



REGULAR ARTICLE

Platinum(II), palladium(II) and gold(I) benzimidazolin-2-ylidene as potential probes for determination of N-heterocyclic carbene donor strengths and steric bulks by DFT calculations

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MS received 23 December 2019; revised 4 March 2020; accepted 5 March 2020

Abstract. Correlation between the donor strength of N-heterocyclic carbenes (NHC) and the M–C_{carbene} bond distances in complexes of the type *trans*-[MX₂(ⁱPr₂-bimy)(NHC)] (MX₂ = PtCl₂, PdBr₂; ⁱPr₂-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) and [Au(ⁱPr₂-bimy)(NHC)]⁺ was investigated for a selection of 20 carbenes. The structures of the complexes were first optimized in gas phase. The bond lengths between metal (Pt, Pd and Au) and the carbene carbon of ⁱPr₂-bimy probe and NHC carbene under studied were then measured. Their correlation to the donor strength, evaluated using Huynh's electronic parameter (HEP) was then examined. The results show good linear fitting between HEP value and Pd–C_{probe} carbene distances or Hirshfeld atomic charge of the ⁱPr₂-bimy probe (C_{probe}), suggesting the possibility of using theoretical approach for evaluation of donor strength for N-heterocyclic carbenes. In addition to the determination of NHC donicity, the optimized geometries can also be utilized as inputs for calculation of the steric properties, namely percent volume buried of the NHC ligands.

Keywords. N-heterocyclic carbene; Huynh's electronic parameter (HEP); platinum(II) carbene; palladium(II) carbene; gold(I) carbene; percent volume buried (%V_{bur}).

1. Introduction

The past few decades has witnessed the transformation of N-heterocyclic carbene (NHC) from a curiosity-driven laboratory discovery into one of the most powerful class of ligands in organometallic chemistry.^{1–5} NHC complexes of transition metals are now found potential applications in various fields, such as drug and advanced material development, and especially in organometallic catalysis.^{5–9} The popularity of NHC ligands can be attributed to their excellent steric and electronic tunability, which can be achieved by judicious choice of N-substituents or varying the NHC backbone (Figure 1).^{10,11}

To quantify electronic properties, or ligand donor strength, of NHCs, there exist several different approaches. For example, to evaluate the ability of a NHC to donate electron density to a metal, one can use Tolman electronic parameter (TEP),¹² rhodium(I) carbonyl-based system, iridium(I) carbonyl-based system,^{13–15} redox potential and the Ligand electronic

parameter (LEP)^{16,17} or ¹³C-NMR based method proposed by Huynh's group (Huynh's electronic parameter—HEP).^{18–20} Though the HEP approach was proposed recently, it has been recognized by organometallic research community and it has gained popularity in the past few years. In principle, the method is based on the ¹³C-NMR spectroscopic analyses of generally stable palladium(II) NHC complexes of the type *trans*-[PdBr₂(ⁱPr₂-bimy)L] (ⁱPr₂-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) (Figure 2). Donor strength of the ligand L is measured by the chemical shift of the ¹³C carbene signal of the ⁱPr₂-bimy reporter ligand (i.e., HEP value). More donating ligand L would lead to a lengthening of the Pd–C_{probe} bond, resulting in a more free-carbene-like ⁱPr₂-bimy and a more down-field shift for the ¹³C-NMR signal of the C_{probe}. Note that the ligand L can be Werner's type or organometallic type ligands, including N-heterocyclic carbenes.

Though the HEP method offers a relatively high resolution measurement of donor strength for various organometallic and classical Werner's type ligands on a unified scale. The main disadvantage of this method, as also for the above-mentioned experimental

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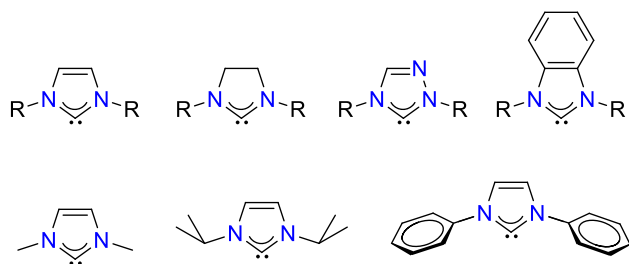


Figure 1. Stereoelectronic turnability of NHC achieved by varying the N-substituents or their backbone.

