Synthesis and Contemporary Applications of Platinum Group Metals Complexes with Acyclic Diaminocarbene Ligands (Review)

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Abstract—Complexes of platinum group metals with acyclic diaminocarbene ligands have found application as transition metal catalysts, photoluminescent materials, chemosensors, and anticancer drugs. This review systematises the studies published to date, analyses the properties and methods of preparation of complexes of platinum group metals with acyclic diaminocarbene ligands, and discusses the latest advances in the use of these compounds for the development of functional materials.

Keywords: carbenes, *N*-heterocyclic carbenes, metal complex catalysis, isocyanides, palladium, platinum, iridium, organometallic activation

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INTRODUCTION

Discovered at the end of the last century, stable aminocarbenes, namely *N*-heterocyclic carbenes (NHCs) and their acyclic diaminocarbene analogues (ADCs), are associated with a high donor ability, which allows them to effectively stabilise electronically and coordinatively unsaturated compounds of transition metals acting as ligands. These properties, combined with low toxicity and moderate chemical stability of NHCs and ADCs, led to their displacement by complexes of traditionally used phosphine derivatives from dominant positions in metal complex catalysis. The unique catalytic properties shown by the complexes of platinum group metals with aminocarbene ligands, led to the discovery of important catalytic reactions, which made it possible to minimise the number of intermediate steps in a number of organic processes. In addition to catalytic processes, complexes of platinum group metals with aminocarbenes are used in medicinal chemistry, in the manufacturing of light-emitting systems, and in sensor applications.

While the synthesis, properties, and applications of complexes with NHCs are discussed in a number of reviews (relevant reviews on structures and synthesis [1–7], catalytic [8–15], luminescent [16–19], medical [20–24] applications, and use in supramolecular chemistry [25]), the corresponding surveys on complexes with acyclic diaminocarbenes are rare and focus mostly on their use as catalysts in organic synthesis (until 2012) [26, 27] and the reactivity of acyclic diaminocarbene ligands [28]. Compared to NHCs, acyclic diaminocarbenes have unique, and as a rule, stronger donor properties, while the absence of a cyclic system allows rotation along the nitrogen–carbon bond, leading to significant changes in the steric and electronic characteristics of the ligand, which is reflected, in particular, in photoemission properties and catalytic activity of the complexes.

The number of publications has now reached a level where new research is timely (more than 50 papers dedicated to ADC complexes of platinum group metals in the last five years). Highly efficient catalytic systems developed in recent years for carrying out cross-coupling [29–31], Heck [32], borylation [33], and hydrosilylation [34–36] reactions, including those performed in an aqueous medium [37] and under photocatalysis with visible light [38], examples of their application in the creation of photoluminescent materials [39–42], chemosensors [39, 43, 44], and potential drugs [36, 45–47] require systematisation and critical analysis.

The main aims of this review are to introduce modern approaches to the preparation of new types of complexes of platinum group metals with ADC ligands, to rationalise the differences between NHCs and ADCs, and to discuss the use of complexes of platinum group metals with ADC ligands in catalysis, materials science, photophysics, and other fields of modern science.

STRUCTURE OF ACYCLIC DIAMINOCARBENES AND THEIR LIGAND PROPERTIES

According to the IUPAC nomenclature, carbene (H_2C:) or its derivatives (X_2C:) are electrically neutral

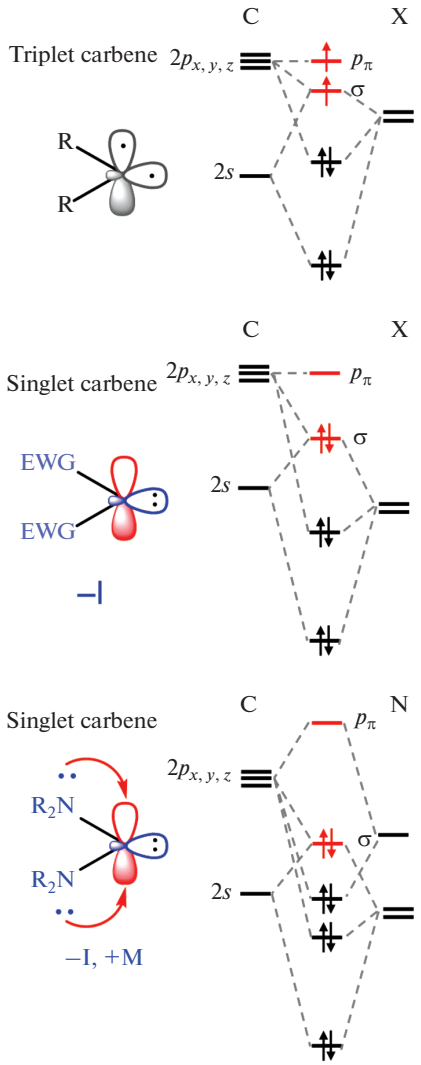


Fig. 1. Correlation diagrams of orbital energies for molecules of singlet and triplet carbenes, showing the influence of inductive and mesomeric effects of substituents.

particles in which a carbon atom is covalently bonded to two monovalent groups of any type or to a divalent group and carries two nonbonding electrons [48]. The geometry of the carbene carbon atom can be linear or angular [1]; linear geometry based on an *sp*-hybridised carbon atom carrying two nonbonding degenerate *p*-orbitals is practically not encountered. Most carbenes have an angular configuration, in which the carbon atom is intermediate between *sp*- and sp^2-hybridisation. When passing from a linear configuration to an angled one, the degeneracy of *p*-orbitals is elevated: one of the *p*-orbitals remains unchanged in energy (it is conventionally denoted as p_π), while the other *p*-orbital acquires a partial *s*-character and thus is energetically stabilised relative to the initial one (it is conventionally denoted as σ). The formed σ- and p_π-orbitals are relatively close in energy, but are separated by a significant energy gap from the occupied and vacant skeletal MOs. Since the carbene carbon atom carries two electrons not taking part in the formation of bonds, the carbene particle can be in a triplet state (two non-bonding electrons occupy σ- and p_π-orbitals with parallel spin orientation) or in a singlet state (two non-bonding electrons occupy an orbital with antiparallel spin orientation).

Chemical properties of triplet carbenes are close to the properties of free radicals and are even more reactive than the latter because of the presence of two half-filled MOs instead of one [49]. Singlet carbenes can have a dual reactivity: a double-occupied and moderate-energy MO gives them nucleophilic anion-like properties, and a vacant low-energy MO results in electrophilic cation-like properties. Since carbene is electrically neutral as a whole, its HOMO energy is lower than that of the corresponding anions; similarly, the energy of LUMO is higher than that of the corresponding cations. This predetermines, on the one hand, the moderate (in comparison with cations and anions in the gas phase) reactivity of carbenes, and on the other hand, a significant effect of substituents at the carbene carbon atom on the energy and electron density of both boundary MOs, which, in turn, determines a wide variety of carbene properties.

The multiplicity of the ground state of carbene is determined by the relative energies of σ- and p_π-orbitals. The singlet ground state is predominant when energy difference between the σ- and p_π-orbitals is significant. Quantum-chemical calculations have shown that an energy difference of about 2 eV is required to stabilise the singlet state [50]. An energy difference of less than 1.5 eV between the relative energies of the σ- and p_π-orbitals favours the triplet state [50].

In the simplest carbene, methylene (H_2C:), the orbitals are close in energy; therefore, their population with electrons is governed by the Pauli principle; for methylene, the triplet is the ground state, and the singlet is the excited state [51]. The addition of substituents to the carbene centre changes the relative stability of these states. Electron-acceptor substituents inductively stabilise the bonding σ-orbital, increasing its *s*-character, while the energy of the *p*-orbital remains nearly unchanged. As a result, the $\sigma–p_\pi$ gap increases, and the singlet state becomes preferable (Fig. 1). As in the case of dichlorocarbenes, for which the singlet state is ground [52, 53], and in the case of diaminocarbenes, two electronegative nitrogen atoms stabilise the singlet state and increase the stability of carbene.

Mesomeric effects also play a significant role in carbene stabilisation. They consist in the interaction between carbon p_π-orbitals and the corresponding *p*- or π-orbitals of two substituents [50, 54]. In the case of

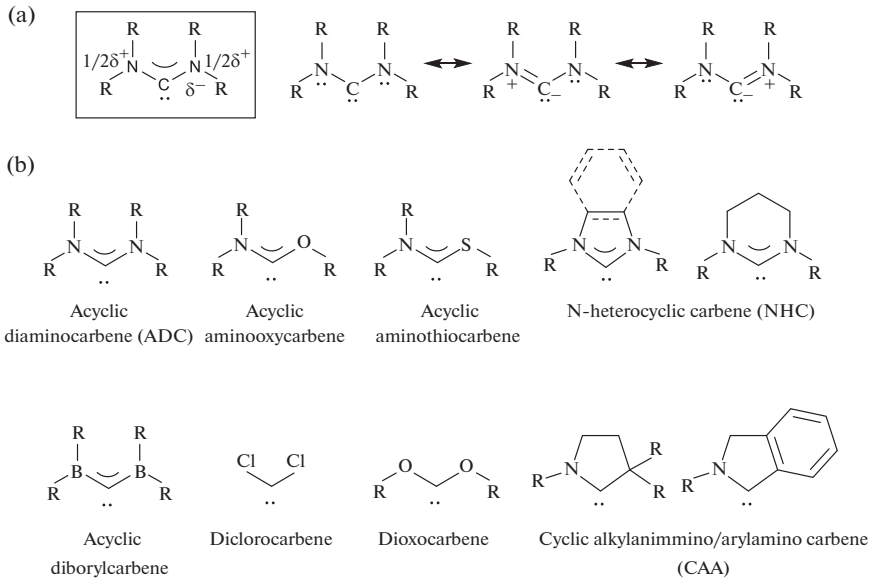


Fig. 2. (a) Mesomeric effects in the stabilisation of the diaminocarbene structure and (b) examples of heteroatom-stabilised singlet carbenes.

π-electron donating groups, such as halides, NR_2, PR_2, OR, SR, and SR_3, the energy of the vacant p_π-orbital increases due to the interaction with a symmetric combination of lone pairs of substituents [55–57]. Since the σ-orbital remains practically unchanged, the $\sigma–p_\pi$ gap increases and the singlet state becomes more preferable. The effect of the π-donor ability of substituents to stabilise carbenes can be demonstrated by comparing acyclic diaminocarbenes and dialkoxycarbenes: amino groups have a higher π-donor ability compared to alkoxy groups. It has been shown experimentally that bis(*N*-piperidyl)carbene $(CH_2)_5N–C–N(CH_2)_5$ exists in solution at room temperature for a day [58], while the lifetime of dimethoxycarbene MeO–C–OMe in solution at room temperature is only 2 ms [59].

The interaction of the π-electrons of the substituents with the p_π-orbital of the carbene carbon atom leads to the formation of a four-electron three-centre π-system, in which the C–X bond acquires a partial π-character. Such carbenes are best described by the superposition of two zwitterionic structures with a negative charge at the centre of the carbene (Fig. 2a). The data of X-ray diffraction studies of acyclic diaminocarbenes indicate the planar structure of nitrogen atoms and the partial π-character of the C–N bonds [58, 60, 61]; the latter is confirmed by large rotation barriers of substituents around the C–N bond in solution (13 kcal/mol), determined for acyclic diaminocarbenes through variable temperature NMR spectroscopy [60, 62].

Examples of heteroatom-stabilised singlet carbenes are shown in Fig. 2b, among which diaminocarbenes are the most important representatives of this class of compounds [1].

An important feature of diaminocarbenes is their pronounced ligand properties in complexes of transition metals [63]. The tendency of ADCs and their analogues to complexation is associated with the possibility of the formation of the $M–C_{carbene}$ 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 with a vacant electron-deficient p_π-orbital of a carbene carbon atom. As a rule, the ADC ligand is an effective σ-donor and a weak π-acceptor (Fig. 3) [64].

