Received 00th January 20xx,

*a St Petersburg University, 7/9 Universitetskaya Nab., Saint Petersburg*

*199034, Russian Federation. E-mail: m.kinzhalov@spbu.ru*

*b Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69*

*7ZD, UK, E-mail: konstantin.luzyanin@liverpool.ac.uk*

† Electronic Supplementary Information (ESI) available. CCDC 2133432, 2133433, 2134335. For ESI and crystallographic data in CIF or another electronic format see DOI: 10.1039/x0xx00000x

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Experimental and Computational Tuning of Metalla-*N*-Heterocyclic Carbenes at Palladium(II) and Platinum(II) Centers

Maria V. Kashina,a Konstantin V. Luzyanin,b\* Eugene A. Katlenok,a Alexander S. Novikov, a and  
Mikhail A. Kinzhalov a\*

Palladium(II) and platinum(II) complexes featuring metalla-*N*-heterocyclic carbenes (**7**–**12**) were synthesised *via* metal-mediated coupling between equimolar *cis*-[MCl2(CNR)2] (R = 2,6-Me2C6H3 (Xyl), 2,4,6-Me3C6H3 (Mes)] and 2-aminopyridine or 2-aminopyrazine. Thiocyanate complexes **13**–**18** with two thiocyanate ligands were obtained through the ligand exchange in the parent **7**–**12** with NH4CNS in acetone/CH2Cl2. Complexes **13**–**18** were isolated and characterised by HRESI+-MS, IR, 1H and 13C{1H} NMR spectroscopy, single-crystal X-ray diffraction (in the case of **11**, **16**, and **18**). The UV-vis properties (for **7**–**18**) and the electrochemical properties (for **7**–**12**)were also evaluated. To study the electronic structure and bonding nature in the new compounds the quantum theory of atoms in molecules (QTAIM), and Mayer bond order analysis together with extended transition state with the natural orbitals for chemical valence method (ETS-NOCV), were used. X-ray diffraction studies and theoretical considerations indicate that the thiocyanate derivatives **16** and **18** form supramolecular dimer by two symmetrical pairs M1···C5 and S1···C2 short intermolecular contacts between electron reach MII-center and thiocyanate ligand in one side, and electron poor π system of azaheterocycle ring in another side.

Introduction

Transition metal complexes with heteroatom-stabilised carbenes, *i.e.* *N*-heterocyclic (NHCs)[1](#_ENREF_1) and acyclic diaminocarbenes (ADCs)[2](#_ENREF_4) underpin a broad range of applications in catalysis of organic processes;[1c](#_ENREF_3), [2b](#_ENREF_5), [3](#_ENREF_6) they are studied as emissive materials in optoelectronics,[4](#_ENREF_10) and potential anticancer drugs.[2b](#_ENREF_5), [5](#_ENREF_13) Ligand properties of diaminocarbenes are manifested through the formation of the М–Сcarbene σ-bond by transferring a pair of nonbonding electrons from the nucleophilic σ-orbital of the carbene carbon atom to the metal atom M. At the same time, the formation of a π-bond is also possible as a result of the interaction of a metal suitable in symmetry orbital with a vacant electron-deficient *p*π-orbital of a carbene carbon atom. The diaminocarbene ligand is usually an effective σ-donor and a weak π-acceptor, which is reflected in the catalytic and photophysical properties of respective metal complexes. Tuning of the electron-donor capacity of diaminocarbenes, which is crucial for the success of their target applications, has been mainly accomplished by varying the substituents on the nitrogen atoms or the modification of the heterocyclic skeleton (**Figure 1**, A). It was shown that NHC complexes containing a metal atom within the NHC skeleton, named metalla-*N*-heterocyclic carbenes (MNHCs),[6](#_ENREF_16) exhibit stronger electron-donor character by comparison with classical imidazole-2-ylidenes.[7](#_ENREF_17)

In pursuit of our ongoing project on the chemistry of diaminocarbenes,[3c](#_ENREF_8), [8](#_ENREF_18) we have reported that platinum(II)-MNHC species (**Figure 1**, B) work as self-photosensitising transition-metal photocatalysts of the hydrosilylation of alkynes under visible light.[9](#_ENREF_24) In this catalytic reaction the platinum(II)-MNHC catalyst has a dual function: it serves as a light-absorbing species and transition metal catalyst enabling catalytic process.



**Figure 1.** A. Examples of cyclic, *N*-heterocyclic and metalla-*N*-heterocyclic diaminocarbenes. B. The platinum(II)-MNHC catalyst exhibiting photocatalytic properties under visible light irradiation.

Additional strategies for fine-tuning of the properties of complexes of this type are linked to (*i*) the modification of the structure of azaheterocyclic ring (highlighted with a yellow rectangle), (*ii*) the substitution in the aryl rings (highlighted with a cyan rectangle), and (*iii*) the replacement of the anionic ligands at both metal centers (highlighted with a magenta rectangle). An interplay of those will define the application of the complex thus designed towards a specific goal.

The scenario of this work was as follows. We started by preparation of a series of palladium(II)- and platinum(II)-MNHC complexes *via* the metal-mediated coupling of isocyanides with various 2-aminoazaheterocycles. Displacement of chlorides with thiocyanates led to the generation of previously unknown diaminocarbene-thiocyanate derivatives. Electronic structure and bonding nature in the new compounds were assessed by using the quantum theory of atoms in molecules (QTAIM), the natural bond orbital (NBO) analysis, and Mayer bond order analysis together with extended transition state with the natural orbitals for chemical valence method (ETS-NOCV). Analysis of frontier molecular orbital character, energy gaps, and UV/vis spectra by density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches provided insights on the excited states involved in the light absorption and electrochemical processes, in turn related to the potential photocatalytic properties.

Results and discussion

*Preparation and characterisation of metalla-N-heterocyclic diaminocarbenes.*For this study, a series of PdII and PtII MNHC species **7**–**12** were prepared *via* the nucleophilic addition of 2-aminoazaheterocycles **5**, **6** to metal-bound isocyanides in *cis*-[MCl2(CNR)2] (**1**–**4**, M = Pd, Pt). The reaction between any one of **1**–**4** proceeds in CH2Cl2 at RT for *ca*. 1 d and the subsequent workup provided the binuclear diaminocarbene species**7**–**12** in good (84–95%) isolated yields (**Scheme 1**, **Route A**). This process occurs via the intermediate generation of corresponding mononuclear M-ADC species and its nucleophilic addition to unreacted isocyanide material facilitated by deprotonation of M-ADC intermediate by an excess of aminoazaheterocycle used.[9-10](#_ENREF_24)



**Scheme 1.** Preparation of **7**–**18**.

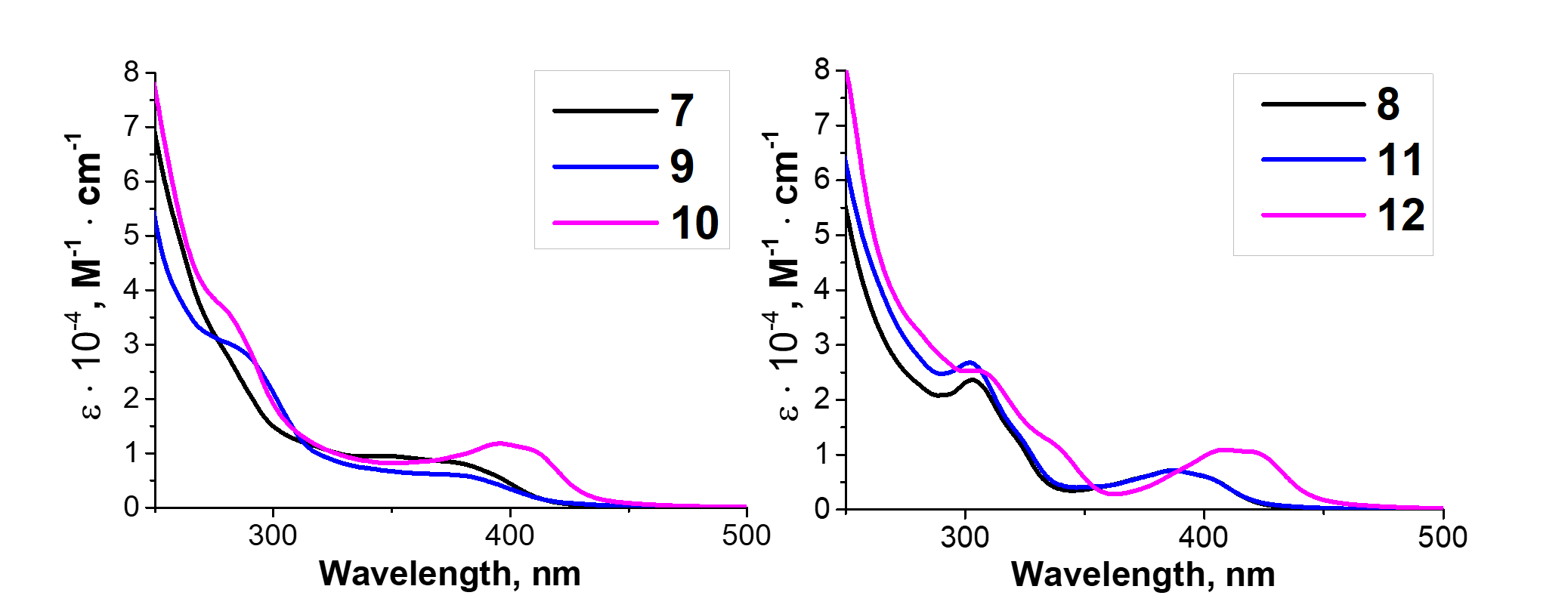
MNHC complexes **7**–**12** are yellow solids stable in the solid state in the 20–80 °C temperature range. New complexes **9**–**12** were characterised by elemental analyses (C, H, N), accurate-mass ESI+-MS, and IR and 1H, 13C{1H}, and 195Pt{1H} NMR spectroscopies (see *Experimental section* for more details), while the authenticity of known species **7**, **8** was confirmed by 1H NMR spectroscopy.[9-10](#_ENREF_24) The intense absorption bands at 1619–1667 cm–1 in FTIR spectra of **7**–**12** was assigned to *ν*(Ccarbene–N) of the NCN moiety. For **7**–**12**, the important 13C resonances of the C atoms in two carbene ligands are different and detected at δC 168 and 182 ppm. This evidences that two NCN groups in **7**–**12** are substantially structurally different; one of them (having the downfield resonance at δC 168 ppm and assigned to C7 carbon) being of the amidine type, whereas another one (having the downfield resonance at δC 182 ppm and assigned to C1 carbon) being of the diaminocarbene type. These δC values for diaminocarbene carbon C1 are downfield relatively to those (*δ*C 157–159) reported for the series of palladium complexes featuring chelated NHC, such as bis(imidazolylidene) palladium dichloride complexes,[7](#_ENREF_17) chelating but are some upfield of the *δ*C 197–201 range observed for the series of palladium complexes featuring chelating acyclic aminocarbene ligands, *i*.*e*. [PdCl{C(N=C(C6R2R3R4R5CON))=N(H)R1}(C=NR1)].[11](#_ENREF_27)