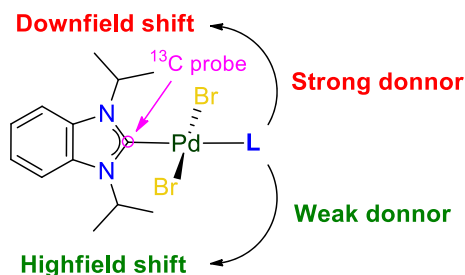


Figure 2. The principle of ligand donor strength determination by HEP approach.

approaches, is that it requires, sometime elaborated, laboratory work to synthesize the compound merely for the purpose of donor strength determination.

Based on the idea that more donating ligand L would lead to a lengthening of the Pt–C_{probe} bond, we expect that DFT theoretical calculation can be utilized to determine the Pd–C_{probe} bond length, offering a mean to evaluate donor strength. It should be noted that, experimentally determined bond distances are strongly affected by various factors, such as crystal quality, crystal packing, solvent molecule in crystal, the temperature at which the data were collected and the bond distance figures often comes with large standard deviations. Therefore, it is, in fact, difficult to compare bond lengths of different compounds. Theoretical calculation, on the other hand, deal with individual molecules in the gas phase and a fixed set of functional and basis sets are used to describe all molecules. As a result, the data come out from calculations are highly reproducible, allowing the comparison of distances with small difference. As a result, it may be possible to develop a merely theoretical approach in complimentary to the HEP approach for ligand donor strength determination. In this manuscript, we present our preliminary result into this direction.

2. Methodology

Complexes of the type *trans*-M(ⁱPr₂-bimy)(NHC), where M = PdBr₂, PtCl₂, Au⁺ (Figure 3), were utilized as platform to evaluate the influence of NHC

donor strength to the respective metal–C_{probe} bond length.

Gas phase structure of all complexes was first optimized using Gaussian[®] 16 software. The B3PW91 hybrid functional were employed for all calculation.^{21,22} The 6-31G(d) basis set was used for H, C, N and Cl.^{23,24} The heavy atoms Pd, Pt, Au and Br were described by Stuttgart–Dresden (SDD) relativistic effective core potential and associated basis sets.²⁵ The imaginary frequency was checked to ensure the stationary point was a minimum. The metal–C_{probe} bond distances were measured for the optimized geometries. The theoretically determined M–C_{probe} (M = Pd, Pt, Au) bond distances were then separately correlated with the HEP values of the respective NHC. Hirshfeld atomic charge for all atoms was calculated at optimized geometries using Multiwfn software.²⁶

3. Results and Discussion

3.1 Collection of N-heterocyclic to examine

In this preliminary work, a set of 20 NHCs,¹⁸ which already had their HEP values reported, was chosen to investigate. Their structures are presented in Figure 4. Noted that the sample collection contains a wide range of NHCs with various different backbones and substituents. The NHC backbones include classical imidazol-2-ylidene (**IMesBn**, **IMes**, **ICy**, **IPr**), substituted imidazol-2-ylidines (**IMes^{Br2}**, **IPr^{Br2}**), and saturated imidazole-driven carbenes (**SIMes**, **SIPrPh**). In addition, nonclassical NHC (abnormal carbene), such as 1,2,3-triazole-4-ylidene (**trz1**, **trz2**, **trz3**, **trz4**, **trz5**, **trz6**), 1,2-pyrazole-3-ylidenes (**pyry1**, **pyry2**, **pyry3**, **pyry4**) and 1,3-imidazole-4-ylidene (**aIBn**) are also included in the collection. The selected NHCs are also bearing various N-substituent

