\underline{H}_3$)$_2$ and NCH$_2$C$\underline{H}_3$ and CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.11 (t, 3H, CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 181.1 (C$_{carbene}$–^{i}Pr$_2$-bimy), 158.5 (C$_{carbene}$–trz), 145.4, 141.0, 134.3, 134.2, 130.1, 129.2, 126.4, 122.3, 113.11, 113.06 (Ar–C), 54.3, 54.2 (NCH), 45.4 (N$\underline{C}$H$_2$CH$_3$), 32.2 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 26.1 (CH$_2\underline{C}$H$_2$CH$_2$CH$_3$), 23.8 (CH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 21.7 (CH($\underline{C}$H$_3$)$_2$), 21.4 (CH($\underline{C}$H$_3$)$_2$), 15.3 (NCH$_2\underline{C}$H$_3$), 14.5 (CH$_2$CH$_2$CH$_2\underline{C}$H$_3$). ESI-MS (positive) *m*/*z*: 618 $[M - Br]^+$. Anal. Calcd for $C_{27}H_{37}Br_2N_5Pd$: C, 46.47; H, 5.34; N, 10.04%; found: C, 46.58; H, 5.65; N, 9.86%.

Synthesis of complex 10

A mixture of salt **d** (132 mg, 0.35 mmol), Ag_2O (49.6 mg, 0.21 mmol) and dimeric complex $[PdBr_2(^iPr_2\text{-bimy})]_2$ (166.6 mg, 0.17 mmol) was stirred in CH_2Cl_2 at ambient temperature for 12 h. Then the suspension was filtered over Celite and the solvent of the filtrate was removed *in vacuo* to give a crude product. Then the crude product was purified using column chromatography (SiO_2, CH_2Cl_2/petroleum ether (v : v) = 2 : 1). The solvent system contains 3‰ triethyl amine. The product was afforded as a yellow solid (124 mg, 0.16 mmol, 48%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.38–8.36 (m, 2H, Ar–H), 7.61–7.58 (m, 3H, Ar–H), 7.52–7.49 (m, 2H, Ar–H), 7.40–7.37 (m, 3H, Ar–H), 7.27–7.26 (m, 2H, Ar–H), 7.15–7.14 (m, 2H, Ar–H), 6.20 (heptet, 1H, NCH, $^3J_{H,H}$ = 7 Hz), 5.98 (heptet, 1H, NCH, $^3J_{H,H}$ = 7 Hz), 5.28 (s, 2H, C$_6$H$_5$C$\underline{H}_2$), 3.07 (t, 2H, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$, $^3J_{H,H}$ = 6 Hz), 2.08–2.05 (m, 2H, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.78 (d, 6H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6 Hz), 1.63 (d, 6H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6 Hz), 1.53–1.49 (m, 2H, CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.01 (t, 3H, CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 12 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 180.8 (C$_{carbene}$–^{i}Pr$_2$-bimy), 159.1 (C$_{carbene}$–trz), 145.9, 140.7, 134.0, 133.9, 133.1, 130.0, 129.7, 129.4, 129.0, 128.1, 126.2, 122.2, 112.92, 112.86 (Ar–C), 54.04, 54.00 ($\underline{C}$H(CH$_3$)$_2$), 53.8 (C$_6$H$_5\underline{C}$H$_2$) 31.7 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 26.1 (CH$_2\underline{C}$H$_2$CH$_2$CH$_3$), 23.5 (CH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 21.5 (CH($\underline{C}$H$_3$)$_2$), 21.2 (CH($\underline{C}$H$_3$)$_2$), 14.2 (CH$_2$CH$_2$CH$_2\underline{C}$H$_3$). ESI-MS (positive) *m*/*z*: 680 $[M - Br]^+$. Anal. Calcd for $C_{32}H_{39}Br_2N_5Pd$: C, 50.58; H, 5.17; N, 9.22%; found: C, 50.44; H, 5.22; N, 8.86%.

Synthesis of complex 11

A mixture of **9** (54.9 mg, 0.08 mmol) and NaOAc (32.3 mg, 0.4 mmol) was stirred in DMSO (5 mL) at 120 °C for 2 h. Then the mixture was suspended in CH_2Cl_2 (20 mL) and washed with deionized H_2O (3 × 10 mL). Drying of the organic phase over Na_2SO_4 followed by removal of the solvent *in vacuo* afforded the crude product as a yellow powder. Then the crude product was purified using column chromatography (SiO_2, CH_2Cl_2/petroleum ether (v : v) = 2 : 1). The solvent system contains 3‰ triethyl amine. The product was afforded as a yellow solid (10 mg, 0.016 mmol, 20%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.64–7.63 (m, 2H, Ar–H), 7.53 (dd, 1H, Ar–H, $^3J_{H,H}$ = 12 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.26–7.24 (m, 2H, Ar–H), 7.04 (td, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 6.81 (td, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 6.40 (dd, 1H, Ar–H, $^3J_{H,H}$ = 12 Hz, $^4J_{H,H}$ = 1.2 Hz), 5.98 (heptet, 2H, NCH, $^3J_{H,H}$ = 7.2 Hz), 4.37 (q, 2H, NC$\underline{H}_2$CH$_3$, $^3J_{H,H}$ = 7.2 Hz), 3.33 (t, 2H, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$, $^3J_{H,H}$ = 6 Hz), 1.79–1.72 (m, 8H, NCH(C$\underline{H}_3$)$_2$ and CH$_2$C$\underline{H}_2$CH$_2$CH$_3$),