The thiocyanate anion NCS− enables several pathways to alter the properties of the metal centres due to its ambidentate nature, allowing the coordination via either S- or N-ends. To the best of our knowledge, only two examples thiocyanate diaminocarbene complexes, *viz.* nickel(II)-NHC with *N*-coordinated thiocyanate[12](#_ENREF_28) and gold(I)-NHC with S-coordinated thiocyanate[13](#_ENREF_29) have been reported. Thiocyanate species demonstrate the better donor abilities and increase dipole moment of complex molecules relative to halide analogues which may lead to the better catalytic activity of thiocyanate species in *i. e.* Kumada-Corriu coupling reaction.[12](#_ENREF_28) In addition, the more donor character of thiocyanate appears to be related to stabilisation of the HOMOs of the complexes and their red-shifted absorption in UV-vis spectrum.[14](#_ENREF_30)

The common method for the preparation of thiocyanate complexes from chloride substrates is metathetic reaction with NaNCS or KSCN in an aqueous or alcohol solution, occasionally aided by AgNO3 to facilitate the chloride subtraction.[15](#_ENREF_32) Metathetic reactions of **7**–**12** with three-fold excess of NH4CNS in acetone/CH2Cl2 at RT for 24 h afforded orange or yellow *bis*(*N*-coordinated thiocyanate) complexes **13**–**18** in good yields (**Scheme 1**, **Route B**). Owing to the poor solubility of complexes **13**–**18** in the most common solvents, all complexes were characterized in solution by means of HR-MS (ESI+) and in the solid state by FTIR, and solid-state 13C CP/MAS NMR. The structures of **16** and **18** were also elucidated by single-crystal XRD.

Complexes **13**–**18** gave satisfactory CHN data, which are consistent with the proposed formulae confirming the replacement of both chloride ligands with thiocyanate. The HRESI+-MS of **13**–**18** exhibit sets of peaks with the characteristic isotopic distribution due to [M + H]+, [M + Na]+ and/or [M – NCS]+ ions. IR spectroscopy was used to identify the coordination modes of thiocyanate in metal thiocyanate complexes.[16](#_ENREF_35) As a general rule, the value of ν(CN) stretch for the thiocyanate of *N*-bonded complexes lies near 2050 cm–1 (strong band) and that of S-bonded complexes is close to 2100 cm–1 (weaker band).[16c](#_ENREF_37) The IR spectra of **13**–**18** measured in KBr revealed two intense absorption bands in the range 2030–2090 cm–1 attributed to the ν(CN) stretch of the *N*-bonded thiocyanate. Additionally, FTIR spectra of **13**–**18** displayed a strong absorption overlapping bands at *ca.* 2200 cm–1 which are also present in spectra of starting **7**–**12** and are attributed to the ν(C≡N) of the isocyanide ligands.

*UV-Vis absorption properties.* All prepared complexes are yellow (**10**–**18**) or yellowish (**7**–**9**) solids, which makes them capable of absorbing light in the visible range. UV-vis absorption spectra of **7**–**12** were measured at ambient temperature in CH2Cl2 solution, while spectra of insoluble compounds **13**–**18** were measured in solid state. UV-vis data for **7**–**18** are summarised in **Table 1** and overlay of spectra are given in **Figures 2** and **3**.



**Figure 2.** UV-vis absorption spectra for **7**–**12** in СH2Cl2 at RT.

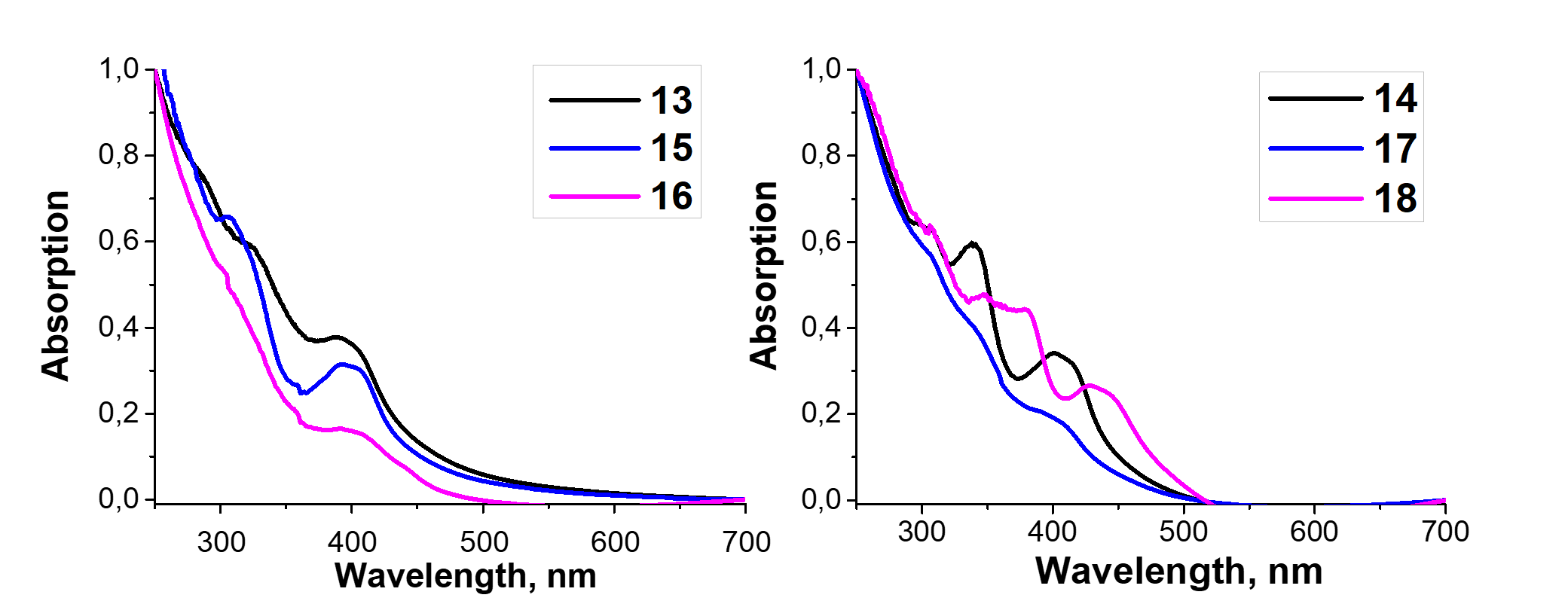
Similar to other palladium[17](#_ENREF_38) and platinum[17a](#_ENREF_38), [17d](#_ENREF_41), [18](#_ENREF_42)cyclometallated complexes, the UV-vis spectra of **7**–**12** contain strong absorption bands below 320 nm [ɛ = (1.15–3.59)×104 M–1cm–1] assigned to π–π\* ligand centred transitions in the xylyl and mesityl moieties (**Figure 2**).[19](#_ENREF_44) The wide intense absorption bands in the 320–450 nm range with characteristic molar extinction coefficients [ɛ = (0.60–1.13)×104 M–1cm–1] can be assigned to a mixed 1L'LCT (ligand-to-ligand charge transfer) and 1ILCT (intraligand charge transfer) transitions based on TD-DFT calculations (see section *TD-DFT calculations*). The energy of the 1L'LCT/1ILCT absorption band are affected by the change of the azaheterocyclic fragment.[20](#_ENREF_45) Complexes with pyridine ring **7**–**9**, **11** show blue-shifted 1L'LCT/1ILCT bands relative to their pyrazine counterparts **10** and **12** (e.g. 364–398 nm [ɛ = (0.60–0.83)×103 M–1cm–1] in **7**–**9**, **11** vs 402–414 nm [ɛ = (1.06–1.13)×103 M–1cm–1] in **10** and **12**).