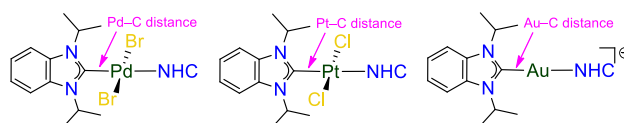
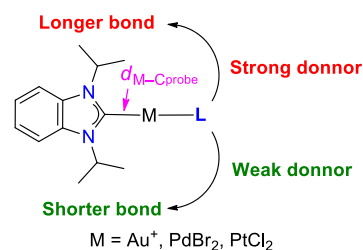


Figure 3. Structures of palladium(II), platinum(II) and gold(III) complexes in this study.

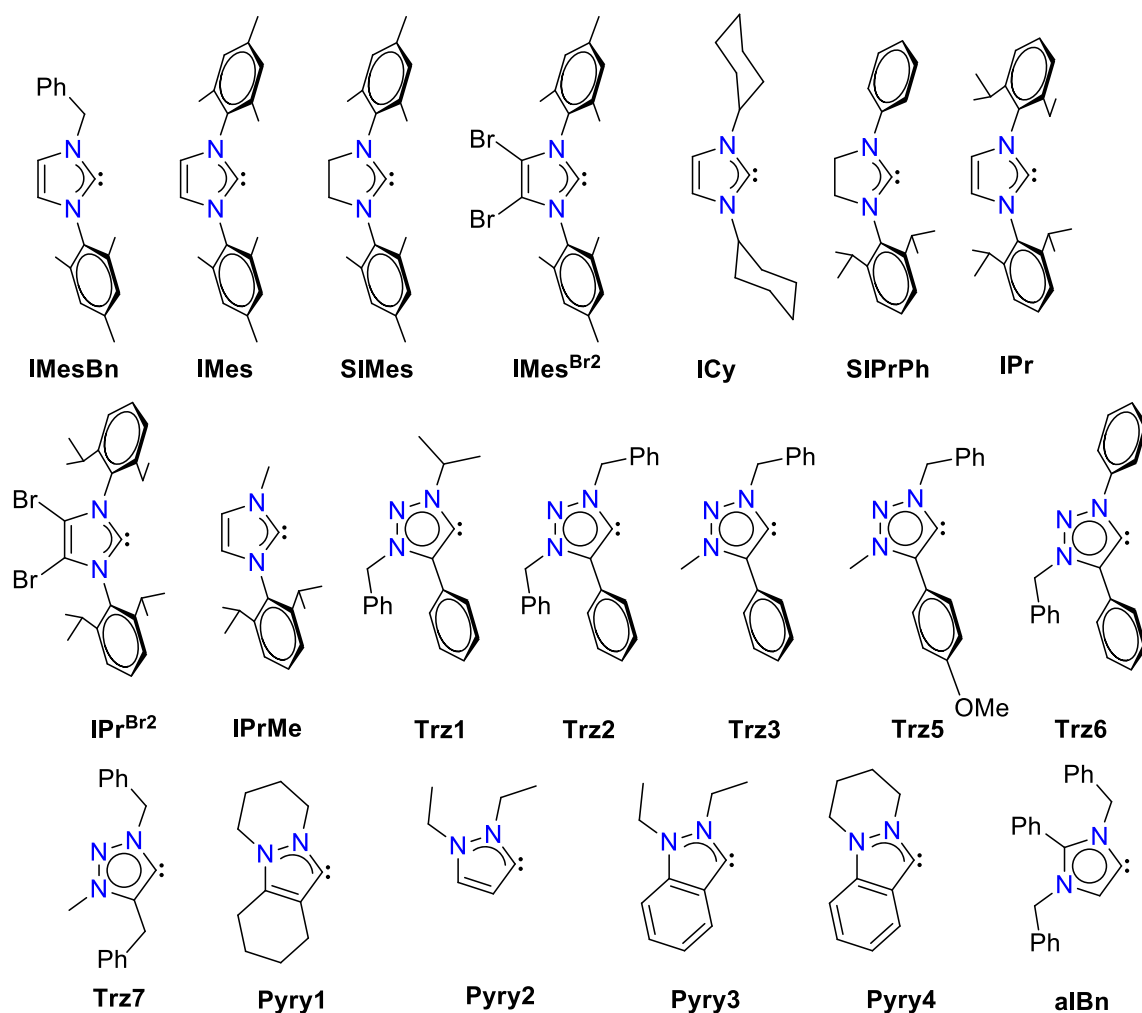


Figure 4. Structures of the 20 N-heterocyclic carbene in this study.

groups, ranging from small, less bulky substituents, for example methyl (**IPrMe**), ethyl (**Piry2**, **Piry3**) to the bulkier isopropyl (**Trz1**), and benzyl (**IMesBn**, **Trz2**, **Trz3**, **Trz5**, **aIBn**). Significantly larger substituents such as mesityl (in **IMesBn**, **IMes**, **SIMes**, **IMes^{Br2}**) or 1,6-diisopropylphenyl (Dipp) in **SIPrPh**, **IPr**, **SIPr**, **IPr^{Br2}**.

3.2 Geometries of the gas phase optimized structures

The geometries of all complexes were first optimized in gas phase. Structures of representative complexes are presented in Figure 5. It can be noted that all the palladium(II) and platinum(II) complexes are essentially squared planar in geometries, coordinated by two halide ligands, a benzimidazol-2-ylidene and a carbene under studied. The gold(I) heterobiscarbene display linear geometries with the gold(I) coordinated

by ⁱPr₂-bimy probe ligand and a NHC under investigation. The most important parameters obtained are distances between the metal centers (Pd, Pt and Au) and the ⁱPr₂-bimy probe carbene (M–C_{probe}) and the carbene under study (M–C_{NHC}) (M = Pt, Pd). The distances are listed in Table 1.

3.3 Correlation between M–C_{probe} and M–C_{NHC} distances and HEP values for the ligands

First of all, the correlation between HEP values and the Pt–C_{probe}, Pt–C_{NHC} in *trans*-[PtCl₂(ⁱPr₂-bimy)(NHC)] and Au–C_{probe}, Au–C_{NHC} in [Au(ⁱPr₂-bimy)(NHC)]⁺ were plotted (Figures 6 and 7).

It can be seen that there is no obvious correlation between Pt–C_{NHC} or Au–C_{NHC} distances and HEP values of the NHCs (Figures 6 and 7). On the other hand, both Pt–C_{probe} and Au–C_{NHC} distances seem to increase as the ligand becomes more