Strong σ-donor and weak π-acceptor properties make ADCs similar in coordination properties to phosphine ligands; however, diaminocarbenes are stronger electron donors than phosphines [65–67]. This is manifested by a stronger metal–ligand bond, which is confirmed by higher bond dissociation energies and shorter metal–ligand bond lengths for diaminocarbene complexes as compared to their phosphine counterparts. Due to the lower electronegativity of carbon in comparison with nitrogen, the lone electron pair on the carbene carbon atom acquires significantly higher energy than in conventional N-donors, for example, in pyridine ligands.

Currently, ADC complexes of many transition metals are known, including complexes with early

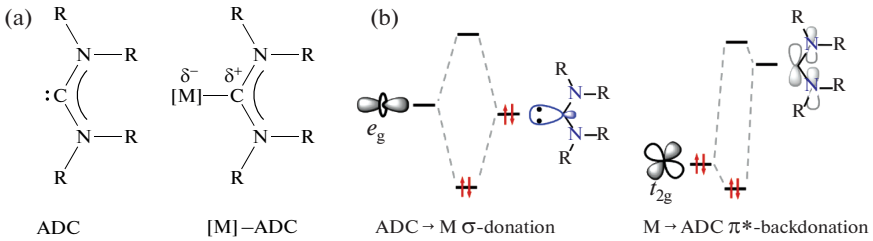


Fig. 3. (a) Acyclic diaminocarbenes (ADC) and their metal complexes; (b) metal–ligand interaction in complexes with acyclic diaminocarbenes.

transition elements kinetically labile in ligand metathesis reactions, such as chromium [68], manganese [69–72], iron [73–79], cobalt [80], copper [81] (as well as mercury [82]); however, coordination compounds of platinum group metals are of the great practical significance.

The high electron-donating properties of ADC ligands stem from their electronic parameters. The Tolman electronic parameter [83] based on measuring the change in the frequency of stretching vibrations of the carbonyl ligand ν(CO) in $[Ni(CO)_3(L)]$ depending on the electron-donating ability of ligand L, as well as systems similar in principle based on carbonyl complexes of rhodium(I) (*trans*-$[RhCl(CO)_2(L)]$) [84] and iridium(I) (*trans*-$[IrCl(CO)_2(L)]$) [85], confirm that diaminocarbenes are more stronger donors than phosphines and carbon monoxide (Fig. 4a). Due to the absence of electron density delocalisation at the heteroaromatic fragment, ADCs, as a rule, have stronger electron donor ligands than five-membered aromatic NHCs. In addition, the donor capacity of ADCs is higher than that of five-membered saturated NHCs, since the larger angle of the $NC_{carbene}N$ bond decreases the *s*-character of the lone electron pair on the carbene carbon atom [60, 63, 86]. According to the Tolman electronic parameter, the donor capacity of ADCs is comparable to the donor capacity of six-membered NHCs [87, 88]. Analysis of the Tolman electronic parameter for asymmetrically substituted ADCs (compounds **1a** and **1b** in Fig. 4a) clearly shows that the donor ability of acyclic diaminocarbene depends on its conformation [88]. An alternative approach to the measurement of electron donor properties based on the measurement of δ_C of the carbene carbon atom of the NHC ligand located in the *trans*-position to the measured ligand in palladium(II) and gold(I) complexes [2, 89, 90] also confirms the high donor ability acyclic of diaminocarbene ligands (Fig. 4b) [91].

Although diaminocarbenes are positioned as strong σ-donor ligands with an insignificant contribution of π-dative interaction, studies have shown that diaminocarbenes can, to a certain extent, acquire electron density by the mechanism of reverse π-donation [64, 88, 92]. The method for evaluating the π-acceptor properties of diaminocarbene ligands, based on the measurement of the chemical shift of ^{77}Se in adducts of diaminocarbene with selenium [93], shows that ADCs, as a rule, are stronger π-acceptors than NHCs (Fig. 4c) [93, 94]. The π-acceptor ability of ADCs depends primarily on the volume of substituents at the nitrogen atoms. ADCs having at least one non-bulky substituent at each of the nitrogen atoms, for example, diaminocarbenes such as $(Mes(Me)N)_2C$: (compound **1a**) and $(Dipp(Me)N)_2C$: (compound **2** in Fig.4c) [88, 95], exhibit moderate electrophilic properties. Alder's tetraisopropyl-substituted diaminocarbene $(^iPr_2N)_2C$: (compound **3** in Fig. 4c) [60] has intermediate electrophilicity and is close to cyclic alkylaminocarbenes (CAACs) in its π-acceptor properties [96]. Carbene $(^iPr_2N)_2C$: exhibits ambiphilic properties, as evidenced by its chemical activity, in particular, the ability to activate small molecules, such as carbon monoxide [97]. To date, ADCs with a bulky 2,2,6,6-tetramethylpiperidine substituent (compound **4** in Fig. 4c) is the most electrophilic diaminocarbene among the investigated ones. According to the results of quantum chemical calculations, the minimum energy corresponds to the conformer in which the 2,2,6,6-tetramethylpiperidine fragment is perpendicular to the N_2C plane. In this conformer, π-conjugation of the lone pair of electrons of the nitrogen atom with the carbene carbon atom is impossible, the energy of LUMO decreases and, consequently, the electrophilicity increases [94]. In most cases, the synergistic nature of the metal–ligand interaction does not allow one to estimate the individual contribution of the σ-donor and π-acceptor properties of the carbene ligands.

The key difference between acyclic diaminocarbenes and cyclic analogues is the absence of a covalent fragment connecting both nitrogen atoms. The absence of a ring in ADCs allows the rotation of substituents around the $C_{carbene}$–N bonds, but free rotation around these bonds limits their partial π-character, which appears due to the conjugation of lone electron pairs of nitrogen atoms and the vacant *p*-orbital of the carbene carbon atom. Experimental [78] and theoretical [98, 99] studies show that in acyclic diamino-

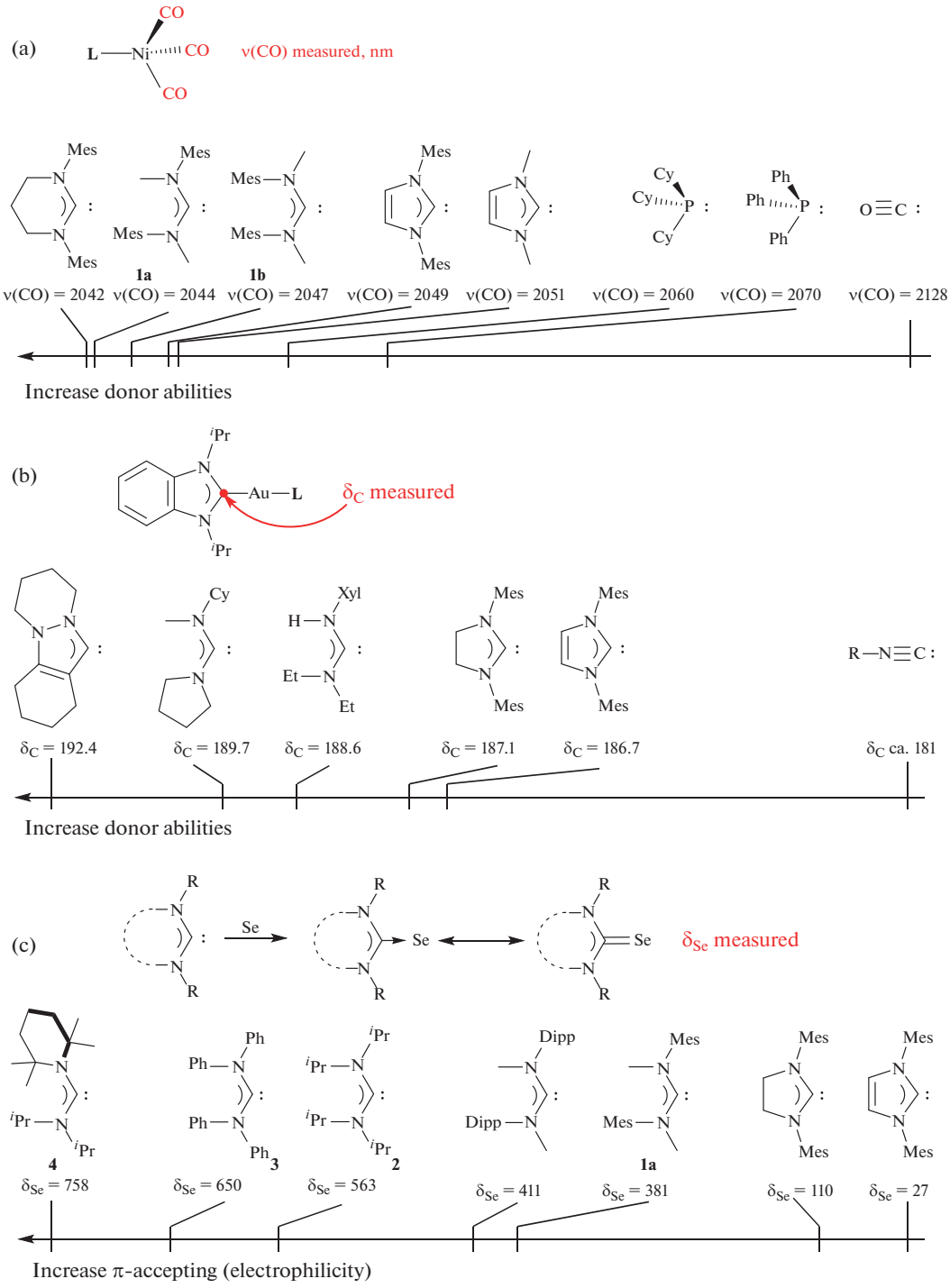


Fig. 4. Evaluation of the electron-donor properties of ADC ligands and comparison with other ligands: (a) electronic Tolman parameter; (b) δ_C carbene carbon atom in mixed ligand NHC complexes; (c) Δ_{Se} in adducts with selenium.

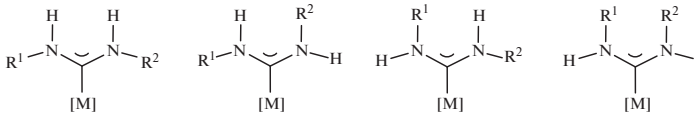
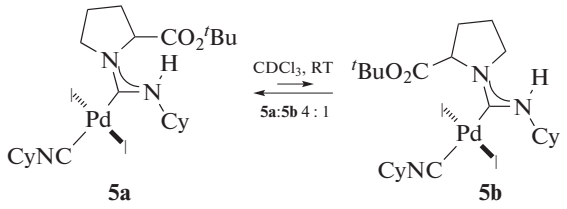


Fig. 5. Conformers of acyclic diaminocarbene ligands in complexes.

carbenes with small substituents and in their complexes with transition metals, the barrier to rotation around the $C_{carbene}$–N bonds does not exceed 13–20 kcal/mol. Monodentate acyclic diaminocarbenes with different substituents at nitrogen atoms have four conformers (Fig. 5).

The geometry of the most preferred conformer in the absence of specific non-covalent interactions depends on how adverse steric interactions are minimised; changes in the relative volumes of substituents at the nitrogen atom can shift the conformational equilibrium in favour of one of the conformers. As an example, asymmetrically substituted ADC complexes of palladium(II) **5** reported in [100], which have a pyrrolidinecarboxylic acid ester as one of the substituents at the carbene carbon atom, exist in solution in the form of an equilibrium mixture of conformers (Scheme 1).



Scheme 1. Equilibrium mixture of conformers fixed in a solution of an asymmetrically substituted ADC palladium(II) complex.

The stabilisation of a particular conformer of ADC ligand can be accomplished via the non-covalent binding of donor and acceptor centres in the structure of the complex. ADC complexes in which nitrogen atoms are bonded to one or more hydrogen atoms can act as hydrogen bond donors and form non-covalent interactions with various nucleophilic particles [28]. The formation of hydrogen bonds restricts the rotation around the C–N bonds in the diaminocarbene fragment, which leads to the stabilisation of a certain conformation (Fig. 6). In particular, cationic ADC complexes with outer-sphere halide anions can be stabilised in the solid phase and in solution in the *syn*,*syn*-configuration due to the formation of the three-centre (bifurcate) hydrogen bond N–H···Cl···H–N between NH-fragments of a diaminocarbene ligand and a halide anion (structure **6**) [101–105].