**Table 1.** UV-Vis absorption data for **7**–**18**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Chloride complexes | | Thiocyanate complexes | |
| Complex | Absorption: λmax, nm (ε · 10−4, M−1cm−1) | | Complex | Absorption: λmax, nm (ε · 10−4, M−1cm−1) |
| in CH2Cl2 | solid state | solid state |
| **7** | 277sh (3.20), 364 (0.83) | 281sh, 417 | **13** | 285sh, 324, 389 |
| **8** | 303 (2.36), 318sh (1.35) 393 (0.64) | 310, 404 | **14** | 304, 339, 403 |
| **9** | 283sh (2.89), 378sh (0.60) | 293, 375 | **15** | 308, 394 |
| **10** | 281 (3.59), 402 (1.13) | 291sh, 407 | **16** | 310sh, 400 |
| **11** | 303 (2.53), 321sh (1.62), 398 (0.66) | 311, 427 | **17** | 305sh, 338sh, 395 |
| **12** | 311 (2.49), 338sh (1.15), 414 (1.06) | 308, 428 | **18** | 307sh, 379, 431 |

This could be explained by decrease of the LUMO energy in case of complexes **10** and **12** withpyrazine species due to the additional intercalation electron negative nitrogen atom in the azaheterocyclic fragment. Variation of the aryl fragment of the CNR or the corresponding daiminocarbene ligands induces no significant change in the positions of the 1L'LCT/1ILCT bands and only exerts minimal influence on the extinction coefficients (e.g. 364–393 nm [ɛ = (0.64–0.83)×103 M–1cm–1] in **7**, **8** vs 378–414 nm [ɛ = (0.60–1.13)×103 M–1cm–1] in **9**–**12**).

The UV-vis spectra of the **13**–**18** (KBr pellets) demonstrate similar absorption profiles to spectra of the **7**–**12** (**Figure 3**). Replacing the both chloride ligands with thiocyanate ligands leads to a significant increase in the HOMO energy and, consequently, the red shift of the long-wavelength bands (*ca*. 30 nm) in absorption spectra. These differences in optical absorption underline the significantly stronger electron donation from thiocyanate ligands compared to that of the chloride ligands.[14](#_ENREF_30), [21](#_ENREF_46)

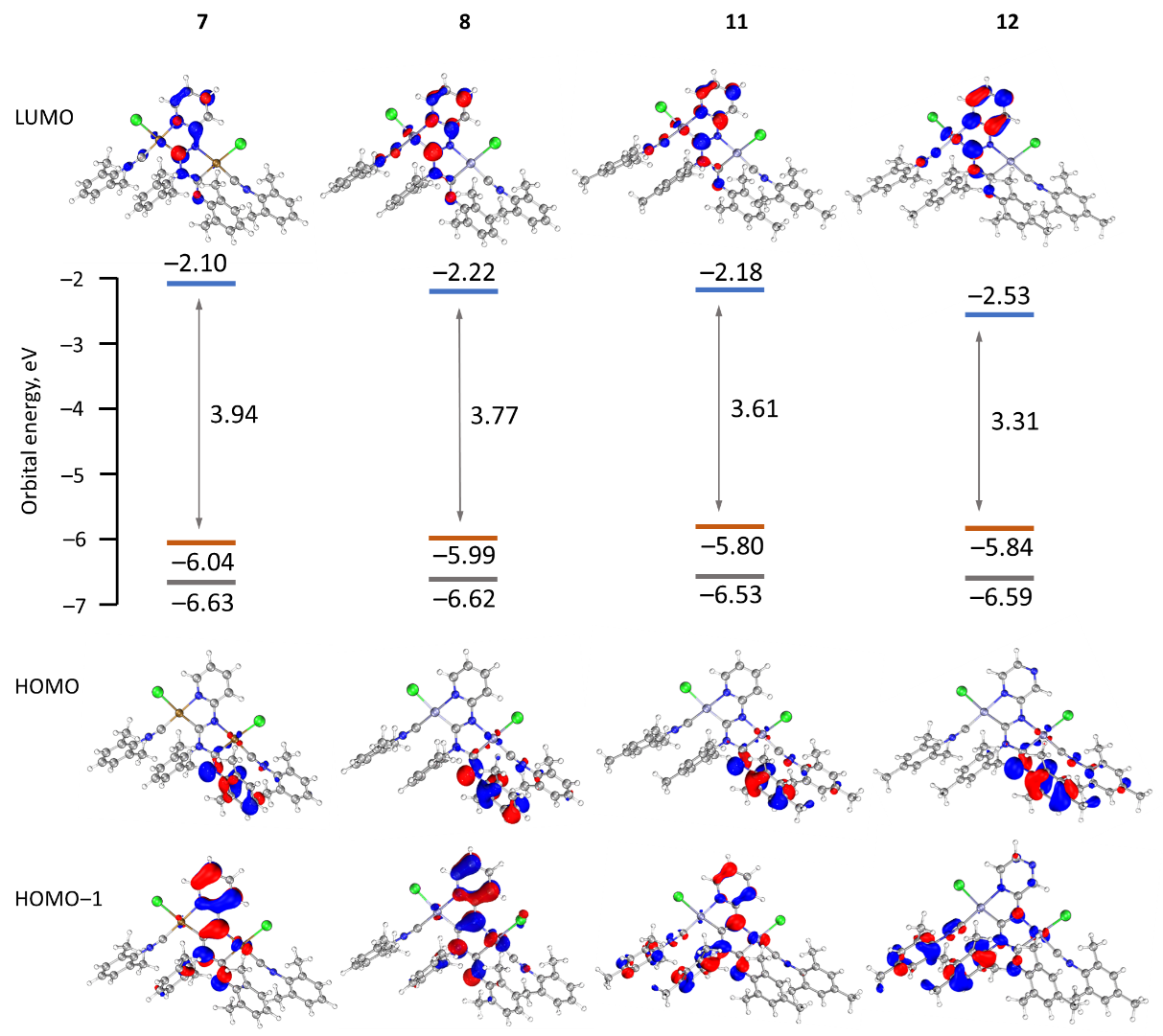


**Figure 3.** Normalized UV-Vis absorption spectra for **13**–**18** in solid state (KBr) at RT.

*Frontier molecular orbitals analysis.*To gain insight into the electronic structures and the optical properties of the obtained complexes time-dependent DFT calculations on **7**, **8**, **11**,and **12** were undertaken. The theoretically predicted structures are in good agreement with experimental X-ray structures (**Table S4** in SI). In general the computed bond lengths are close to the experimental ones which indicating a sufficient accuracy of the selected computational protocol.[22](#_ENREF_48) The main difference concludes in slightly elongation of coordination bonds (by 0.01–0.03 Å) and CN triple bonds (0.03–0.04 Å) in the optimized structures compared to experimental, due to relaxation of cyclic metal including systems.

**Figure 4** shows the shape and energy of the frontier molecular orbitals for **7**, **8**, **11** and **12**, while the FMO compositions are given in the **Table S6**. In all cases, high occupied molecular orbitals (HOMOs) are delocalized by the π molecular orbitals on the aryl ring connected with the exocyclic nitrogen atom of diaminocarbene species (contribution of aryls > 80%), while the contribution of the metal *d* orbitals is insignificant (<5%). The energy of the HOMO orbitals of **7**, **8**, **11** and **12** are similar, while the lowest unoccupied molecular orbitals (LUMOs) is localized over the entire diaminocarbene (22–34%) and azaheterocycle (38–54%) species. The large contribution (12–16%) from the metal *d* orbitals in LUMO may be related with the absence of luminescence for **7**–**12** at RT due to population of a metal-centred state.[23](#_ENREF_52)

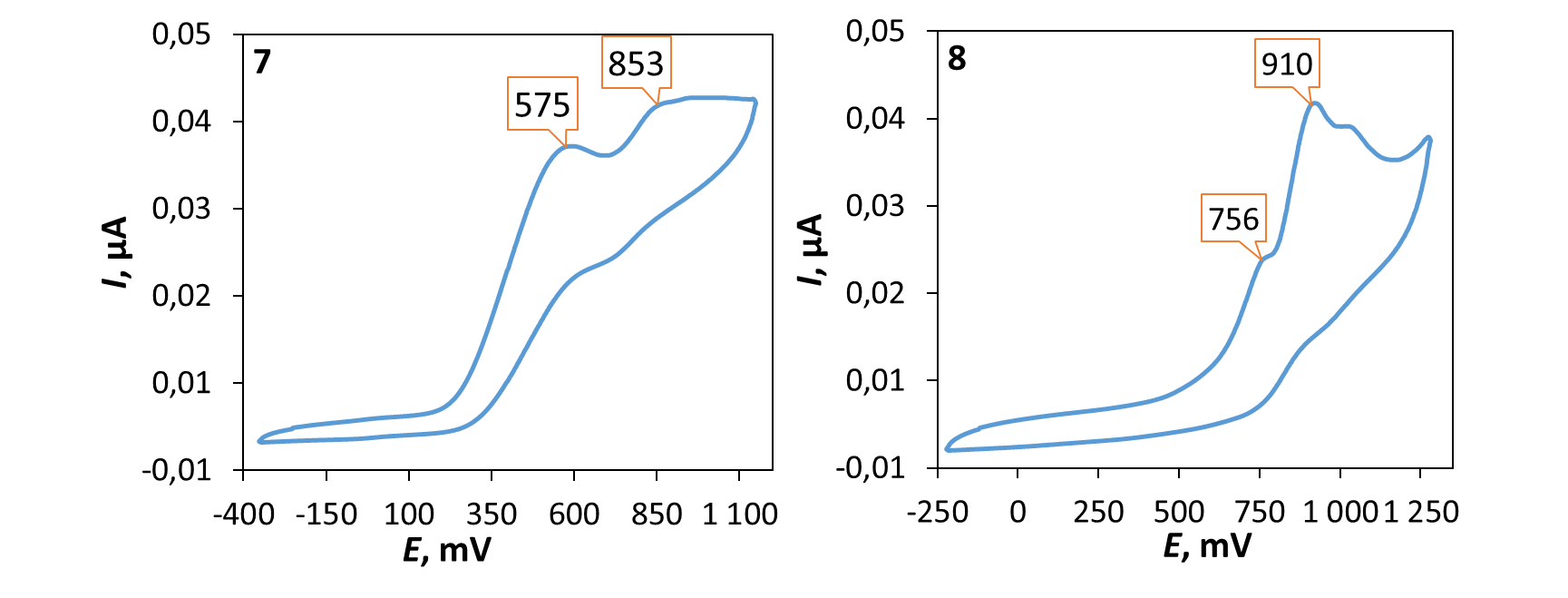
The HOMO–LUMO energy difference varies considerably between 3.94 eV (**7**) and 3.31 eV (**12**). The small HOMO–LUMO gap of **12** withpyrazine species comes from the low lying LUMO which is affected by the additional intercalation electron negative nitrogen atom in the azaheterocyclic fragment. There is clearly a correlation between the HOMO–LUMO energy difference and the red-shifted absorption bands determined experimentaly for **10** and **12** with pyrazine ring relative to their pyridine counterparts **7**–**9**, **11**.