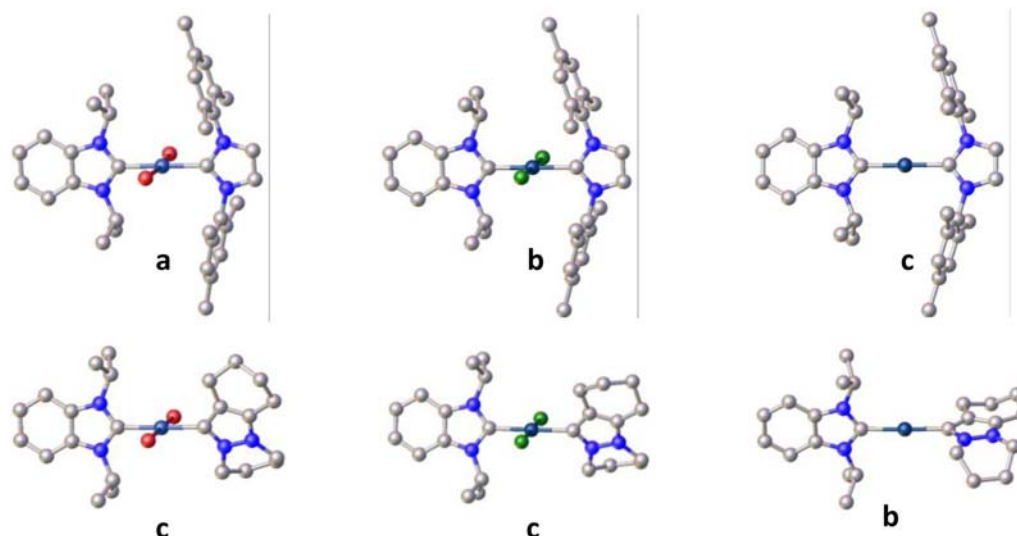


Figure 5. Optimized structures of selected complexes (a) *trans*-[PdBr₂(ⁱPr₂-bimy)(IMes)]; (b) *trans*-[PtCl₂(ⁱPr₂-bimy)(IMes)]; (c) [Au(ⁱPr₂-bimy)(IMes)]⁺; (d) *trans*-[PdBr₂(ⁱPr₂-bimy)(Pyr1)]; (e) *trans*-[PtCl₂(ⁱPr₂-bimy)(Pyr1)]; (f) [Au(ⁱPr₂-bimy)(Pyr1)]⁺.

Table 1. M–C_{probe} and M–C_{NHC} bond lengths in their complexes.

No.	NHC	HEP value	<i>trans</i> -PdBr ₂ (ⁱ Pr ₂ -bimy)(NHC)		<i>trans</i> -PtBr ₂ (ⁱ Pr ₂ -bimy)(NHC)		[Au(ⁱ Pr ₂ -bimy)(NHC)] ⁺	
			Pd–C _{probe}	Pd–C _{NHC}	Pt–C _{probe}	Pt–C _{NHC}	Au–C _{probe}	Au–C _{NHC}
1	IMesBn	178.3	2.02541	2.05034	2.03132	2.04385	2.0515	2.04402
2	IMes	177.2	2.01576	2.07025	2.02663	2.05101	2.04876	2.03909
3	SIMes	177.6	2.02070	2.07281	–	–	2.05266	2.0519
4	IMes^{Br2}	175.6	2.01113	2.07569	–	–	2.04761	2.03986
5	ICy	181.2	2.03502	2.03813	2.03563	2.04238	2.05254	2.04884
6	SIPrPh	178.7	2.02752	2.04244	2.03546	2.03378	2.0517	2.04963
7	IPr	177.5	2.01816	2.06116	2.02805	2.04400	2.05007	2.04162
8	IPr^{Br2}	175.3	2.01312	2.07656	2.02594	2.05016	2.04899	2.04264
9	IPrMe	178.8	2.02733	2.03986	2.03177	2.03604	2.05172	2.04553
10	Trz1	181.2	2.03291	2.03177	2.03311	2.03768	2.05232	2.04307
11	Trz2	180.8	2.03236	2.03254	2.03394	2.03690	2.05175	2.04096
12	Trz3	180.8	2.03234	2.03323	2.03429	2.03696	2.05171	2.04202
13	Trz5	181.0	2.03255	2.03325	2.03434	2.03793	2.0518	2.04186
14	Trz6	180.3	2.02874	2.03322	2.02968	2.03423	2.0507	2.0436
15	Trz7	180.2	2.03259	2.03675	2.03543	2.03655	2.05262	2.04247
16	Pyr1	184.0	2.03975	2.02816	2.03947	2.03378	2.05631	2.04269
17	Pyr2	182.4	2.03672	2.02741	2.03837	2.03088	2.05433	2.04359
18	Pyr3	181.6	2.03576	2.02912	2.03993	2.02895	2.05499	2.04304
19	Pyr4	181.4	2.03484	2.03086	2.03819	2.03131	2.0546	2.04162
20	alBn	181.9	2.03465	2.03591	2.0354	2.03793	2.05323	2.04259

donating (higher HEP values). It is in line with the fact that more donating NHC would lead to an elongation of the distance between the metal center and the probe ⁱPr₂-bimy. However, the linear fitting only results in a correlation with coefficient of 0.82 for Pt–C_{NHC} and 0.86 for Au–C_{NHC}. Such moderate correlation indicates that *trans*-[PtCl₂(ⁱPr₂-bimy)(NHC)] and [Au(ⁱPr₂-bimy)(NHC)]⁺ are not ideal system for the theoretical determination of NHC donor strength.