The *anti*-configuration at one of the nitrogen atoms can be achieved due to the intermolecular pair N–H···Cl hydrogen bonds between the NH fragments of the diaminocarbene ligand and the halide ligand at the metal atom of the neighboring molecule (structure **7**) [106]. It was found [106] that in compound **8** there is a pairwise cooperative intermolecular interaction with the formation of chalcogenic and hydrogen bonds S···Cl/H···Cl, which stabilise the specific conformer of the ADC ligand not only in the solid phase but also in solution.

When substituents with hydrogen bond acceptors are introduced into the structure of the diaminocarbene moiety, an intramolecular hydrogen bond can form, which fixes the diaminocarbene moiety in the *amphi*-conformation, as in the case of palladium(II) ADC complexes with the 4-aryl-substituted thiazole-2-yl substituent (structure **8**) [106]. A similar stabilisation of the diaminocarbene fragment in the *amphi*-conformation also occurs in the case of ADC complexes of other late transition metals with a pyridin-2-yl substituent, namely, in the complexes of gold [107–112] and iron [113]. Stabilisation of a certain conformer can also be achieved due to π–π interactions between aryl substituents (structure **10**) [88, 114], C–H···π interactions (structure **11**) [99], and anagostic H···M interactions (structure **12**) [101]. In mixed-ligand diaminocarbene/isocyanide complexes **13** with aryl substituents, a certain conformer can be stabilised due to the formation of an intramolecular π-hole···π interaction [115]. These interactions also control the conformational structure of acyclic diaminocarbene complexes both in the solid phase and in solution. The formation of hydrogen bonds with NH fragments of the diaminocarbene ligand can not only change the conformational stability but also lead to isomerisation of the coordination polyhedron [116].

The presence of additional donor centres in the diaminocarbene ligand can lead to the formation of C,X-chelate and X,C,X-pincer complexes, in which conformations are fixed at one or both nitrogen atoms, respectively. Nitrogen and carbon atoms (examples of C,N- and C,C-chelate complexes are presented in Section 3.4), sulphur [117] and phosphorus atoms (representative examples of C,P-chelates (compounds **14** and **15**) [118–120] and P,C,P-pincers (compound

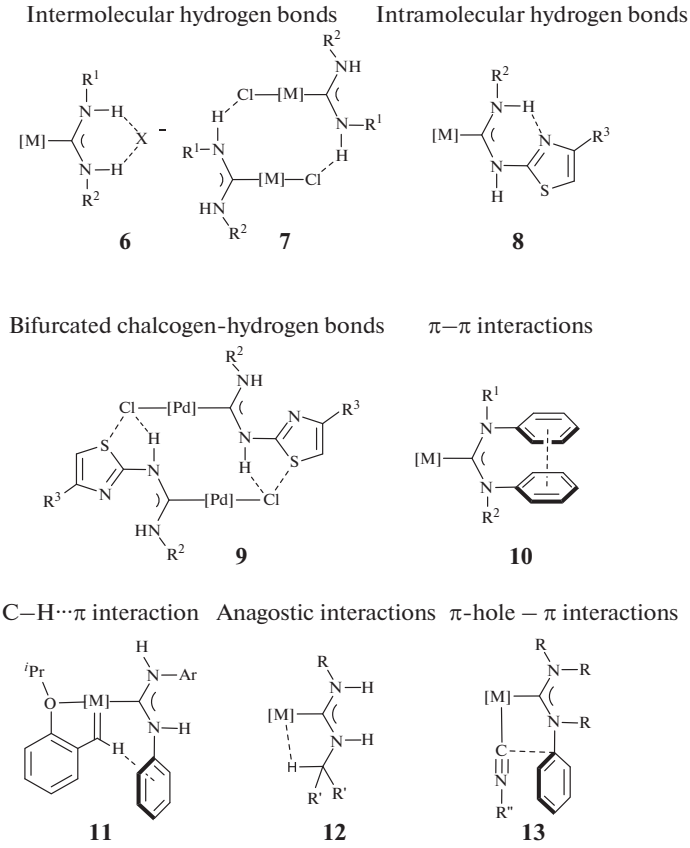


Fig. 6. Examples of non-covalent interactions involved in the stabilisation of the ADC ligand conformer.

16) [102] are shown in Fig. 7a) can act as additional donor centres X in C,X-chelate complexes.

It is fundamentally important that conformational transitions cause changes in the energy of the boundary σ- and p_π-orbitals and lead to significant changes in the steric and electronic characteristics of the ligand. In particular, the conformational isomers of ADC complexes exhibit different energies of the ^{3}MLCT-transition, which is reflected in their photoemission properties (a representative example shown in Fig. 7b) [121], and dissimilar catalytic activity [122].

METHODS FOR PREPARATION OF COMPLEXES OF PLATINUM GROUP METALS WITH ACYCLIC DIAMINOCARBENE LIGANDS

The valuable characteristics of complexes with diaminocarbene ligands determining their catalytic, photophysical, and other applications, are linked to the properties of the metal centre, as well as described by the balance between the donor and steric properties of the diaminocarbene ligand. Each area of application requires complexes with ligands possessing different set of parameters. Ligands are selected, as a rule, empirically, which imposes stringent requirements on the method of their synthesis. The synthetic approach should be modular, allowing an easy introduction of the desired functional groups, versatile, making it possible to obtain a wide range of derivatives, and efficient, providing high reaction yield with a low complexity of the process.

A number of experimental approaches to the synthesis of complexes with diaminocarbene ligands (Fig. 8) [26–28] have been proposed, the main of which are (i) deprotonation of formamidinium salts with subsequent coordination of the thus generated carbene to a metal centre (Direct complexation), (ii) oxidative addition of C-chloriminium to a metal centre (Oxidative addition), (iii) lithium-halogen exchange followed by transmetalation (Transmetalation), (iv) metal-promoted nucleophilic addition to isocyanide ligands (Metal-mediated addition), and (v) the insertion of isocyanide at the M–N bond (Insertion).

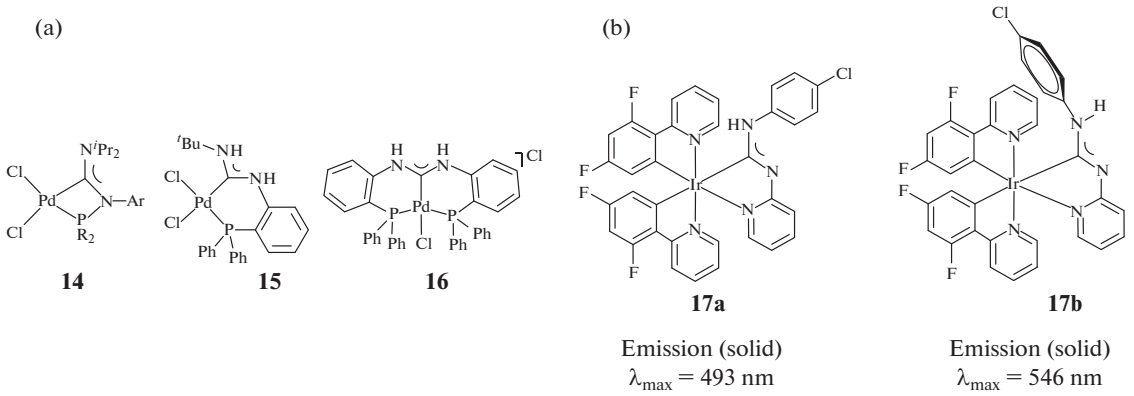
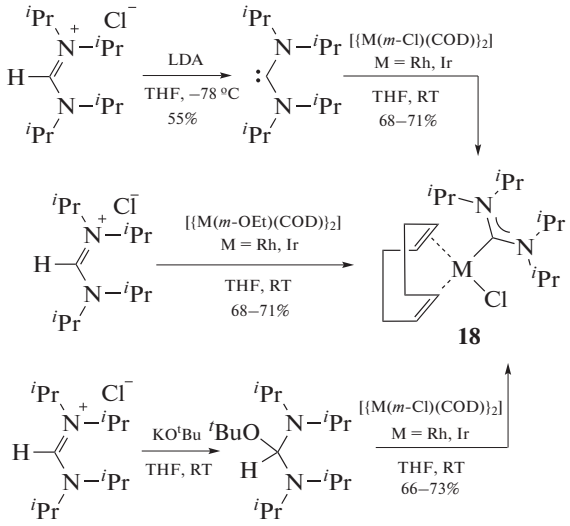


Fig. 7. (a) C,P-chelate and P,C,P-pincer complexes with ADC-ligands; (b) conformational isomers of the ADC complex showing different photoemission properties.

Direct Complexation

Direct complexation between the metal centre and free carbene obtained from precursors in situ is the main method for the synthesis of *N*-heterocyclic carbene complexes [123, 124]. As precursors for the synthesis of their acyclic analogues ([M]-ADC), as a rule, *N,N,N′,N′*-tetrasubstituted formamidinium salts are used, the deprotonation of which leads to the formation of free carbene [27, 125]. Deprotonation of *N,N,N′,N′*-tetrasubstituted formamidinium salts requires strong bases such as LDA, KH/KO^{t}Bu or LiN(SiMe$_3$)$_2$ [60, 67, 126]. Scheme 2 shows representative examples of rhodium(I) and iridium(I) complexes synthesised by direct coordination of diaminocarbene obtained from the corresponding formamidinium precursors [87].



Scheme 2. Representative examples of rhodium(I) and iridium(I) complexes synthesised by direct coordination of diaminocarbene.

The main disadvantage of this method is the limited synthetic availability of *N,N,N′,N′*-tetraalkylformamidinium salts, the preparation of which is associated with significant problems [127, 128]. In addition, the disadvantage of this method is the ability of the

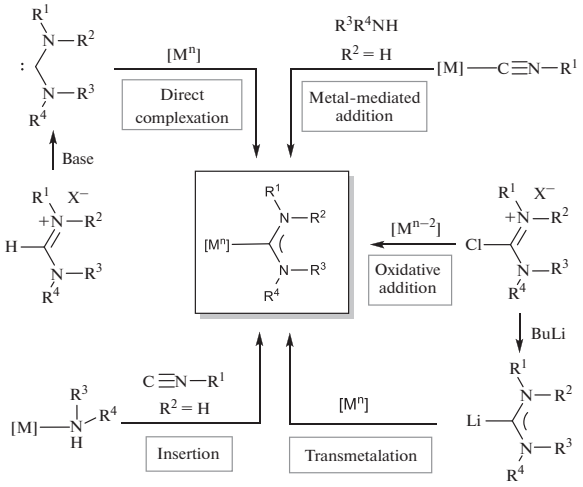


Fig. 8. Experimental approaches to the synthesis of complexes with acyclic diaminocarbene ligands.

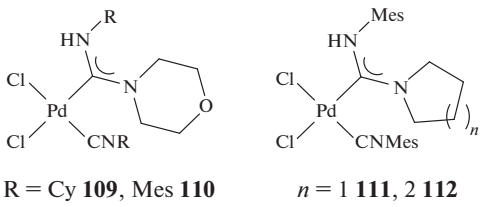
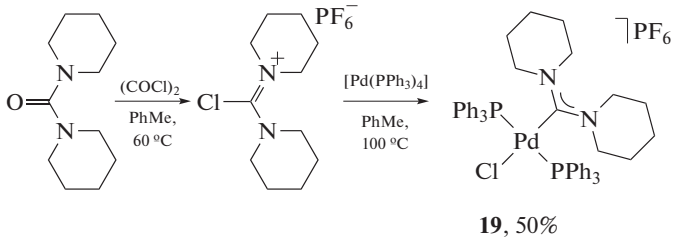


Fig. 9. Structures of compounds **109**–**112**.

formed free carbene, if it is not stabilised by bulky substituents, to participate in the side reactions of oxidation, dimerization, alkene elimination, and others [58, 61, 119, 120, 125]. Substituted thioureas, which form diaminocarbene upon reduction, can also act as precursors, but this approach is limited to a few examples [129, 130].