**Figure 4**. Calculated molecular orbital energy HOMO–LUMO gaps and surface plots of the HOMO–1, HOMO and LUMO for **7**, **8**, **11** and **12**.

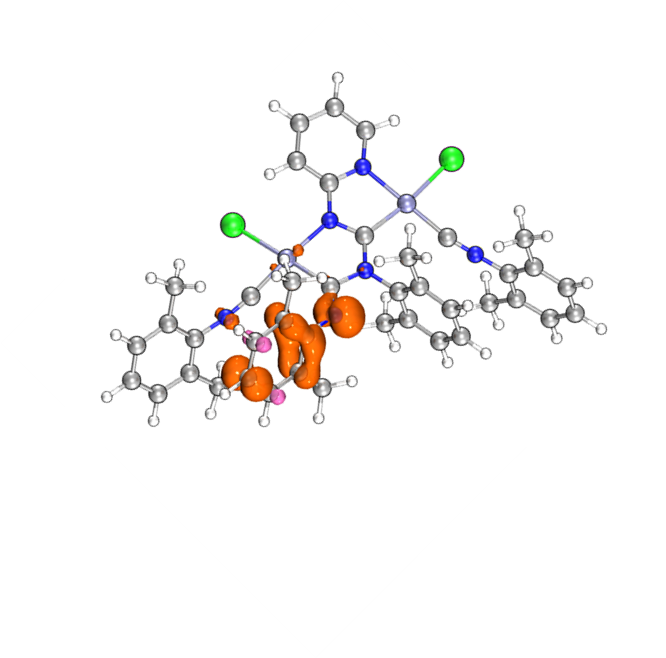
*TD-DFT calculations.* TD-DFT calculations were carried out to elucidate the nature of the transitions in the absorbance profile. The simulated based on TD-DFT calculations and the experimental UV-vis spectra of all complexes have a good agreement. Calculated absorption spectra for **7**, **8**, **11** and **12** reasonably reproduce the experimental spectral profiles (**Figure S7**). The absorption band in 320–450 nm range are resulted by combination of the most intense transfers appearing at *ca.* 340–360 nm (f *ca.* 0.123–0.156) and at *ca.* 393–410 nm (f *ca*. 0.031–0.038) associated correspondently with HOMO→LUMO (91–92 %) and HOMO-1→LUMO (91–94 %) transitions (**Table S5** in SI).

*Electrochemical studies.*The electrochemical properties of **7**–**12** were examined using cyclic voltammetry (CV) in dichloromethane solution (**Figure 5**). Palladium complexes **7**, **9** and **10** exhibit two irreversible oxidation waves in the ranges of 0.48–0.58 and 0.83–0.85 V, which corresponds multistep oxidation processes (Subsequent oxidation processes is probably assigned to the next step of the oxidation of the mono oxidized species[24](#_ENREF_53)). Platinum complexes **8**, **11** and **12** are oxidized at more positive potentials than their corresponding palladium counterparts and first intense irreversible oxidation peak was observed in the range of 0.72–0.77 V.



**Figure 5.** Cyclic voltammograms of **7** and **8** in СH2Cl2 at RT (potentials gives in mV *vs.* Fc+/Fc). Oxidation potentials (mV) of **9** 483, 833; **10** 718, 968; **11** 566, 850; **12** 740, 1028.

It is worth noting that, complexes with mesityl substituent **9**–**12** xylylsubstituents are oxidized easier than their corresponding analogues **7** and **8** with xylyl substituent. To interpret the electrochemical behaviour of the complexes, quantum-chemical calculations were performed for **7**, **8**, **11** and **12** and their mono oxidized forms at the level of the DFT theory. The plot of the spin density calculated for oxidized forms **7**, **8**, **11** and **12** (**Figure 6** and **S8**) demonstrate that the first oxidation process can be associated with the oxidation of the aryl fragment connecting to exocyclic nitrogen atom.



**Figure 6.** A plot of the spin density calculated for [**8**]+.

*X-Ray diffraction studies of chloride species.* Single crystals of **11**were obtained by the slow evaporation of CH2Cl2 solution.Crystals of **11** are yellow and possess low symmetry *P1* space group (**Figure 7**). In **11**, both metal centers acquire the distorted square-planar coordination environment. The CNR ligands are in *cis*-position to the C atoms of {C(NR)N(R)CN(NC4H3X)} (X = CH, N); the latter forms the dinuclear bicyclic framework.

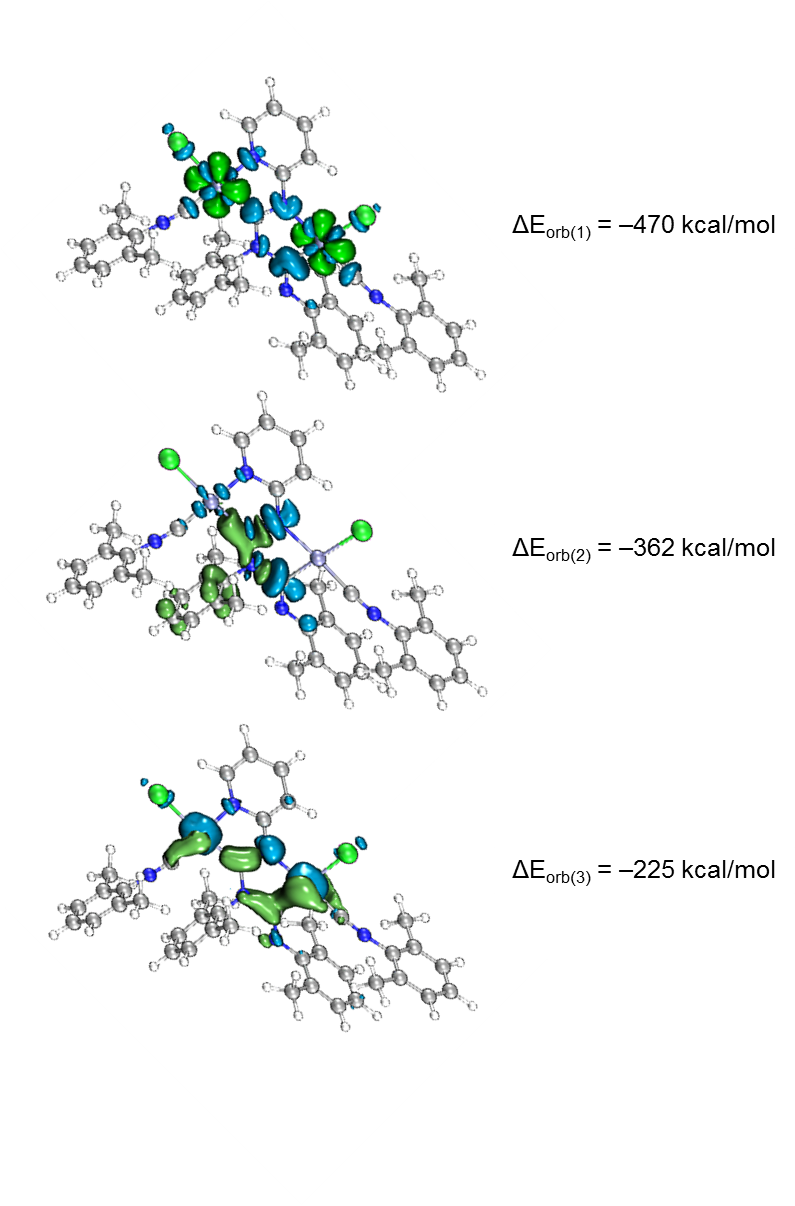
The bond lengths of the two coordinated CN groups are in the interval of 1.136(8)–1.146(8) Å, typical for the CN triple bonds in isocyanide PdII and PtII complexes.[3d](#_ENREF_9), [25](#_ENREF_54) The Pt–Ccarbene distances are slightly smaller than typical Pt–C bonds (1.995–2.023 Å)[5c](#_ENREF_15), [26](#_ENREF_60) reported for the relevant PtII–ADC complexes and are close to Pt–C distances in Pt-NHC complexes (1.970–1.991 Å).[27](#_ENREF_62) On the other side, the Pt–C bond lengths are sufficiently larger than those in Pt-NHCs, where NHC is included into an extended rigid π-system (1.906–1.970 Å)[28](#_ENREF_65) and in Pt-CAAC complexes (1.942–1.967 Å).[29](#_ENREF_66) The bond lengths in the first carbene moiety C1–N1 (1.350(7) Å) and C1–N3 (1.341(7) Å) are similar and are between single CN bond (e.g., 1.469(10) Å) in amines[30](#_ENREF_68) and double CN bond (e.g., 1.279(8) Å) in imines[30](#_ENREF_68) distances indicating a substantial delocalization of the electron density. In the second carbene the endocyclic C7–N3 bond of the metallacycle is typical single (1.450(7) Å), while the exocyclic C7–N4 is typical double (1.268(7) Å) indicating low degree of delocalization in these NCN carbene fragment. Structure of this carbene moiety is therefore closer to the amino(imino)carbene or diamonocarbene-like structures reported previously.[31](#_ENREF_69) All other bond lengths in **11** are normal, and their values agree with those reported for previously reported **7**,[10b](#_ENREF_26) **8**[9](#_ENREF_24) and otherrelated diaminocarbene and isocyanide species.[8c](#_ENREF_20), [10a](#_ENREF_25), [32](#_ENREF_71)



**Figure 7.** View of **11** with the atomic numbering schemes. Solvent molecule and hydrogen labels were omitted for simplicity. The crystal data, and selected bond lengths and angles are given in the **SI**, section **S1**.