The correlation between HEP values of a NHC and Pd–C_{probe} and Pd–C_{NHC} distances in *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] were plotted (Figure 6). Generally, more donating NHCs lead to shorter Pd–C_{NHC} bond distances. However, the correlation between HEP value and Pd–C_{NHC} distance is not strong, showing the R² value of 0.85 for linear fitting, which is consider not a very strong correlation. On the other hand, stronger positive correlation is observed for HEP value and Pd–C_{probe} distance (Figure 8).

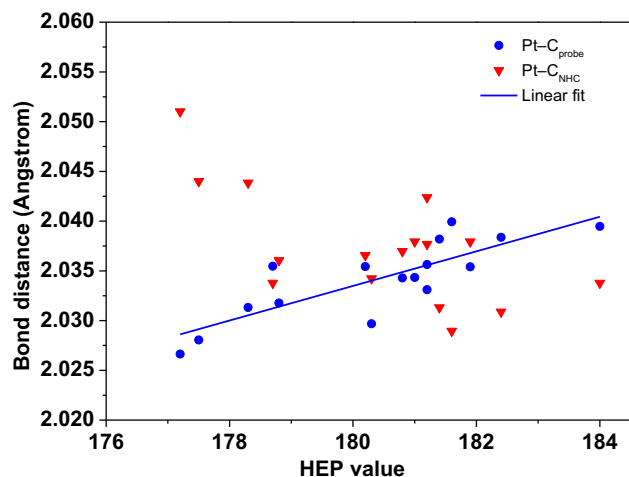


Figure 6. Plot of Pt-C_{probe} and Pt-C_{NHC} distances vs HEP values.

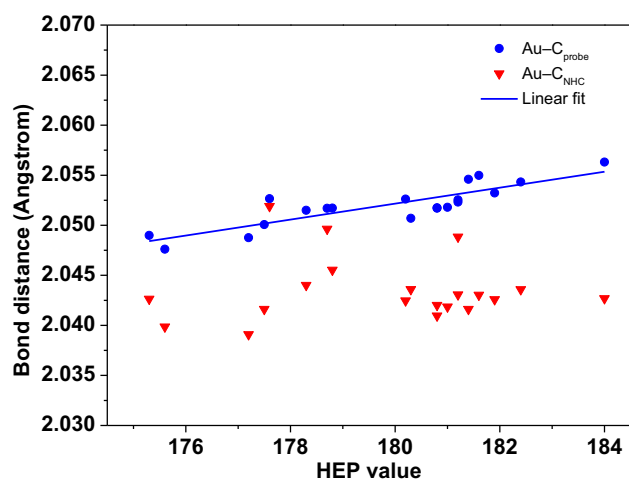


Figure 7. Plot of Au-C_{probe} and Au-C_{NHC} distances vs HEP values.

Linear fitting shows that the two parameters can be interconvertible by the mathematical equation

$$[d_{\text{Pt-C}_{\text{probe}}}] = 0.00352 \times [\text{HEP}] + 1.396$$

The strong correlation was indicated by the high R² value of 0.97 for the data set of 20 data points. Such strong correlation suggests the possibility to utilize the Pd-C_{probe} distances obtained from theoretically optimized molecular structure of the *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] complexes as a means to calculate the donor strength (HEP value) of NHC ligands.