Oxidative Addition

The reaction of oxidative addition of formamidinium salts can occur only at metal centres in the zero oxidation state, and the use of this method is limited to a few examples for the preparation of palladium(II) ADC complexes (Scheme 3) [131, 132].

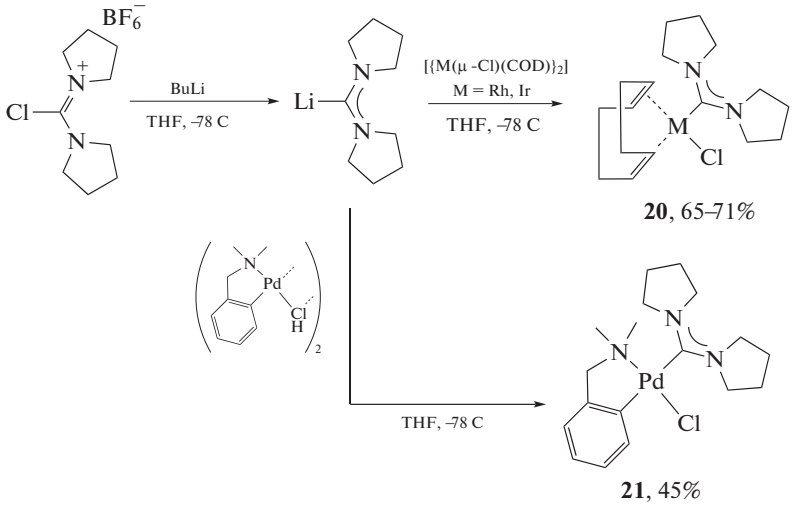


19, 50%

Scheme 3. Oxidative addition of formamidinium salts, leading to the formation of ADC-complexes of palladium(II).

Transmetalation

An alternative approach to the preparation of ADC complexes of platinum group metals is based on the interaction of lithiated formamidinium salts with coordinatively unsaturated metal precursors (Scheme 4) [132, 133]. However, the high reactivity of organolithium compounds imposes significant restrictions on the nature of substituents in diaminocarbene fragments. Therefore, as far as we know, the use of this method is represented by a few examples of the preparation of palladium(II), rhodium(I), and iridium(I) ADC species [132, 133].



20, 65–71%

21, 45%

Scheme 4. Approach to the preparation of ADC-metal complexes by interaction of lithiated formamidinium salts with coordination-unsaturated metal precursors.

Approach Consisting of Metal-Mediated Addition to Isocyanide Ligands

The metal-mediated interplay of isocyanides with N-centred nucleophiles (NH-nucleophiles) is the most promising method for the preparation of complexes with acyclic diaminocarbene ligands [134, 135], insofar as application of this method allows to adjust the electron-donor and steric properties of the diami-

nocarbene ligand by varying the substituents, which is achieved by selection of a suitable isocyanide–nucleophile pair. The metal-promoted interaction of isocyanides with NH-nucleophiles was discovered a little over a hundred years ago by L. A. Chugaev, who was a professor at Saint Petersburg State University, at that time known as the Imperial Petrograd University, when studying the interaction of methyl isocyanide with hydrazine promoted by platinum(II) [136]. Due to its versatility, over the past 20 years, the isocyanide approach has been extended to many other metal centres and nucleophiles [135, 137].

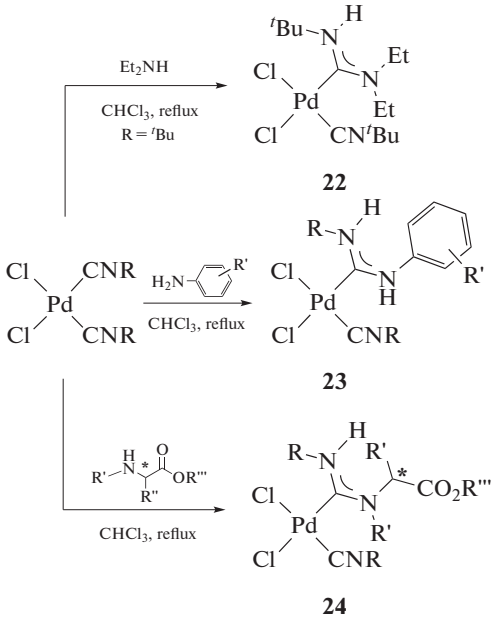
In the free state, the isocyanide carbon atom has a nucleophilic character; therefore, in the absence of electrophilic particles, including compounds of transition metals, isocyanides do not interact with amines and alcohols [63]. The coordination of isocyanides to metal centres in high oxidation states and depleted in electrons increases the partial positive charge on the isocyanide carbon atom, leading to an increase in its electrophilicity [134, 135]. To carry out the metal-promoted combination of isocyanides with NH-nucleophiles, a metal centre is required that ensures sufficient activation of the isocyanide. These metal centres include late transition metals in relatively high oxidation states: palladium(II), platinum(II), gold(I/III), and others. Another prerequisite is the use of strong and moderately strong nucleophiles.

The overwhelming majority of examples of nucleophilic addition to coordinated isocyanides known in the literature is reduced to interaction with N-nucleophiles (amines) [134, 138] and O-nucleophiles (alcohols) [76, 139–144]. These reactions lead to the formation of "classical" monodentate diaminocarbene (when the coordinated isocyanide is attacked by the N-donor centre) and amino(oxo)carbene ligands (when the coordinated isocyanide is attacked by the O-donor centre). At the same time, in the presence of an additional N'-nucleophilic centre in the molecule of the joining N-nucleophile, compounds of a more complex structure can be formed, including those containing C,N- and C,C'-chelate diaminocarbene ligands [138]. Often, such complexes are more stable than complexes containing "classical" monodentate C-coordinated diaminocarbene ligands.

It is important to note that our discussion will not focus on an encyclopaedic listing of the available data. Instead, we will strive to analyse the main driving forces behind the formation of compounds of one type or another, which will undoubtedly facilitate and stimulate further research in this area. The flow of the section is related to the properties of nucleophile, namely the number of N-nucleophilic centres and their mutual arrangement.

Addition of monofunctional NH-nucleophiles. Interaction of isocyanide complexes *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt) with various monofunctional NH-nucleophiles, such as aliphatic [101, 145–151] and aromatic amines [140, 152–154], including amino acid derivatives [100], as a rule, flows through only one isocyanide ligand and leads to complexes with one acyclic diaminocarbene ligand and one isocyanide ligand. Representative examples of these reactions are shown in Scheme 5. The reaction usually proceeds under mild conditions with good rates and high yields. The use of chiral isocyanides or nucleophiles makes it possible to synthesise optically active diaminocarbene complexes [100], which are promising for use as catalysts in asymmetric synthesis [26, 27].

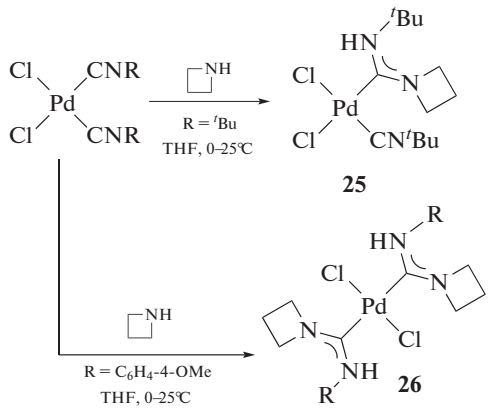
An empirical indicator of the electrophilic nature of an isocyanide ligand in its metal complexes is the force constant of CN bond vibrations, which correlates with the value of the relative positive charge on the carbon atom (the higher the force constant, the greater the positive charge). In the review [134], based on an analysis of experimental data, it was concluded that a complex should be attacked in which $\Delta\nu = \nu(CN)_{coord} - \nu(CN)_{free} \geq 40$ cm^{-1}. According to IR spectroscopy data, $\nu(C{\equiv}N)$ in *cis*- $[MCl_2(CNR)_2]$ is 90–115 cm^{-1} higher than in free isocyanides, which indicates a significant increase in the electrophilicity of the isocyanide carbon atom during coordination and thus indirectly indicates a significant increase in reactivity as compared to nucleophiles. The high electrophilic activation of isocyanides explains the ability of *cis*-$[MCl_2(CNR)_2]$ complexes to react with nucleophiles of different basicity.



Scheme 5. Interaction of isocyanide complexes of *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt) with monofunctional NH-nucleophiles, resulting in mono-ADC-complexes.

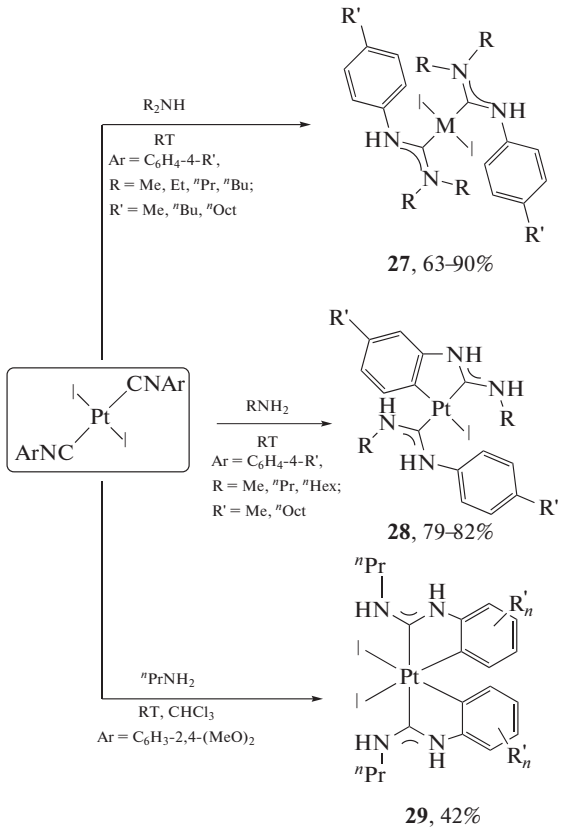
The absence of a reaction for the second isocyanide ligand in *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt) when using

an excess of amine results from the fact that the resulting diaminocarbene ligand is a stronger donor than the isocyanide ligand [148] and therefore it deactivates the isocyanide ligand in nucleophilic addition reactions. The nucleophilic attack of both isocyanide ligands in the reaction with monofunctional nucleophiles is realised only by strong nucleophiles, for example, aliphatic [155–157] or cycloaliphatic amines [158], and/or upon activation of isocyanides by electron-withdrawing substituents (Scheme 6) [159]. Depending on the nature of the substituent in the isocyanide, the interaction of *cis*-$[PdCl_2(CNR)_2]$ with amines can lead to both monocarbene (**25**) and *bis*-carbene complexes (**26**). The interaction of complexes with aromatic isocyanides occurs simultaneously at both isocyanide ligands, while when a less active *tert*-butyl isocyanide complex is used in reactions with nucleophiles, the reaction proceeds only at one of them [158].



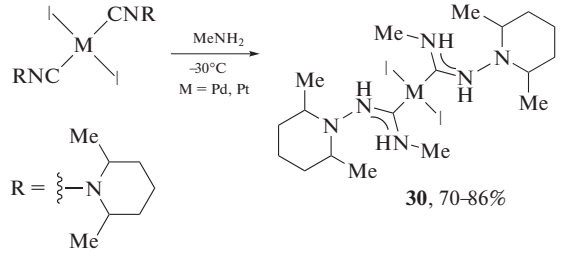
Scheme 6. Example of a nucleophilic attack on both isocyanide ligands leading to the generation of bis-carbene derivatives.

The interaction of *trans*-$[PtI_2(CNAr)_2]$ with primary and secondary amines proceeds at both isocyanide ligands and leads to bis-carbene complexes **27**–**29**. Depending on the reaction conditions and the nature of the amine, nucleophilic addition can be accompanied by a further reaction of *ortho*-metalation of the aryl fragment with the formation of C,C-chelate diaminocarbene complexes of platinum(II) and platinum(IV) (Scheme 7) [155–157, 160]. In particular, when carrying out the reaction with primary amines, the process is accompanied by the stage of *ortho*-metalation of the aryl fragment of one of the formed ADC ligands and leads to platinum(II) compound **28**. Double-cyclometalated platinum(IV) complex **29** can be synthesised by carrying out the reaction of *trans*-$[PtI_2(CNAr)_2]$ with an excess of primary amine in chloroform, the latter acts not only as a solvent but also as an oxidising agent, reducing to dichloromethane.