*DFT analysis of ligand properties in chloride species* **7**–**12***.* To shed the light on the nature of the bonding in these compounds, the quantum theory of atoms in molecules (QTAIM),[33](#_ENREF_75) and Mayer bond order analysis,[34](#_ENREF_76) as well as the extended transition state method and the natural orbitals for chemical valence scheme (ETS-NOCV),[35](#_ENREF_77) were used.

Bader’s theory of atoms in molecules provides a unique way to analyse the electron density, *ρи*.[33](#_ENREF_75) The most important property to assign a bond is the presence of a bond critical point (BCP) which is a point of electron and energy densities along the bond path. It is quite interesting to compare the M1–C1 bonds, which involves the metalla-*N*-heterocyclic carbene C1 atoms, with the almost equivalent M2–C7 bonds, which engage the only formal acyclic diaminocarbene C7 atom. BCP for both pairs M–Ccarbene bonds show a moderate value of electron density (ρb 0.070–0.091 e) and a positive value of the laplacian. Since a covalent bond in transition metal complexes is characterized by small value of ρb and small and positive values of ∇2ρ(**r**) due to the diffuse character of the electron distribution,[36](#_ENREF_78) the best descriptor to ascertain the type of interaction is the local energy electronic density H(**r**).[37](#_ENREF_79) All of these M–Ccarbene have negative values of H(**r**) at the BCPs. The listed parameters indicate a significant degree of covalency. Another similar criterion was proposed by Espinosa[38](#_ENREF_80) on the basis of the ratio |V(**r**)|/G(**r**) for closed shell interaction, |V(**r**)|/G(**r**) < 1 and for shared shell interaction, |V(**r**)|/G(**r**) > 2. The interaction is taken as an intermediate type if the ratio falls between these two limits.[39](#_ENREF_81) The BCPs of M–Ccarbene bonds have a |V(**r**)|/G(**r**) value 1.47–1.70 and it is taken as evidence for partial covalent nature. At the same time, the values for the ρb bond and |V(**r**)|/G(**r**) for all M–Ccarbene bonds are higher than for the M–Cl, M–CCNR and M–N bonds, all this indicates that the M–Ccarbene is more covalent. Values for the local topological properties at the BCP of these two type bonds M–Ccarbene are close enough (**Table S7**), and are comparable to those obtained from theoretical electronic energy density for the M–Ccarbene bonds of the other diaminocarbene complexes.[37](#_ENREF_79), [40](#_ENREF_82) The calculated Mayer bond orders (MBOs) of the M–Ccarbene bonds are similar for both M–Ccarbene bonds of each complex (0.5512 and 0.5491 for **7** and 0.9907 and 1.0678 for **8**) and are larger than the MBOs of the M–CCNR bonds (0.2675 and 0.2753 for **7** and 0.9029 and 0.9058 for **8**). The values of the topological parameters at BCPs of the Ccarbene–N bonds are all typical for covalent bonds between nonmetal atoms with some degree of delocalization.[41](#_ENREF_84) The MBOs for Ccarbene–N bonds in the N1–C1–N3 moiety are higher than 1 and very similar 1.2570–1.3101), which support the previous proposal that the unsaturation of the C atom of a diaminocarbene is alleviated by π-donation of electron density from the filled *p*π orbitals of the N atoms to the empty *p*π orbital of the carbene carbon.[42](#_ENREF_85) The MBOs for Ccarbene–N bonds in the second N3–C7–N4 moiety are different (C7–N4 0.9715–0.9989 for C7–N3 and 1.6346–1.6752 for C7–N4) as evidenced by XRD data.



**Figure 8.** Shape of the deformation densities Δρ(1)–(3) that correspond to ΔEorb(1)–(3). The direction of the charge flow of the deformation densities is blue (loss of electron density) → green (gain of electron density).

The coordination bonding in binuclear diaminocarbene complexes was understood by employing an extended transition state (ETS)[43](#_ENREF_86) together with the natural orbitals for chemical valence (NOCV)[35](#_ENREF_77), [44](#_ENREF_87) method. This method can be employed to quantify the bonding interactions in the complexes between the metal center and the surrounding ligands in a chemically intuitive manner. The ETS-NOCV scheme in this manner, gives quantitative (ΔEorb) data about the strength of orbital interactions in chemical bonds.[45](#_ENREF_88)

The ETS-NOCV calculations for **7** and **8** were carried out using PBE0/ZORA-def2-TZVP geometries with the ADF program package.[46](#_ENREF_91) The fragmentation pattern shown in the **Figure S9**, where the C1–N1, C7–N3 and all M–L bonds were fragmented homolytically in the frozen geometry of the complex molecule for this purpose. The major contribution to the total orbital interaction comes from the three orbital term ΔEorb(1)−ΔEorb(3) (90%), indicating a strong covalent bonding (**Figure 8**). The strongest pairwise orbital interaction (ΔEorb(1), –470 kcal/mol) comes from the ligand to metal σ dative interactions, which is provided by 41% of a total ΔEOrb. Then, the second term (ΔEorb(2), –362 kcal/mol) is associated with the coupling of *p* orbitals in diaminocarbene moieties. The last ΔEorb(3) (–225 kcal/mol) is due to the π-back-donation from metal centers to carbene ligands and comprises only 20% of the total ΔEOrb energy.

*X-Ray diffraction studies of thiocyanate derivatives.* Single crystals for **16** and **18** were formed in situ in reaction mixture (**Figure 9** and **S1**).The **16** and **18** form pale orange isomorphous through the Pd/Pt atom exchanges in the molecular crystals.[5c](#_ENREF_15), [25d](#_ENREF_57), [25e](#_ENREF_58) Both thiocyanate ligands in **16** and **18** are bound to the metal centers by the N atom, which is in full agreement with the data of IR spectroscopy. The M1−N8 and M2−N9 distances were within the range of typical values for Pd−N[16b](#_ENREF_36), [47](#_ENREF_92) and Pt−N[16a](#_ENREF_35), [47](#_ENREF_92) coordination bonds reported for relevant *N*-ligated thiocyanates. Both M1–N8–C45 and M2–N9–C46 angles due to the thiocyanate binding are considerably different: one thiocyanate in **16** and **18** is coordinated to the metal atom in a somewhat linear fashion (M1–N8–C45 169.1(12)–178.5(3)°), while the other adopts a bent configuration with the corresponding angle (M2–N9–C46) in the range of 147.0(4)–159.1(4)°. Subsequent theoretical studies (section **S3.1**) and analysis of the CCDC (section **S4**) showed that the differences are associated with the effect of crystal packing.



**Figure 9.** View of **18** with the atomic numbering schemes. Solvent molecule and hydrogen labels were omitted for simplicity. Crystal structure of **16** is given in the Section **S1** in SI alongside selected bond lengths and angles.



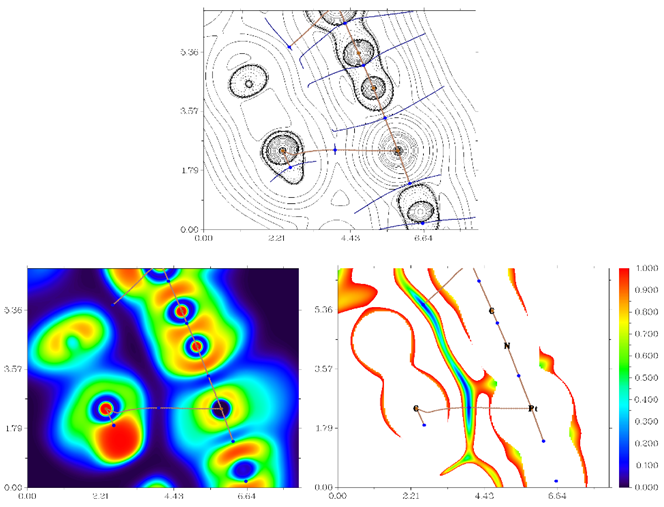
**Figure 10.** Views of dimers of **18**. Dotted lines indicate the Pt1···C5 and S1···C2 contacts. Thermal ellipsoids are shown with 50% probability.

The polycyclic organometallic skeletons of thiocyanate complexes **16** and **18** are almost identical to chloride species (**Figures S2** and **S3**). Thiocyanate is a type of ligand that can be explored as a potential crystal-driving supramolecular synthon generator in biochemistry[48](#_ENREF_93) and material[49](#_ENREF_94) chemistry. The versatile of interacting centers in NCS mainly associated with sulfur and the nitrogen atoms allows it to be involved in hydrogen[50](#_ENREF_96), halogen[51](#_ENREF_97) bonding and π[52](#_ENREF_98) interactions. The Hirshfeld surface analysis for the XRD structures of **16** and **18** indicates the domination of the contacts that involve hydrogen atoms, specifically, H-H, C-H, S-H, and N-H (section **S5** in SI). The H-H contacts provide the largest contributions to the molecular Hirshfeld surfaces, because the fraction of these atoms is maximal and the Hirshfeld surfaces analysis does not disclose the attractive or repulsive nature of these contacts. Apart from the contacts involving H atoms, **16** and **18** exhibit two pairs M1···C5 and S1···C2 short intermolecular contacts forming supramolecular dimer (**Figure 10**).