3.4 Atomic charge on C_{probe} and HEP values of NHC ligands

It is also interesting to look at atomic charge of the C_{probe} carbon atom in those *trans*-[PdBr₂(ⁱPr₂-

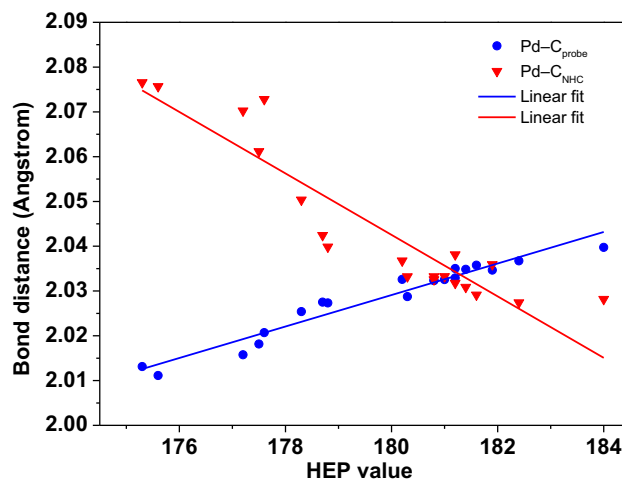


Figure 8. Correlation between Pd-C_{NHC}, Pd-C_{probe} and HEP values.

bimy)(NHC)] and to examine correlation between the charges and donor strength of NHC ligands. Hirshfeld charge for the C_{probe} carbon atoms in the complexes is listed in Table 2.

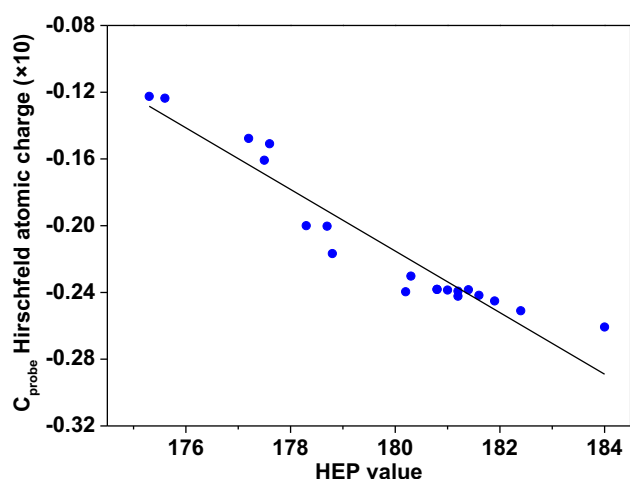
It is clearly shown from the data that all the carbon atoms of the *i*Pr₂-bimy probe (C_{probe}) carry a negative charge, and higher charge density is found for those with more donating NHC. The correlation between C_{probe} Hirshfeld atomic charge and the respective HEP value is plotted in Figure 9. Linear fitting results in regression equation [C_{probe} charge] = 0.00185 × [HEP] + 0.311, with a high coefficient of 0.95.

3.5 Percentage volume buried (%Vbur) for the NHC carbenes using the gas phase optimized geometries of *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)]

In general, besides electronic, steric property of ligands is a key factor that control properties and reactivity of a complexes. Immense effort has been devoted into developing methodologies for evaluation of the steric property of ligands. Among the available approach, the recently proposed percent volume buried^{27,28} can be considered as a convenient approach. By definition, percent volume buried is the percentage of metal coordination sphere occupied by a specific ligands. To calculate percent volume buried (%Vbur) for a ligand, one would need to provide X-ray determined molecular structure of the complex, from which a free web-based tool (SambVca 2) would process and give the %Vbur as outcome results.²⁹ Since the calculation requires structures of the complexes, which cannot always be grown as single

Table 2. C_{probe} Hirschfeld atomic charge in the complexes.