Scheme 7. Interaction of *trans*-$[PtI_2(CNAr)_2]$ with amines leading to the preparation of bis-carbene derivatives **27**–**29**; subsequent *ortho*-metalation of the aryl fragment with the formation of C,C-chelated diaminocarbene complexes.

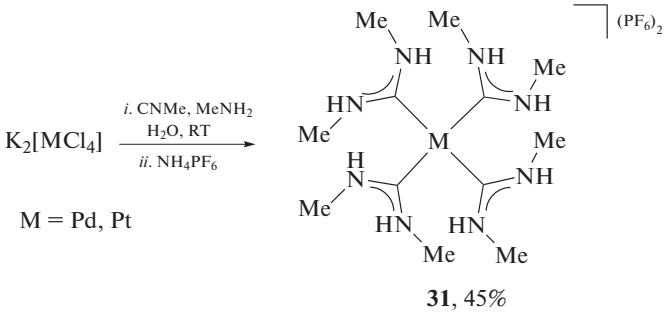
The interaction of *N*-isocyanodialkylamines in the coordination sphere of palladium(II) and platinum(II) with amines proceeds under mild conditions, leading to the formation of bis-diaminocarbene complexes **30** in a good preparative yield (Scheme 8) [159]. It should be noted that the use of *N*-isocyanodialkylamines shows promise for the preparation of new diaminocarbene complexes due to their high reactivity [159, 161–164].



Scheme 8. Interaction of N-isocyanodialkylamines in the coordination sphere of palladium(II) and platinum(II).

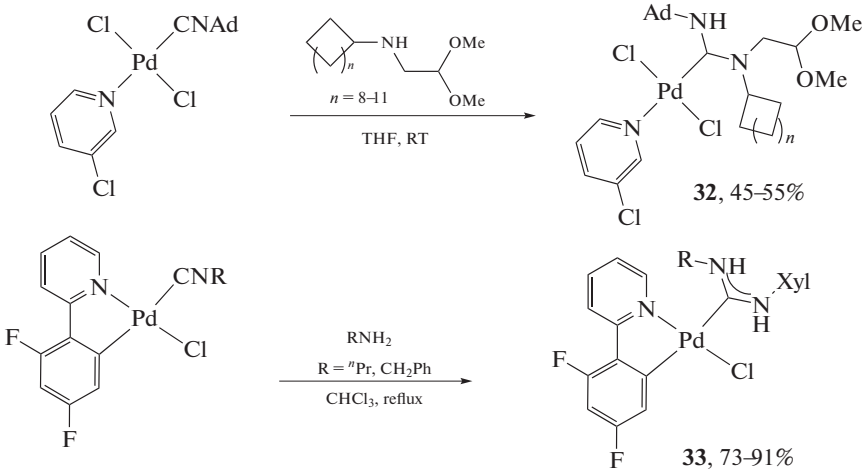
Heteroleptic tetrakis(acyclic diaminocarbene) complexes of palladium(II) and platinum(II) **31**

can be synthesised by the interaction of potassium tetrachloropalladate/tetrachloroplatinate with methyl isocyanide and methylamine (Scheme 9) [165–167]. Despite the apparent simplicity of the method, currently known examples are limited to compounds with methyl substituents; therefore, it is difficult to estimate the synthetic potential of the method.



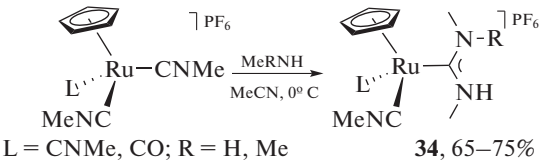
Scheme 9. Heteroleptic tetrakis-ADC complexes of palladium(II) and platinum(II).

The interaction of monoisocyanide complexes of palladium(II) and platinum(II) with amines, as expected, leads to the formation of monodentate acyclic diaminocarbene complexes (representative examples are shown in Scheme 10) [33, 43, 47, 168, 169]. Due to the high electrophilic activation of isocyanides by the indicated metal centres, the reactions, as a rule, proceed under mild conditions and lead to a wide range of acyclic diaminocarbene complexes in a good preparative yield.



Scheme 10. Examples of the interaction of monoisocyanide complexes of palladium(II) and platinum(II) with amines.

Methyl isocyanide ligands in the cyclopentadienyl complexes of ruthenium(II) add methylamine and dimethylamine to form acyclic diaminocarbene ligands (Scheme 11) [170]. When the reaction is carried out at low temperature, the resulting monocarbene complexes **34** can be isolated in good preparative yield; when the reaction is carried out at a higher temperature in a large excess of amine, bis-carbene complexes are formed; however, the latter are unstable in the absence of an excess of amine and upon standing form monocarbene compounds **34** [28, 170].

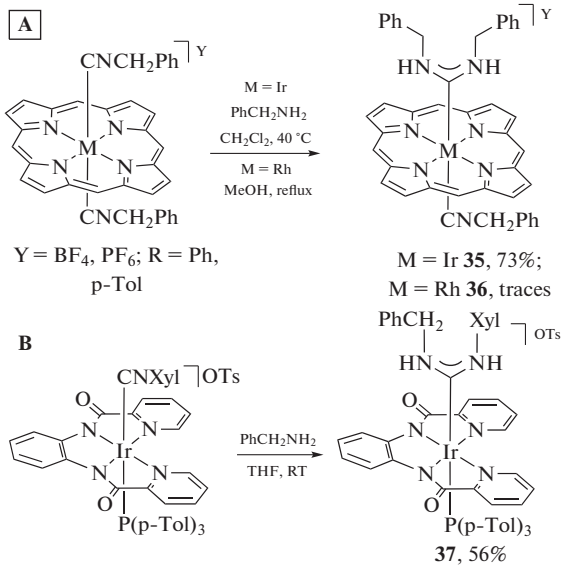


Scheme 11. Interaction of methyl isocyanide ligands in cyclopentadienyl complexes of ruthenium(II) with amines.

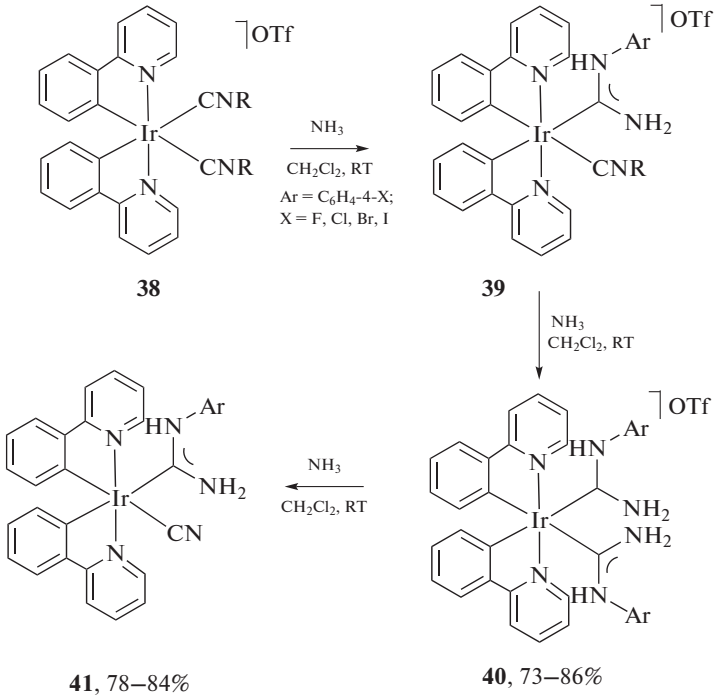
Porphyrin complexes of iridium(III) with axial isocyanide ligands combine with amines to form the corresponding ADC complexes (Scheme 12a) [171]. At a

stoichiometric ratio of reagents, the reaction proceeds only at one isocyanide ligand and leads to compound **35** in a good preparative yield. The authors note that the transformation of the second isocyanide ligand is possible in the presence of a ten-fold excess of amine; however, the formed bis-ADC-complex was detected only in solution and was not isolated in a pure form. ADC-derivatives of rhodium(III) porphyrin complexes **36** can be obtained by refluxing the corresponding bis-isocyanide complexes in methanol [172]. The axially located isocyanide ligand in the iridium(III) complex with the tetradentate pyridinecarboxamide ligand reacts with amines in a similar way (Scheme 12b) [173].

Due to the influence of cyclometalating σ-donor ligands, iridium(III) in bis-cyclometalated complexes is a weak electrophilic activator of isocyanides ($\Delta\nu = \nu(CN)_{\text{isocyanide ligand}} - \nu(CN)_{\text{uncoordinated isocyanide}} = 4–32\ cm^{-1}$ [174–177]); therefore, only isocyanide ligands activated by acceptor substituents enter into the reaction of nucleophilic addition. The interaction of bis-isocyanide complexes **38** with ammonia leads to the quantitative formation of bis(diaminocarbene) complexes **40** (Scheme 13) [178]. In this case, the addition of ammonia to the first and second isocyanide ligands in **38** occurs at similar rates, which already at the initial stage leads to the formation of an inseparable mixture of compounds **39** and **40** and makes it impossible to obtain pure complexes **39** according to this reaction. It is interesting to note that further exposure of compounds **40** in an ammonia atmosphere leads to the fragmentation of one of the diaminocarbene ligands to form a cyanide complex (Scheme 13, compound **41**).

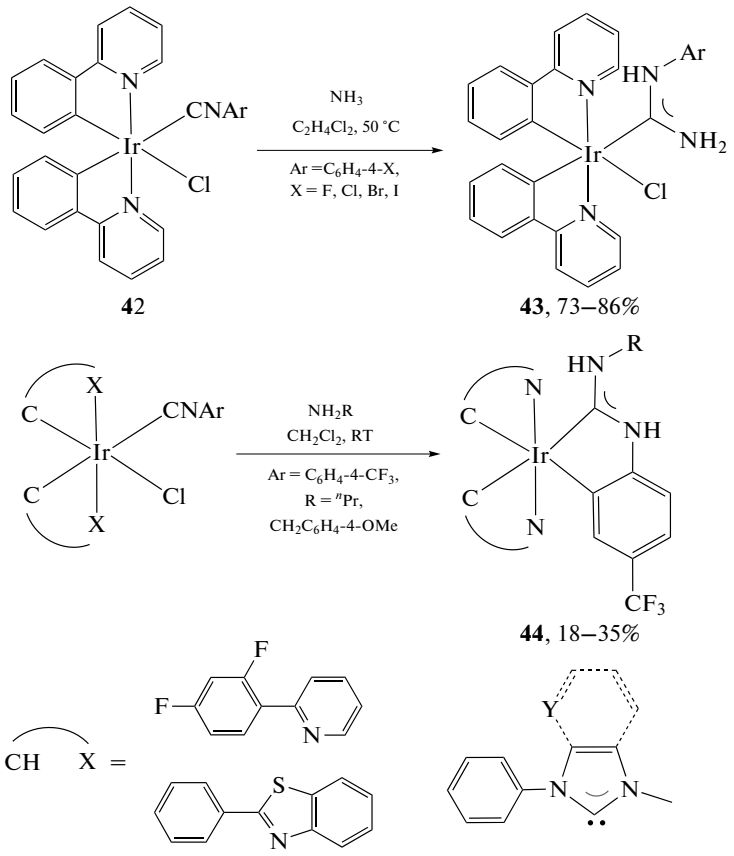


Scheme 12. Interaction of porphyrin (A) and pyridine-carboxamide (B) complexes of iridium(III) containing axial isocyanide ligands with amines.



Scheme 13. Interaction of cyclometalated iridium(III) complexes containing isocyanide ligands with amines.