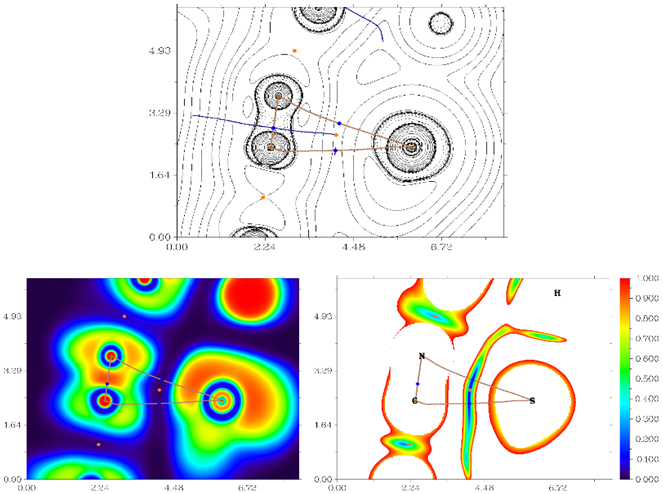
The distances between the M1···C5 and S1···C2 interacting atoms are slightly larger than the sum of Bondi’s vdW radii (102–109%),[53](#_ENREF_100) but are comparable with the sum of Alvarez's (86–89% for M1···C5 and 99% for S1···C2)[54](#_ENREF_101) vdW radii. The latter suggests that the observed noncovalent interactions can exist. To confirm or disprove the hypothesis on the existence of noncovalent interactions between MII-center and C5 atom and between S-center of thiocyanato and C2 atom, a further computational study was carried out.

QTAIM analysis[33](#_ENREF_75) for model supramolecular associates (**16**)2and (**18**)2shows appropriate bond critical points (3, –1) (BCPs) for discussed contacts (**Figures 11**, **12**, **S11** and **S12**, **Table S11**). In the case of (**18**)2, the formally bifurcated *μ*2-S···[PtII,C] contact (**Figure 12**), while in the case of (**16**)2 a S1···Pd2 contact (**Figure S12**), are formed. The low magnitudes of electron density (0.005–0.008 a.u.), the positive values of the Laplacian of electron density (0.015–0.021 a.u.), and the positive energy density close to zero (0.001 a.u.) in the BCPs, as well as the balance between the Lagrangian kinetic energy G(**r**) and potential energy density V(**r**) at the BCPs (ratio |G(**r**)|/V(**r**) > 1) reveal that these contacts are purely noncovalent.[38](#_ENREF_80)

The Electron Localization Function[55](#_ENREF_102) (ELF) projections for the M1···C5 contacts were plotted along with CPs and bond paths (**Figures 11** and **S11**). ELF projections show increased ELF areas around PdII and PtII atoms near the bond paths connecting metal centers and azaheterocycle species that can be interpreted as filled *dz2* orbitals. The M···C bond paths that connect metal centers and C5 atom from azaheterocycle species go through these *dz2* and π\* orbitals. On the ELF projections plotted for the S1···C2 contacts sulfur lone pair is clearly visible near the bond paths; also, the electron density depletion regions associated with the π-holes are easily identified in the ELF basins. Reduced density gradient (RDG) analyses confirm the fact that all discussed contacts are clearly attractive.



**Figure 11**. Contour line diagram of the Laplacian of electron density distribution ∇2ρ(**r**), bond paths, and selected zero-flux surfaces (left panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, right panel) analyses for Pt1···C5 intermolecular contacts in (**18**)2. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps are presented in a.u.



**Figure 12**. Contour line diagram of the Laplacian of electron density distribution ∇2ρ(**r**), bond paths, and selected zero-flux surfaces (left panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, right panel) analyses for *μ*2-S···[PtII,C] intermolecular contact in (**18**)2. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps are presented in a.u.

The comparison of the crystal structures of the thiocyanate derivatives with those of the chloride species (**Figures S4**, **S5**) revealed significant changes occurred on the anion exchange. If the crystal structure of chloride species is predominantly held by C-H···X (X = Cl, N) hydrogen bonds with no involvement of the MII-center, the change from Cl to NCS as the anionic ligand favors the formation of M···C interactions.

Conclusions

In the course of this study, a series of new binuclear palladium(II) and platinum(II) metalla-*N*-heterocyclic carbene (MNHC) type complexes were prepared via metal-mediated coupling between *cis*-[MCl2(CNR)2] (R = Xyl, Mes) and 2-aminopyridine or 2-aminopyrazine nucleophiles. Characterization of **7**–**12** thus obtained by HRESI+-MS, IR, 1D 1H, 13C{1H}[,](#_ENREF_1) 195Pt{1H} NMR and 2D HSQC(1H, 13C), HMBC(1H, 13C) spectroscopy as well as by single-crystal XRD revealed the difference in diaminocarbene ligands where the both Ccarbene–N bonds in MNHC moiety are in agreement with data for classical diaminocarbenes, while the second NCN fragment is ADC-like carbene due to the rather double and single C–N bonds character. QTAIM reveals that the M–Ccarbene bonds are characterized by low to moderate values of electron density ρb, positive values of the laplacian ∇2ρ and negative values of local electronic energy densities, H(**r**)-signifying that these M–Ccarbene bonds have significant degree of covalency. The UV-vis absorption spectrum of MNHC species characterized by the wide intense absorption in the 320–414 nm range assigned to 1L'LCT/1ILCT transactions which is important in visible light photocatalysis. The absorption characteristics are governed by the nature of the azaheterocycle fragment and complexes with pyrazine pyridine ring (**10** and **12**) show 20–40 nm red-shifted bands relative to their pyrazine counterparts (**7**–**9** and **11**). In contrary, the parent CNR fragments have more effect on the electrochemical properties of the MNHC compounds and species with mesityl substituents (**9**–**12**) are oxidized at lower potential than their corresponding xylyl analogues (**7** and **8**).

The first palladium(II) and platinum(II) diaminocarbene thiocyanate derivatives **13**–**18** were synthesized from corresponding starting chlorides **7**–**12** by metathetic reaction with NH4NCS. In these complexes, the both thiocyanate ligands are *N*-bound as confirmed by IR spectroscopy and single-crystal XRD. Replacing the both chloride ligands with thiocyanate ligands leads to a significant increase in the HOMO energy and, consequently, the red shift of the long-wavelength bands (*ca*. 30 nm) in absorption spectra. Isomorphous crystal structures of the thiocyanate derivatives **16** and **18** exhibit two symmetrical pairs M1···C5 and S1···C2 short intermolecular contacts between electron reach MII-center and thiocyanate ligand in one side, and electron poor π system of azaheterocycle ring in another side; observed noncovalent interactions provide supramolecular dimer.

Together, the experimental and computational data provide an insight into the flexible character of MNHC species. Our future studies are focused on exploring the photocatalytic properties of the [M]-MNHCs derived from reactions of metal-activated RNCs and various 2-aminoazaheterocycles to develop useful catalytic systems and to establish catalyst structure−activity relationships in various visible light activated systems.

Experimental

**Materials and Instrumentation.** Solvents, organic reagents and NH4SCN were obtained from commercial sources and used as received. Isocyanide complexes *cis-*[MCl2(CNR)2] (M = Pd, R = Xyl **1**,[31a](#_ENREF_69) Mes **2**;[10b](#_ENREF_26) M = Pt, R = Xyl **3**,[56](#_ENREF_105) Mes **4**[57](#_ENREF_106)) were prepared as reported earlier. C, H, and N elemental analyses were carried out on a Euro EA 3028 HT CHNSO analyzer. Mass-spectra were acquired on Bruker micrOTOF spectrometer equipped with ESI source; a CH2Cl2/MeOH mixture was used as the solvent. The instrument was operated at positive ion mode using *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI+) and the capillary exit at +(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow was 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra were recorded on Bruker Tensor 27 FTIR instrument (4000–2400 cm–1, resolution 2 cm–1) in KBr pellets. The UV/vis absorption spectra in CH2Cl2 solution were recorded on a Shimadzu UV-2500 spectrophotometer in a quartz cuvette with l = 1.0 mm with the complex’s concentration 0.03 mM. A Shimadzu UV-1800 spectrophotometer was used to measure the UV/vis absorbance of solid-state complexes. The 13C CP/MAS NMR spectra were acquired using a double-resonance 4 mm MAS Bruker probe at a resonance frequency of 101 MHz under 14 kHz MAS. The CP contact time in all experiments was 3.5 μs with a delay between acquisitions of 1 sec and number of scans was collected 20000. Suitable single crystals were selected and mounted on a MiTeGen tip via crystallographic oil. Data were collected using a Rigaku XtaLAB Synergy, Single source at home/near, HyPix diffractometer equipped (monochromated Cu*Kα* radiation, λ = 1.54184 Å) at 100(0) K. In each case, the structure was solved with a ShelXT[58](#_ENREF_107) structure solution program using Intrinsic Phasing and refined with a ShelXL[58](#_ENREF_107) refinement package incorporated in the OLEX2 program package[59](#_ENREF_108) using Least Squares minimization. Empirical absorption correction was applied in CrysAlisPro[60](#_ENREF_109) program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The CVs were measured using an Autolab PGSTAT302N voltammetric analyzer at a scan rate of 100 mV s–1. A glassy carbon and a platinum wire were used as the working and counter electrodes, respectively. The sample solutions (*ca.* 5 mM) in 0.1 M [*n*Bu4N](BF4)–CH2Cl2. Ag/AgNO3 (0.01 M AgNO3 in MeCN) was used for the reference electrode and the potential values were corrected against Fc+/Fc couple (E1/2 = 0.52 V vs. Ag/AgNO3 in CH2Cl2).