1.61 (t, 3H, $NCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz), 1.60 (d, 6H, $NCH(C\underline{H}_3)_2$, $^3J_{H,H}$ = 7.2 Hz), 1.56–1.50 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.99 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 6 Hz).^{13}C NMR ($CDCl_3$, 150 MHz): 193.0 ($C_{carbene}$–^{i}Pr$_2$-bimy), 162.0 ($C_{carbene}$–trz), 148.6, 148.0, 144.0, 139.7, 134.4, 129.2, 128.3, 126.5, 124.6, 122.5, 114.9, 113.4 (Ar–C), 54.5 ($\underline{C}H(CH_3)_2$), 44.7 ($N\underline{C}H_2CH_3$), 33.1 ($\underline{C}H_2CH_2CH_2CH_3$), 24.9 ($CH_2\underline{C}H_2CH_2CH_3$), 23.3 ($CH_2CH_2\underline{C}H_2CH_3$), 21.7, 21.6 ($CH(\underline{C}H_3)_2$), 16.0 ($NCH_2\underline{C}H_3$), 14.7 ($CH_2CH_2CH_2\underline{C}H_3$). ESI-MS (positive) *m*/*z*: 536 $[M - Br]^+$. Anal. Calcd for $C_{27}H_{36}BrN_5Pd$: C, 52.56; H, 5.88; N, 11.35%; found: C, 53.01; H, 5.55; N, 11.16%.

Synthesis of complex 12

A mixture of **10** (68.4 mg, 0.09 mmol) and NaOAc (36.9 mg, 0.45 mmol) was stirred in DMSO (5 mL) at 120 °C for 2 h. Then the mixture was suspended in CH_2Cl_2 (20 mL) and washed with deionized H_2O (3 × 10 mL). Drying of the organic phase over Na_2SO_4 followed by removal of the solvent *in vacuo* afforded the crude product as a yellow powder. Then the crude product was purified using column chromatography (SiO_2, CH_2Cl_2/petroleum ether (v : v) = 5 : 1). The solvent system contains 3‰ triethyl amine. The product was afforded as a yellow solid (13.4 mg, 0.02 mmol, 22%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.65–7.62 (m, 2H, Ar–H), 7.59 (dd, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.41–7.36 (m, 3H, Ar–H), 7.30–7.29 (m, 2H, Ar–H), 7.26–7.24 (m, 2H, Ar–H), 7.06 (td, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 6.83 (td, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 6.42 (dd, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 1.2 Hz), 5.98 (heptet, 2H, NCH, $^3J_{H,H}$ = 7.2 Hz), 5.53 (s, 2H, $C_6H_5C\underline{H}_2$), 3.27 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{H,H}$ = 7.8 Hz), 1.74 (d, 6H, $CH(C\underline{H}_3)_2$, $^3J_{H,H}$ = 6 Hz), 1.63–1.59 (m, 8H, $CH(C\underline{H}_3)_2$ and $CH_2C\underline{H}_2CH_2CH_3$), 1.49–1.45 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.91 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 192.9 ($C_{carbene}$–^{i}Pr$_2$-bimy), 162.7 ($C_{carbene}$–trz), 149.2, 139.7, 134.4, 134.0, 129.8, 129.6, 128.4, 128.3, 124.6, 122.5, 115.1, 113.4 (Ar–C), 54.5 (NCH), 53.4 ($C_6H_5\underline{C}H_2$), 32.7 ($\underline{C}H_2CH_2CH_2CH_3$), 25.0 ($CH_2\underline{C}H_2CH_2CH_3$), 23.3 ($CH_2CH_2\underline{C}H_2CH_3$), 21.7 ($CH(\underline{C}H_3)_2$), 21.6 ($CH(\underline{C}H_3)_2$), 14.6 ($CH_2CH_2CH_2\underline{C}H_3$). ESI-MS (positive) *m*/*z*: 598 $[M - Br]^+$. Anal. Calcd for $C_{32}H_{38}BrN_5Pd$: C, 56.60; H, 5.64; N, 10.31; found: C, 57.31; H, 5.25; N, 9.56%. Although the elemental analysis results are slightly outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

X-ray diffraction studies

X-ray data for complexes **5** and **7** were collected with an Agilent Xcalibur Eos Gemini diffractometer using Mo-K_α radiation. For complex **6**, the data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. For complex **10**, the data were collected on a Rigaku XtaLAB P200 MM003 diffractometer. Structural solution was carried out with the Olex2 program.[19] The structure was solved using direct methods. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table SI-1.† CCDC 1824536–1824539† contain the supplementary crystallographic data for this paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Beijing Natural Science Foundation (Grant No. 2164057) and the National Natural Science Foundation of China (Grant No. 21502122) for financial support.

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