The interaction of monoisocyanide complexes of iridium(III) **42** with an excess of gaseous ammonia leads to the formation of diaminocarbene complexes **43** (Scheme 14) [39]. At the same time, when primary and secondary aliphatic amines are used as nucleophiles, the nucleophilic addition reaction is accompanied by metalation of the aromatic substituent to form C,N-chelate diaminocarbene complexes **44** [41].

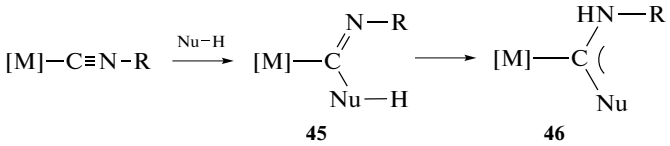


Scheme 14. Interaction of monoisocyanide complexes of iridium(III) **42** with ammonia and amines.

Experimental kinetic studies [140, 143, 179–183] and quantum chemical calculations [184–186] indicate that the reaction leads to the formation of acyclic diaminocarbene ligands as a result of the attack of NH nucleophiles on coordinated isocyanides has a common second order [179–181], i.e. the formation of an associate occurs at a stage that determines the reaction rate. A slight increase in enthalpy and a decrease in the entropy of activation of the reaction ($\Delta H = 9.4 \pm 0.1$ kcal/mol, $\Delta S = -35.1 \pm 1.7$ kcal/mol for the reaction of *cis*-$[PdCl_2(CNPh)(PPh_3)]$ with *para*-toluidine) also indicate the progress of the reaction through the formation of an associate [140]. At the rate-limiting stage, the reaction rate should depend on the nature of the substituents both in both the isocyanide ligand and the attacking nucleophile: the introduction of electron-withdrawing substituents into the isocyanide molecule and/or electron-donating substituents into the nucleophile molecule should lead to an increase in the reaction rate, which is observed experimentally [181]. An increase in the solvent polarity slows down the reaction rate, which is probably because of the greater stabilisation of the attacking amine as compared to the transition state leading to the association in polar solvents, most likely formation of hydrogen bonding [183].

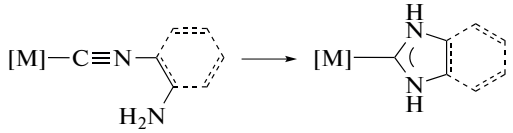
According to the theoretical studies using the density functional theory method, the mechanism of CNXyl ligand coupling in the complex *cis*-$[PtCl_2(CNXyl)(CNMe)]$ with various NH nucleophiles ($HNMe_2$, $HN{=}CPh_2$, $H_2N{-}N{=}CPh_2$) is a stepwise associative process and includes the addition of a nucleophile to the isocyanide carbon atom, deprotonation of the resulting intermediate compound **45** (for example, with a second nucleophile molecule or another base from the reaction mixture), and protonation of the isocyanide nitrogen atom to form reaction product **46** (Scheme 15) [184]. Nucleophilic addition

is the rate-limiting step of the entire process. According to the data of quantum chemical calculations performed for different types of nucleophiles ($HNMe_2$, $HN{=}CPh_2$, $H_2N{-}N{=}CPh_2$), the total activation energy is almost independent of the nature of the nucleophile and amounts to 19.8–22.4 kcal/mol [184]. Proton transfer during the transition from intermediate **45** to compound **46** can occur stepwise or concurrently. According to the data of quantum-chemical calculations of the studied nucleophiles ($HNMe_2$, $HN{=}CPh_2$, $H_2N{-}N{=}CPh_2$), the proton transfer is realised as a stepwise process, while the coordinated proton transfer (both through the four-centre transition state and through the six-membered transition state with participation of an additional nucleophile molecule) is thermodynamically less favourable.



Scheme 15. Stepwise mechanism of the coupling of a CNXyl ligand in complex *cis*-$[PtCl_2(CNXyl)(CNMe)]$ with various NH-nucleophiles.

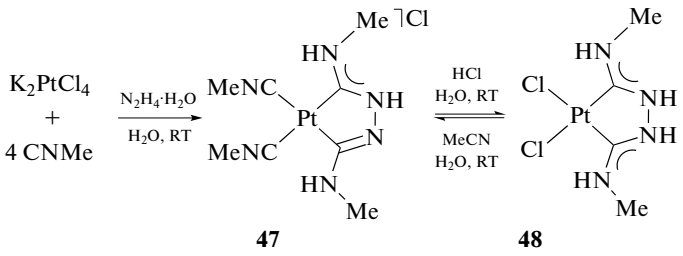
It should be noted that the use of β-amino-functionalised isocyanides which undergo spontaneous cyclisation upon coordination to metal centres [164, 187] serves as a reliable method for the synthesis of complexes with N-heterocyclic carbene ligands (Scheme 16) [3].



Scheme 16. Spontaneous cyclisation of β-amino-functionalised isocyanides.

Addition of N,N'-polynucleophiles. In the presence of an additional N'-nucleophilic centre in the molecule of the attaching N-nucleophile, compounds of a more complex structure, including those with C,N- and C,C'-chelate diaminocarbene ligands, can be formed. Examples of the combination of N,N'-polynucleophiles with isocyanide ligands in palladium(II) complexes have been analysed in detail in the review [138]; therefore, only general regularities characteristic of all platinum group metals are given below.

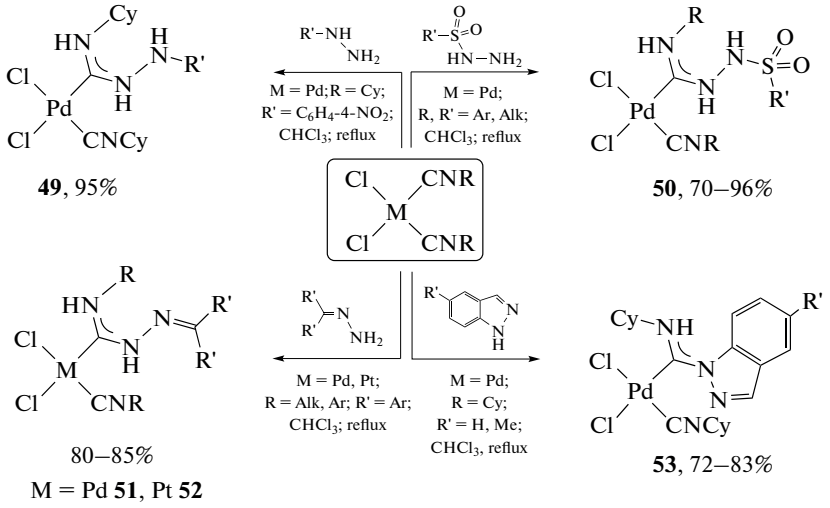
It is most logical to systematise the interaction of N,N'-polynucleophiles with isocyanide complexes based on the mutual arrangement of nucleophilic centres. For N,N'-polynucleophiles with adjacent nucleophilic centres that have the same (hydrazine, *N,N'*-dimethylhydrazine) or similar nucleophilicity of nitrogen atoms (*N*-monoalkyl-substituted hydrazines), the most characteristic are reactions with *cis*-bis-isocyanide or tetrakis-isocyanide complexes leading to the formation of a C,C'-chelate bis-diaminocarbene complex. Insofar as these compounds were originally described by Professor L. A. Chugaev [136], later they started to be called as "Chugaev type" complexes [188, 189]. The interaction of the in situ generated tetrakis(methylisocyanide)platinum(II) complex with hydrazine leads to the formation of red compound **47** (Chugaev's red salt, Scheme 17), which, under the action of a hydrochloric acid solution, converts into yellow complex **48** (Chugaev's yellow salt). Complex **48** can be converted back to **47** by interaction with methyl isocyanide [188].



Scheme 17. Interaction of in situ generated tetrakis(methyl isocyanide)complex of platinum(II) with hydrazine.

Later in the scientific groups of A. Balch [73, 166, 188, 190–194], L. M. Slaughter [32, 195–198], and T.S. Teets [40, 199] it was found that the reaction is of general nature and synthetic procedure can be extended to other isocyanides, substituted hydrazines, and metal centers such as palladium(II) [32, 188, 193, 195, 198], iridium(III) [40, 199], gold(III) [200], and iron(II) [73, 79]. The ease of formation of a C,C'-chelate product when using hydrazine and monosubstituted hydrazines can be explained by a combination of several co-directional factors, namely: (i) the nucleophilicity of hydrazine is higher than that of amines and ammonia, which is associated with the α-effect [201, 202]; (ii) the combination of the second isocyanide group occurs as an intramolecular process, which facilitates the reaction; (iii) the positive charge of the complex ion promotes a nucleophilic attack on the isocyanide ligand [203].

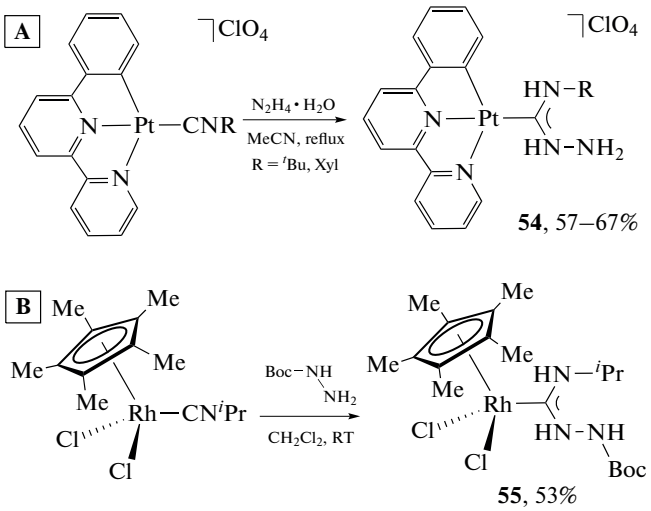
Hydrazine derivatives with a strongly reduced nucleophilicity of one of the reaction centres (hydrazones [34, 204–207], hydrazides of carboxylic and sulfonic acids [29, 37, 208], *N*-Boc-hydrazine [209], 4-nitrophenylhydrazine [210, 211], *N*,*N*-diphenylhydrazine [212], and indazoles [213]) lead predominantly to the formation of monoaddition products (Scheme 18). Despite the presence of two nucleophilic centres, only one of them is usually activated, while the second centre is deactivated by a structural fragment or an electron-withdrawing substituent reducing its nucleophilicity. It should be noted separately that the addition of indazole [213] to a coordinated isocyanide is one of the few examples [117, 213] when the NH-nucleophilic centre is included in the aromatic system. Compounds **53** have a structure similar to that of arylaminocarbene complexes [96]; in this case, diaminocarbene is stabilised due to partial disruption of the aromatic system of the heteroaryl fragment [213].



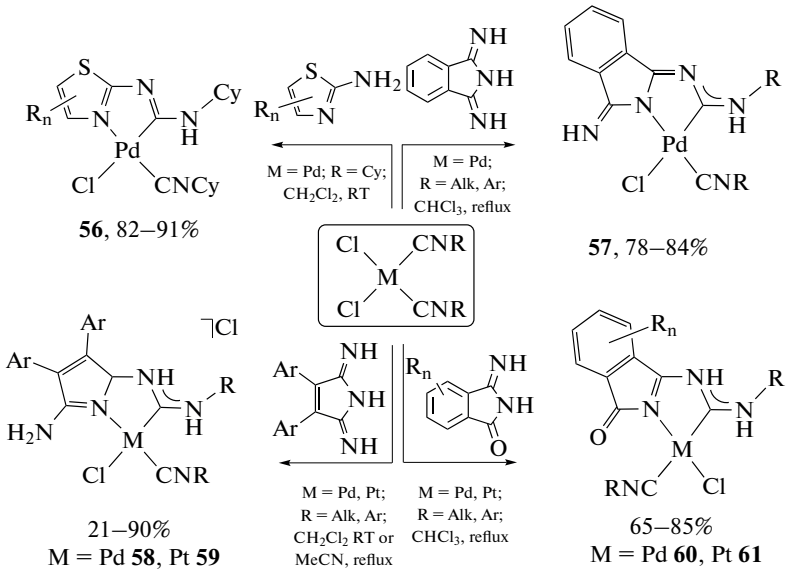
Scheme 18. Nucleophilic attack of hydrazine derivatives on isocyanides coordinated to palladium(II) and platinum(II) metal centres.