**Synthetic work.** *General procedure for the synthesis of* ***7****–****12****.*A mixture of solid [MCl2(CNR)2] (**1**–**4**, 0.10 mmol) and aminoazaheterocycles **5**, **6** (0.20 mmol) was dissolved in CH2Cl2 (5 mL) and left to stand at RT for 24 h. During the reaction time, the mixture of turned from pale yellow to lemon yellow. After 24 h, the reaction mixture was filtered to remove a precipitated **5·**HCl or **6·**HCl and then was slow evaporated in air at RT to give yellow crystals of **7**–**12**. The solids of **7**–**12** were separated by decantation and washed with three 2 mL portions of Et2O and then dried in airat RT.

**9.** Yellow solid(37 mg, yield 78%). Anal. Calcd. For C45H48N6Cl2Pd2: C, 56.5; H, 5.1; N, 8.8; found: C, 56.7; H, 5.4; N, 9.0. [М – Cl]+ calcd for C45H48N6ClPd2+ 921.1703, found 921.1706. IR (KBr, selected bands, cm–1): ν(C–H) 2920 (s), 2854 (s); ν(C≡N) 2189 (s); ν(Ccarbene–N) 1629 (s); δ(C–H from Мes) 855 (s). 1H NMR (CDCl3, 400.13 MHz, δ): 9.10 (d, 3*J*H,H = 8.5 Hz, 1H, H3), 9.06 – 8.99 (m, 1H, H5), 7.84 (ddd, 3*J*H,H = 8.8 Hz, 3*J*H,H = 7.4, 4*J*H,H = 1.7 Hz, 1H, H4), 7.03 – 6.94 (m, 1H, H6), 6.91 (s, 2H, *m*-H from Мes), 6.82 (s, 2H, *m*-H from Мes), 6.68 (s, 2H, *m*-H from Мes), 6.46 (s, 2H, *m*-H from Мes), 2.41 (s, 6H, 2Мe), 2.31 (s, 3H, Мe), 2.26 (s, 15H, 3Мe), 2.23 (s, 6H, 2Мe), 2.02 (s, 6H, 2Мe), 1.47 (s, 3H, Мe), 1.46 (s, 3H, Мe). 13C{1H} NMR (101 MHz, CDCl3, δ): 195.0 (Ccarbene–N), 167.0 (Ccarbene–N), 162.8 (C=N), 147.7 (*p*-C from Мes), 146.7, 141.5 (C3, C4), 140.7 (*ipso*-C from Мes), 140.0, 139.8, 138.9 (*p*-C from Мes), 136.2, 133.9, 133.9 (*o*-C from Мes), 133.7 (*p*-C from Мes), 128.5, 128.3, 128.1, 127.2 (*m*-C from Мes), 124.9, 124.2 (*ipso*-C from Мes), 118.3, 117.2 (C5, C6), 21.2, 21.1, 20.1, 20.0 (Мe’s), 19.5, 19.3 (2Мe’s), 18.4 (4Мe).

**10.** Yellow solid(42 mg, yield 88%). Anal. Calcd. For C44H47N7Cl2Pd2: C, 55.2; H, 5.0; N, 10.2; found: C, 54.8; H, 5.0; N, 10.6. [M + H]+ calcd for C44H48N7Cl2Pd2+ 958.1417, found 958.1412. IR (KBr, selected bands, cm–1): ν(C–H) 2916 (s), 2853 (s); ν(C≡N) 2199 (s), 2189 (s); ν(Ccarbene–N) 1632 (s); δ(C–H из Мes) 854 (s). 1H NMR (CDCl3, 400.13 MHz, δ): 10.37 (d, 4*J*H,H = 0.7 Hz, 1H, H3), 8.89 (dd, 3*J*H,H = 3.1 Hz, 4*J*H,H = 1.0 Hz, 1H, H5), 8.32 (d, 3*J*H,H = 3.3 Гц, 1H, H6), 6.93 (s, 2H, *m*-H from Mes), 6.83 (s, 2H, *m*-H from Mes), 6.69 (s, 2H, *m*-H from Mes), 6.48 (s, 2H, *m*-H from Mes), 2.40 (s, 6H, 2Me), 2.32 (s, 3H, Me), 2.26 (s, 3H, Me), 2.02 (с, 6H, 2Me), 2.26 (с, 3H, Me), 2.02 (s, 6H, 2Me), 1.47 (s, 6H, 2Me). 13C{1H} NMR (101 MHz, CDCl3, δ): 196.8 (Ccarbene–N), 163.2 (*ipso*-C from Mes), 161.8 (Ccarbene–N), 147.6 (*p*-C from Mes), 142.2 (C3), 140.6 (*p*-C from Mes), 140.2 (*p*-C from Mes), 139.1 (*ipso*-C from Mes), 137.9 (C5), 137.6 (C6), 135.9 (*o*-C from Mes), 134.0 (*o*-C from Mes), 133.9 (*ipso*-C from Mes), 133.9 (*o*-C from Mes), 128.6, 128.3, 128.2 (*m*-C from Mes), 127.0 (*o*-C from Mes), 124.7 and 123.9 (C≡N), 21.2, 21.1, 20.1, 20.0, 19.5 (Me’s), 19.2 (2Me’s), 18.4 (4Me’s).

**11.** Yellow solid(47 mg, yield 83%). Anal. Calcd. For C45H48N6Cl2Pt2: C, 47.7; H, 4.3; N, 7.4; found: C, 47.2; H, 4.3; N, 7.6. [M + H]+ calcd for C45H49Cl2N6Pt2+ 1134.2688, found 1134.2654. IR (KBr, selected bands, cm–1): ν(C–H) 2915 (s); ν(C≡N) 2194 (s); ν(Ccarbene–N) 1667 (s), 1619 (s); δ(C–H from Mes) 771 (s). 1H NMR (CDCl3, 400.13 MHz, δ): 9.36 – 9.07 (m, 2H, H5 + H3), 8.02 – 7.73 (m, 1H, H4), 7.05 (t, 3*J*H,H = 6.6 Hz, 1H, H6), 6.92 (s, 2H, *m*-H from Mes), 6.82 (s, 2H, *m*-H from Mes), 6.68 (s, 2H, *m*-H from Mes), 6.42 (s, 2H, *m*-H from Mes), 2.40 (s, 6H, 2Me), 2.32 (s, 3H, Me), 2.27 (s, 15H, 3Me), 2.25 (s, 6H, 2Me), 2.04 (s, 6H, 2Me), 1.45 (s, 3H, Me), 1.40 (s, 3H, Me). 13C{1H} NMR (101 MHz, CDCl3, δ): 183.6 (Ccarbene–N), 168.3 (Ccarbene–N), 153.0 (C=N), 148.3 (*p*-C from Mes), 145.1, 141.7 (C3, C4), 140.1, (*ipso*-C from Mes), 139.9, 139.6, 138.6 (*p*-C from Mes), 136.2, 134.0, 133.9 (*o*-C from Mes), 133.1 (*p*-C from Mes), 128.5, 128.2, 128.1, 126.7 (*m*-C from Mes), 125.2, 124.6 (*ipso*-C from Mes), 117.7, 116.9 (C5, C6), 21.2, 21.1, 20.1, 19.9 (Me’s), 19.5, 19.0 (2Me’s), 18.4 (4Me’s). 195Pt{1H} NMR (CDCl3, 86.02 MHz, δ): -3756, -3796.

**12.** Yellow solid(53 mg, yield 94%). Anal. Calcd. For C44H47N7Cl2Pt2: C, 46.6; H, 4.2; N, 8.6; found: C, 44.8; H, 4.4; N, 8.4. [M + H]+ calcd for C44H48N7Cl2Pt2+ 1135.2640, found 1135.2664. IR (KBr, selected bands, cm–1): ν(C–H) 2915 (s); ν(C≡N) 2208 (s), 2190 (s); ν(Ccarbene–N) 1634 (s); δ(C–H from aryls) 835 (s). 1H NMR (CDCl3, 400.13 MHz, δ): 10.50 (s, 1H, H3), 9.10 (d, 3*J*H,H = 3.0 Hz, 1H, H6), 8.38 (d, 3*J*H,H = 3.4 Hz, 1H, H5), 6.94 (s, 2H, *m*-H from Mes), 6.83 (s, 2H, *m*-H from Mes), 6.70 (s, 2H, *m*-H from Mes), 6.44 (s, 2H, *m*-H from Mes), 2.39 (s, 6H, 2Me), 2.33 (s, 3H, Me), 2.28 (s, 3H, Me), 2.27 (s, 6H, 2Me), 2.25 (s, 6H, 2Me), 2.04 (s, 6H, 2Me), 1.47 (s, 3H, Me), 1.41 (s, 3H, Me). 13C{1H} NMR (101 MHz, CDCl3, δ): 185.05 (Ccarbene–N), 162.89 (*ipso*-C from Mes), 153.62 (C2), 148.11 (*p*-C from Mes), 141.98 (C3), 141.80 (*p*-C from Mes), 140.20 (*p*-C from Mes), 139.93 (*ipso*-C from Mes), 139.88 (C3), 138.73 (*p*-C from Mes), 137.06 (C5), 135.97 (*o*-C from Mes), 135.84 (*o*-C from Mes), 134.34 (C6), 134.00 (*o*-C from Mes), 133.30 (*ipso*-C from Mes), 132.64 (*ipso*-C from Mes), 129.08 (*o*-C from Mes), 128.58, 128.57, 128.26, 128.09 (*m*-C from Mes), 126.55 (*o*-C from Mes), 125.05 and 124.30 (C≡N), 21.19 (Me’s), 21.07 (Me’s), 20.06 (Me’s), 19.90 (Me’s), 19.42 (2Me’s), 18.97 (2Me’s), 18.32 (4Me’s). 195Pt{1H} NMR (CDCl3, 86.02 MHz, δ): ‒3718, ‒3803.