No.	NHC	HEP	C _{probe} charge	No.	NHC	HEP	C _{probe} charge
1	IMesBn	178.3	-0.0200	11	Trz2	180.8	-0.0123
2	IMes	177.2	-0.0148	12	Trz3	180.8	-0.0261
3	SIMes	177.6	-0.0124	13	Trz5	181.0	-0.0251
4	IMes^{Br2}	175.6	-0.0242	14	Trz6	180.3	-0.0242
5	ICy	181.2	-0.0238	15	Trz7	180.2	-0.0238
6	SIPrPh	178.7	-0.0238	16	Pyry1	184.0	-0.0245
7	IPr	177.5	-0.0218	17	Pyry2	182.4	-0.0239
8	IPr^{Br2}	175.3	-0.0200	18	Pyry3	181.6	-0.0239
9	IPrMe	178.8	-0.0151	19	Pyry4	181.4	-0.0230
10	Trz1	181.2	-0.0161	20	alBn	181.9	-0.0239

**Figure 9.** Very strong correlation between Hirschfeld atomic charge of the C_{probe} and HEP value.

crystals suitable for X-ray diffraction, the calculation for %V_{bur} can sometime become a challenging task. In this work, we propose the usage of optimized geometries as input for the calculation.

Percent volume buried values for the NHCs, calculated using optimized geometries of the respective *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] complexes are listed in Table 3.

The results are in line with chemical intuition, the NHC with bulky 2,6-diisopropylphenyl N-substituents, such as **SIPrPh**, **Ipr** and **IPr^{Br2}** are the ones with higher %V_{bur} with the value of 32.1%, 31.2% and 32.1%, respectively. The carbenes with more flexible alkyl substituents (benzyl, methyl, isopropyl) are less bulky, having the %V_{bur} of 19.1% (**IMesBn**), 28.7% (**IPrMe**), 27.2% (**Trz1**), 27.8% (**Trz2**) and 28.1% (**Trz3**). Notably, the abnormal carbenes, bearing only one N-substituent neighbored to the carbene carbon are the least bulky ligands. For example, **alBn** with only one benzyl group next to the carbene carbon has

Table 3. %V_{bur} of the NHC in this study, calculated using optimized geometries of *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] complexes.

No.	NHC	%V _{bur}	No.	NHC	%V _{bur}
1	IMesBn	29.1	11	Trz2	27.8
2	IMes	31.1	12	Trz3	28.1
3	SIMes	34.5	13	Trz5	28.3
4	IMes^{Br2}	31.6	14	Trz6	29.6
5	ICy	26.5	15	Trz7	28.1
6	SIPrPh	32.1	16	Pyry1	24.8
7	IPr	31.2	17	Pyry2	24.3
8	IPr^{Br2}	32.1	18	Pyry3	26.4
9	IPrMe	28.7	19	Pyry4	26.4
10	Trz1	27.2	20	alBn	25.5

the %V_{bur} of 25.5% only. Similarly, the **Pyry2** carbene with only one ethyl substituent also has low %V_{bur} of 24.3%.

4. Conclusions

Correlation between the donor strength of N-heterocyclic carbenes (NHC) and the M-C_{carbene} bond distances in complexes of the type *trans*-[MX₂(ⁱPr₂-bimy)(NHC)] (MX₂ = PtCl₂, PdBr₂) and [Au(ⁱPr₂-bimy)(NHC)]⁺ was examined for 20 N-heterocyclic carbenes with diverse structures. The results show good correlation between Pd-C_{probe} distances or the atomic charge of the ⁱPr₂-bimy carbene carbon atom (C_{probe}) in the complexes *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] and the HEP values of respective NHCs. It also suggested that the optimized geometries of *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] can be utilized to evaluate the steric properties of the NHC using percent volume buried approach. The approach for using DFT optimized structure of *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] to evaluate donor strength of NHC can be extended to a more

elaborated NHC collection to investigate the applicability of this methodology. Work in this direction is being pursued in our laboratory.

Acknowledgements

This work is funded by National Foundation for Science and Technology Development (NAFOSTED) through Project 104.03-2017.14.

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