The interaction of monoisocyanide complexes with hydrazine derivatives, as expected, leads to the formation of monodentate acyclic diaminocarbene complexes, for example, the interaction of isocyanide complexes of platinum(II) with hydrazine (Scheme 19a) [214] and isocyanide complex of rhodium(III) with *N*-Boc-hydrazine (Scheme 19b) [209].

Symmetrical and unsymmetrical N=C–N polynucleophiles, namely 2-amino azaheterocycles [38, 115, 215–221], 3-imine-isoindolin-1-ones [35, 222, 223], isoindolin-1,3-diimines [224], 1*H*-pyrol-2,5-diimines [36, 225, 226], amidines [116, 227], and *N*,*N*'-diphenylguanidine [228], react with isocyanide ligands in *cis*- $[MCl_2(CNR)_2]$ (M = Pd, Pt) by only one of its nucleophilic centres, while the second nucleophilic nitrogen atom is coordinated to the metal centre, forming a C,N-chelate diaminocarbene ligand (Scheme 20). The general regularity of the reactions of *cis*- $[MCl_2(CNR)_2]$ (M = Pd, Pt) with the indicated N=C–N polynucleophiles is that the interaction proceeds in two stages. First, one N-donor centre is coordinated to the metal centre, as a rule, by substitution of the halide ligand, and then an intramolecular nucleophilic attack by another nucleophilic centre of the N-coordinated polynucleophile at the triple CN bond of the isocyanide proceeds.



Scheme 19. Interaction of monoisocyanide complexes of platinum(II) (A) and rhodium(III) (B) with hydrazine derivatives.



Scheme 20. Coupling of symmetric and asymmetric polynucleophiles N=C–N with isocyanides in *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt) complexes.

The combination of unsymmetrical N=C–N polynucleophiles, such as *N*,*N*'-diphenylguanidine [228] and *N*-phenylbenzamidine [227], leads to the formation of regioisomeric diaminocarbene complexes (Scheme 21). In solution, *N*,*N*'-diphenylguanidine and *N*-phenylbenzamidine exist in tautomeric equilibrium, due to an intramolecular process of proton transfer between N-centres; due to this tautomeric equilibrium, the N-donor centres are similar in their nucleophilicity.

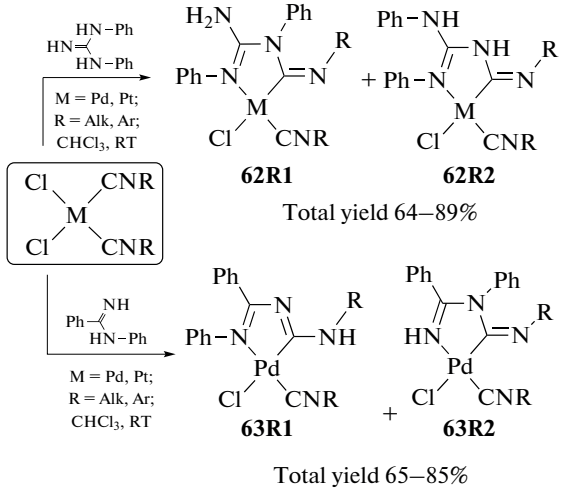
The coordination of *N*,*N*'-diphenylguanidine to the metal centre, which occurs at the initial stage of the reaction with the replacement of the chloride ligand, in all cases occurs with the PhN=C fragment [228]. The subsequent stage of nucleophilic coupling occurs intramolecularly when the carbon atom of the coordinated isocyanide is attacked by one of the two remaining donor centres, namely NHPh (regioisomer **62R1**) or NH_2 (regioisomer **62R2**), which leads to the formation of regioisomeric C,N-chelate diaminocarbene complexes **62** (Scheme 21). The regioisomeric composition is completely defined by the nature of the substituent in the isocyanide ligand; varying the solvent and/or conditions does not lead to a change in the

isomeric composition of the reaction mixture. In addition, for both metal centres, the coupling leads to the regioisomeric mixture of the same composition. The involvement of aryl isocyanides in the reaction leads predominantly to the formation of regioisomer **62R1**, while the use of complexes with alkyl isocyanides increases the proportion of regioisomer **62R2**.

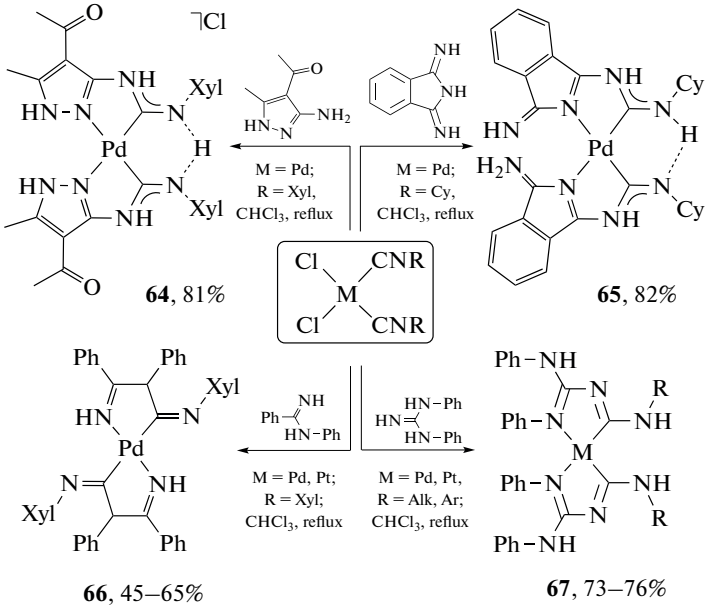
In the case of *N*-phenylbenzamidine, the regioisomeric composition is also determined by the nature of the substituent in the isocyanide ligand [227]. When an aromatic isocyanide (R = Xyl) is used, *N*-phenylbenzamidine is coordinated to the metal centre by the HN=C centre, and the nucleophilic attack is carried out by the NHPh centre of the amidine (**63R1**). If the substituent is a *tert*-butyl group (R = ^{t}Bu), the opposite situation is observed: the amidine is coordinated by the NHPh centre, and the addition to the isocyanide occurs via the HN=C (**63R2**) nucleophilic centre. When cyclohexyl isocyanide (R = Cy) is used, both regioisomers (**63R1** and **63R2**) are formed.

The intramolecular nature of the addition of N=C–N polynucleophiles accelerates the reaction and also makes it possible to form bis-diaminocarbene complexes from bis-isocyanide complexes *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt) when the reaction is carried out in an excess of nucleophile and/or under more stringent conditions (Scheme 22) [216, 224, 227, 228].

Bis-diaminocarbenes **66** and **67** can also be obtained when complexes **62** and **63** were allowed to react with an additional amount of the corresponding nucleophile [227, 228].



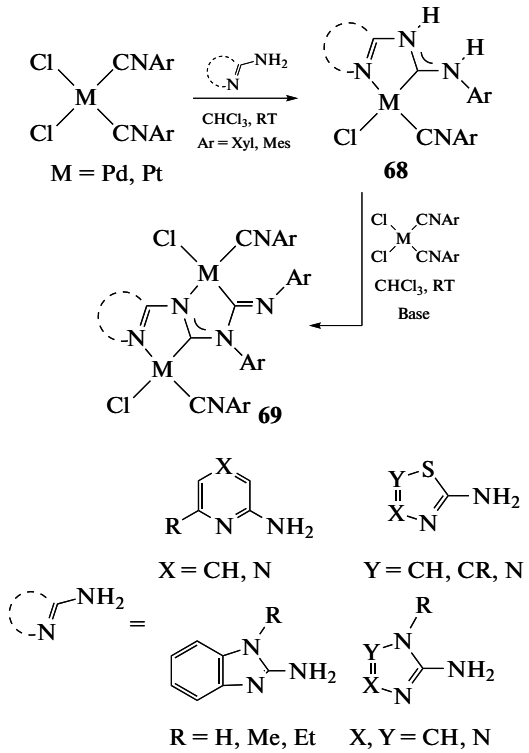
Scheme 21. Coupling of *N,N'*-diphenylguanidine and *N*-phenylbenzamidine with isocyanides in palladium(II) and platinum(II) complexes, leading to the formation of regioisomeric diaminocarbene complexes.



Scheme 22. Formation of bis-diaminocarbene complexes from bis-isocyanide complexes *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt).

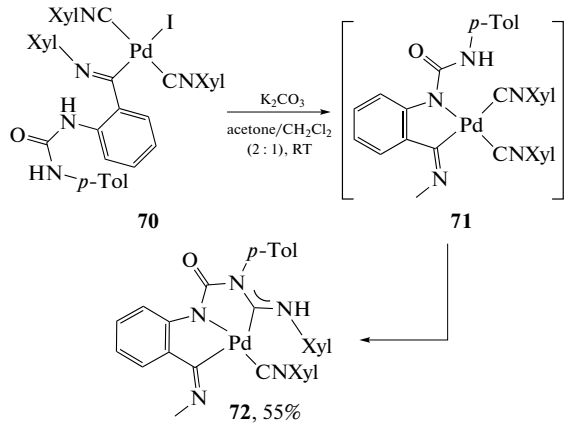
Diaminocarbene complexes of palladium(II) and platinum(II) **68** formed as a result of the reaction of nucleophilic coupling of aryl isocyanides in *cis*-$[MCl_2(CNAr)_2]$ (M = Pd, Pt) with α-amino azaheterocycles, can react with the second molecule of the isocyanide complex of *cis*-$[MCl_2(CNAr)_2]$ with the

formation of binuclear diaminocarbene complexes **69** (Scheme 23, the reactivity of acyclic diaminocarbene in transition metal complexes is described in detail in the review [28]) [38, 115, 215–217, 219–221, 229].



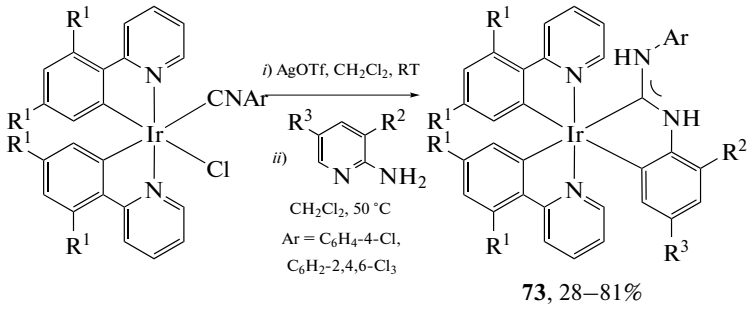
Scheme 23. Interaction of diaminocarbene complexes of palladium(II) and platinum(II) with initial isocyanide complex *cis*-$[MCl_2(CNAr)_2]$, leading to binuclear diaminocarbene derivatives.

The synthesis of a palladium(II) complex **72** with a diaminocarbene ligand of the C,N,C-pincer type can also be considered as one of the examples for the addition of NCN nucleophiles (Scheme 24) [230]. Compound **70**, containing a monodentate ligand with a urea fragment, under basic conditions is annelated twice leading to **72**. The reaction mechanism consists in deprotonation of one of the acidic (NH) hydrogen atoms of the urea fragment with a base and substitution of the iodide ligand with the formation of intermediate **71**. Under the reaction conditions, intermediate **71** spontaneously cyclises by intramolecular nucleophilic addition of the second N-donor group of urea to the coordinated isocyanide.



Scheme 24. Synthesis of palladium(II) complex with diaminocarbene ligand of C,N,C-pincer type.

The interaction of isocyanide complexes of iridium(III) with α-amino azaheterocycles also leads to the formation of compounds **73** with a C,N-chelate diaminocarbene ligand; however, in the case of this metal centre, additional use of silver salts is necessary for preliminary removal of halide ligands due to the high kinetic inertness of the iridium metal centre(III) in ligand metathesis reactions (Scheme 25) [121].