*General procedure for the synthesis of* ***13****–****18****.*The mixture of **7**–**12** (0.05 mmol) with three-fold excess of NH4CNS (0.15 mmol) was suspended in acetone/CH2Cl2 mixture (v/v 3:1, 2 mL) at RT. The reaction mixture was stirred overnights to give yellow solution over the yellow or orange precipitate. These precipitate of **13**–**18** was separated by centrifugation, washed with two 2 mL portions of H2O and dried in air at RT.

**13.** Yellow solid(35 mg, yield 74%). Anal. Calcd. For C43H40N8S2Pd2: C, 54.6; H, 4.3; N, 11.9; S, 6.8, found C, 54.3; H, 4.8; N, 11.5; S, 6,6. [M + Na]+ calcd for C43H40N8S2Pd2Na+ 969.0784, found 969.0796. IR (KBr, selected bands, cm–1): ν(C≡N) 2204 (s), ν(NCthiocyanate) 2064, 2087 (s); ν(Ccarbene–N) 1605, 1634 (s); δ(C–H from aryls) 778 (s). 13C CP MAS NMR: 136.75, 136.42, 134.39, 133.46, 132.51, 131.36, 130.76, 129.55, 128.80, 127.96, 127.16, 125.82 (C and CH from aryls), 118.49 and 117.77 (C≡N), 21.42, 20.78, 19.03, 18.30 (Me’s).

**14.** Yellow solid(42 mg, yield 75%). Anal. Calcd. For C43H40N8S2Pt2: C, 46.0; H, 3.6; N, 10.0; S, 5.7, found C, 45.7; H, 3.3; N, 9.8; S, 5,6. [M – NCS]+ calcd for C42H40N7SPt2+ 1063.2363, found 1064.2355. IR (KBr, selected bands, cm–1): ν(C≡N) 2202 (s), ν(NCthiocyanate) 2072, 2094 (s); ν(Ccarbene–N) 1611, 1627 (s); δ(C–H from aryls) 777 (s). 13C CP MAS NMR: 166.7, 151.0, 145.1, 144.5, 136.7, 133.7, 130.7, 128.7, 127.9, 126.8, 126.2 (C and CH from aryls), 118.4 and 117.0 (C≡N), 21.5, 20.9, 20.5, 19.0, 18.6, 18.4, 17.8 (Me’s).

**15.** Yellow solid(34 mg, yield 68%). Anal. Calcd. For C47H48N8S2Pd2: C, 56.3; H, 4.8; N, 11.2; S, 6.4, found C, 55.8; H, 4.3; N, 10.8; S, 6,6. [M – NCS]+ calcd for C46H48N7SPd2+ 944.1766, found 944.1744. IR (KBr, selected bands, cm–1): ν(C≡N) 2187 (s), ν(NCthiocyanate) 2071, 2100 (s); ν(Ccarbene–N) 1619 (s); δ(C–H from aryls) 763 (s). 13C CP MAS NMR: 166.2, 140.3, 136.1, 134.8, 129.3, 127.0 (C and CH from aryls), 118.5 and 115.6 (C≡N), 20.0, 19.0 (Me’s).

**16.** Yellow solid(36 mg, yield 71%). Anal. Calcd. For C46H47N9S2Pd2: C, 55.1; H, 4.7; N, 12.6; S, 6.4, found C, 54.8; H, 4.6; N, 12.8; S, 6,4. [M – NCS]+ calcd for C46H48N7SPd2+ 945.1718, found 945.1716. IR (KBr, selected bands, cm–1): ν(C≡N) 2193 (s); ν(NCthiocyanate) 2057; ν(Ccarbene–N) 1625 (s); δ(C–H from aryls) 855 (s). 13C CP MAS NMR: 140.1, 137.9, 135.5, 135.1, 134.2, 133.7, 132.7, 131.5, 128.8 (C and CH from aryls), 19.8, 19.3, 19.1 (Me’s).

**17.** Yellow solid(54 mg, yield 77%). Anal. Calcd. For C47H48N8S2Pt2: C, 48.0; H, 4.0; N, 9.5; S, 5.4, found C, 47.6; H, 3.7; N, 9.5; S, 5,6. [M + H]+ calcd for C47H49N8S2Pt2+ 1180.2814, found 1180.2850. IR (KBr, selected bands, cm–1): ν(C≡N) 2205 (s), ν(NCthiocyanate) 2030, 2062 (s); ν(Ccarbene–N) 1608 (s); δ(C–H from aryls) 854 (s). 13C CP MAS NMR: 196.81 and 190.60 (Ccarbene–N), 160.66, 154.03, 150.48, 141.46, 138.79, 135.41, 133.29, 130.58, 129.43, 127.34, 126.07, 124.60 (C and CH from aryls), 116.12 and 114.59 (C≡N), 20.81, 20.04, 18.11, 16.06 (Me’s).

**18.** Yellow solid(47 mg, yield 80%). Anal. Calcd. For C46H48N9S2Pt2: C, 46.8; H, 4.0; N, 10.7; S, 5.4, found C, 46.3; H, 3.6; N, 10.6; S, 5,5. [M + H]+ calcd for C46H48N9S2Pt2+ 1180.2750, found 1180.2754. IR (KBr, selected bands, cm–1): ν(C≡N) 2202 (s), ν(NCthiocyanate) 2055, 2097 (s); ν(Ccarbene–N) 1604, 1629 (s); δ(C–H from aryls) 845, 860 (s). 13C CP MAS NMR: 185.6 (Ccarbene–N), 161.9, 153.5, 147.5, 145.3, 142.2, 140.8, 140.2, 139.7, 138.0, 136.2, 135.7, 135.1, 134.9, 133.8, 131.2, 130.1, 128.9, 128.4, 128.0, 125.5, 122.7 (C and CH from aryls), 119.0 and 118.4 (C≡N), 24.1, 21.9, 21.4, 19.7, 19.1, 18.4, 17.1 (Me’s).

**Computational details.** *DFT/TD-DFT studies for complexes* ***7****,* ***8****,* ***11*** *and* ***12.***The full geometry optimization of all complexeswas carried out at the DFT level of theory using the PBE0[61](#_ENREF_110) functional with the atom-pairwise dispersion correction with the Becke–Johnson damping scheme (D3BJ)[62](#_ENREF_112) with the help of the ORCA package (version 5.0.2).[63](#_ENREF_114) Zero-order regular approximation (ZORA)[64](#_ENREF_116) was employed to account for relativistic effects. The ZORA-def2-TZVP(-f)[64](#_ENREF_116) basis sets were used for the H, C, N, F, O and S atoms while the SARC-ZORA-TZVP basis sets were used for the Pd and Pt atoms.[65](#_ENREF_117) The Hessian matrix was calculated analytically for the optimized structures to prove the location of correct minima (no imaginary frequencies). Combination of the “resolution of identity” and the “chain of spheres exchange” algorithms (RIJCOSX)[66](#_ENREF_118) in conjunction with the auxiliary basis sets SARC/J were used.[67](#_ENREF_119) The SCF calculations were tightly converged (TightSCF). Numerical integrations during all DFT calculations were done on a dense grid (DEFGRID3). TD-DFT calculations were performed by means of the conductor polarizable continuum model (CPCM)[68](#_ENREF_120) solvation model. 60 vertical transition energies to the lowest singlet excited states with significant oscillator strengths, and their characters calculated allowed to simulate a large portion of the absorption spectra and are listed in **Tables S5**. Calculations of the lowest 10 singlet–singlet excitation energies at the optimized geometries are satisfied to gain the nature of the long wavelength light absorption of the complexes. QTAIM, MOs and spin density were calculated using the Multiwfn 3.8 software[69](#_ENREF_121) and visualized with VMD program.[70](#_ENREF_124)

*DFT studies for complexes* ***16*** *and* ***18****.* The single point calculations based on the experimental X-ray geometries of **16** and **18** and full geometry optimization procedure for isolated model structures have been carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD[71](#_ENREF_125) with also the help of Gaussian-09[72](#_ENREF_126) program package. For palladium and platinum atoms the quasi-relativistic pseudopotentials MWB28 and MWB60 and the appropriate contracted basis sets[73](#_ENREF_127) were used, the 6-31G\* basis sets were used for other atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader[33](#_ENREF_75) has been performed by using the Multiwfnprogram (version 3.7).[74](#_ENREF_128) The Cartesian atomic coordinates for all model structures are presented in **Table S12**, Supporting Information.

*Hirshfeld analysis.* The Hirshfeld molecular surfaces were generated by CrystalExplorer17 program.[75](#_ENREF_129) The normalized contact distances, dnorm,[76](#_ENREF_131) based on Bondi’s van der Waals radii,[53](#_ENREF_100) were mapped into the Hirshfeld surface (**Table S13** and **Figures S15**, **S16**). In the color scale, negative values of dnorm are visualized by the red color indicating contacts shorter than the sum of van der Waals radii. The white color denotes intermolecular distances that are close to van der Waals contacts with dnorm equal to zero. In turn, contacts longer than the sum of van der Waals radii with positive dnorm values are colored with blue.

Author Contributions

M.V.K. − conceptualization, investigation (synthesis and physicochemical study), writing; K.V.L. − conceptualization, writing; E.A.K. – investigation (UV-vis spectroscopy and electrochemical study, computational study for **7**, **8**, **11** and **12**), writing; A.S.N. – investigation (computational study for **16** and **18**), writing; M.A.K.− conceptualization, writing, project administration.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Russian Science Foundation (project 21-73-10083). The electrochemical studies were performed by E.A.K. in the framework of the Russian Foundation for Basic Research project 19-29-08026. Measurements were performed at Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, and Computing Centre (all belong to St Petersburg University).

Keywords

diaminocarbene • NHC • organometallics • platinum complexes • palladium complexes

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