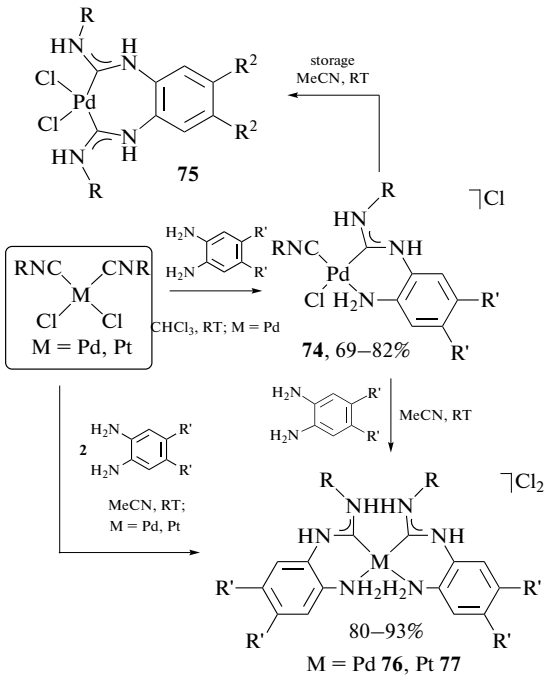


Scheme 25. Interaction of isocyanide complexes of iridium (III) with α-aminoazheterocycles.

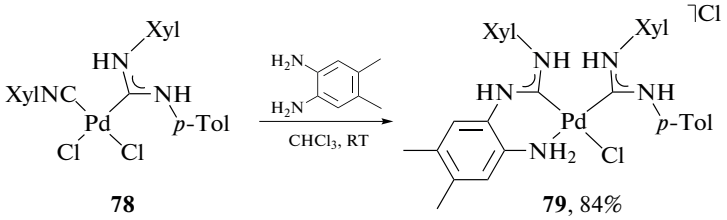
In 1,2- and 1,3-diamine molecules, nucleophilic centres are located at different carbon atoms. When nucleophilic centres are separated by carbon atoms, on the one hand, their mutual influence on each other decreases, and on the other hand, the structure becomes more flexible, which makes it possible to form complexes with C,N- or C,C'-chelate diaminocarbene ligands during the interaction of these nucle-

ophiles with isocyanide complexes of platinum group metals. The interaction of palladium(II) isocyanide complexes, *cis*-$[PdCl_2(CNR)_2]$ and *o*-phenylenediamines, depending on the stoichiometry of the starting materials and reaction conditions, can lead to compounds of three types (Scheme 26). In all cases, both amino groups interact and the product carries chelated diaminocarbene ligand [103]. On the basis of kinetic studies in [154], it was found that the first stage of reaction between *cis*-$[PdCl_2(CNR)_2]$ and *o*-phenylenediamines is the reversible substitution of the chloride ligand followed by intramolecular nucleophilic addition.

Due to an intramolecular nature of the coupling of 1,2-diamines with coordinated isocyanides, the coupling process occurs even in the case of mixed diaminocarbene/isocyanide complexes, which, as a rule, do not react with monofunctional nucleophiles. Bis-diaminocarbenes **76** can be prepared by reacting **74** with an additional amount of the corresponding *o*-phenylenediamine (Scheme 26) [103]. The interaction of diaminocarbene complex **78** with 1,2-diamine leads to bis-diaminocarbene complex **79** with two types of ADC ligands, namely, monodentate and C,N-chelate (Scheme 27) [154].



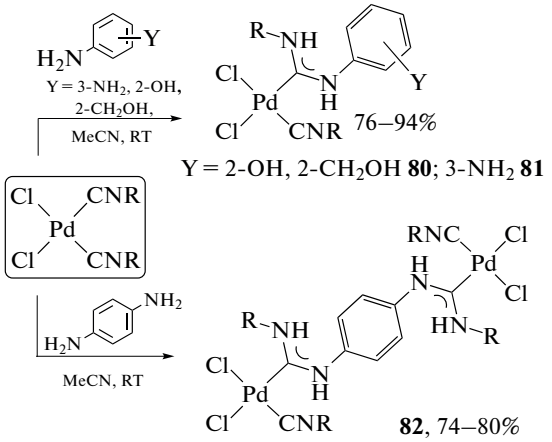
Scheme 26. Interaction of isocyanide complexes of *cis*-$[PdCl_2(CNR)_2]$ with *ortho*-phenylenediamines.



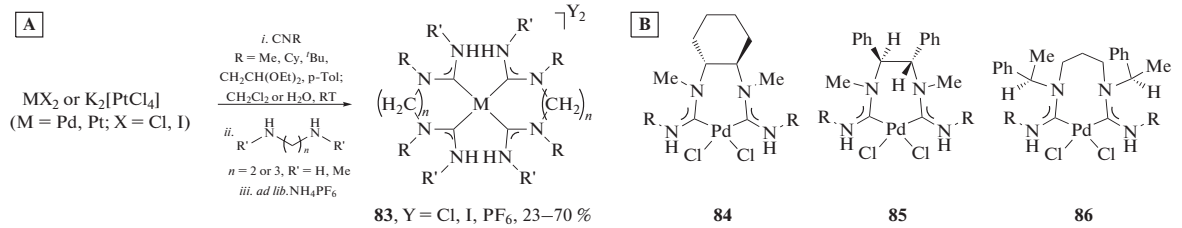
Scheme 27. Formation of a bis-diaminocarbene palladium(II) complex containing two types of ADC ligands.

The interaction of complexes *cis*-$[PdCl_2(CNR)_2]$ with *o*-aminophenol and *o*-aminobenzyl alcohol with the OH group as the second attacking centre (much less basic than NH_2 in *o*-phenylenediamines) leads exclusively to monodentate diaminocarbene complexes **80** (Scheme 28). *m*-Phenylenediamine and *p*-phenylenediamine also interact with *cis*-$[PdCl_2(CNR)_2]$, but the reaction occurs only at one isocyanide ligand (Scheme 28). *m*-Phenylenediamine reacts with only one amino group, forming complexes **81**; *p*-phenylenediamine participates in the reaction with both amino groups, each of which combines with a separate *cis*-$[PdCl_2(CNR)_2]$ molecule to form binuclear compounds **82**.

Homoleptic complexes of palladium(II) and platinum(II) **83**, containing two C,C-chelate bis-diaminocarbene ligands, can be synthesised by one-pot interaction of the corresponding metal salt, isocyanide and 1,2-diaminoethane or 1,3- diaminopropane (Scheme 29a) [231].



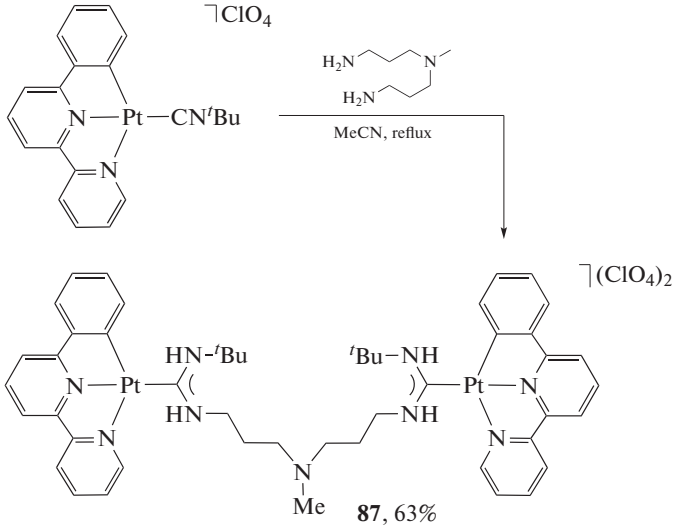
Scheme 28. Interaction of complexes *cis*-$[PdCl_2(CNR)_2]$ with *ortho*-aminophenol and *ortho*-aminobenzyl alcohol.



Scheme 29. (a) Preparation of homoleptic complexes of palladium(II) and platinum(II) containing two C,C-chelate (bis-diaminocarbene) ligands; (b) examples of chiral C,C-chelate (bis-diaminocarbene) complexes of palladium(II).

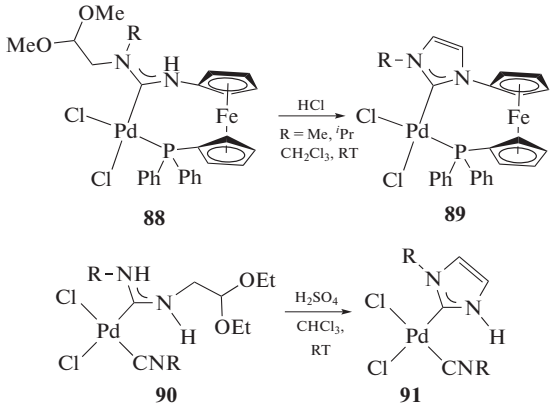
The interaction of optically active diamines, namely substituted 1,2-diaminoethanes [232, 233] and 1,3-diaminopropane [234] with *cis*-$[PdCl_2(CNC_6H_4\text{-}4\text{-}CF_3)_2]$, can be used to obtain chiral C,C-chelate bis-diaminocarbene complexes of palladium(II) **84**–**86** (Scheme 29b). In contrast to the combination of hydrazines, the combination of 1,2- and 1,3-diamines with isocyanide ligands requires more drastic reaction conditions (higher temperature, longer time).

Aliphatic diamines, in which nucleophilic centres are separated from each other by more than three atoms, can react with two equivalents of isocyanide complexes to form binuclear compounds; in this case, the resulting bis-diaminocarbene ligand acts as a linker linking two metal centres (Scheme 30) [214].



Scheme 30. Bis-diaminocarbene linker connecting two metal centres.

Therefore, the method for the synthesis of diaminocarbene complexes based on the reactions of metal-activated isocyanides with N-centred nucleophiles is simple and versatile and leads to acyclic diaminocarbene complexes of platinum group metals with a defined structure, which is controlled by the structure of nucleophile and the choice of the reaction conditions. This method complies with the principles of "green chemistry", as it is "atom-economic" and leads to high yields of target products. Note that the complexes formed during the metal-promoted coupling contain at least one hydrogen substituent at the nitrogen atom of the diaminocarbene fragment; therefore, such compounds can be further functionalised using alkylation or annulation reactions (Scheme 31, the reactivity of acyclic diaminocarbenes in transition metal complexes is described in detail in the review [28]).

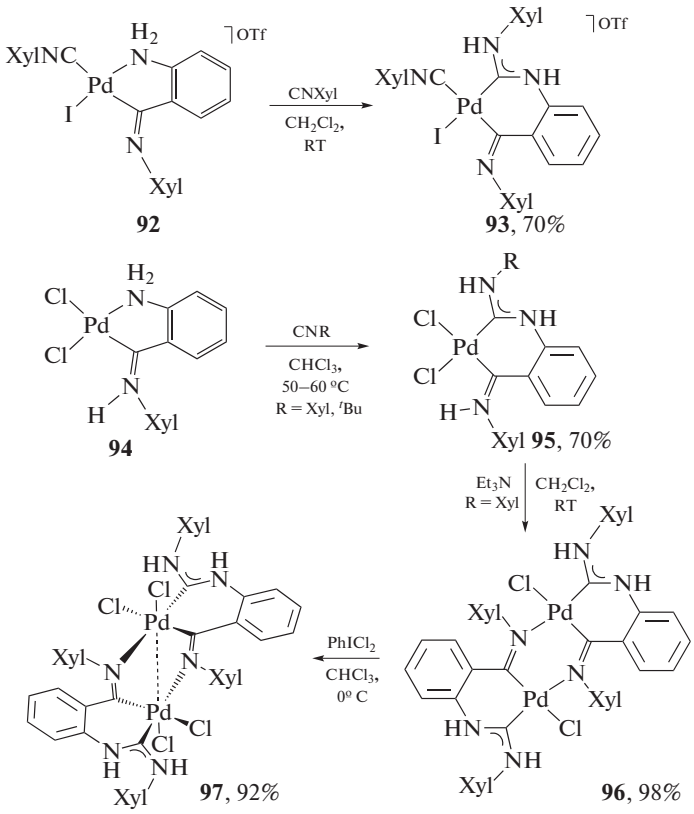


Scheme 31. Examples of annelation of acyclic diaminocarbene complexes.

Insertion of Isocyanides at the Metal-Nitrogen Bond

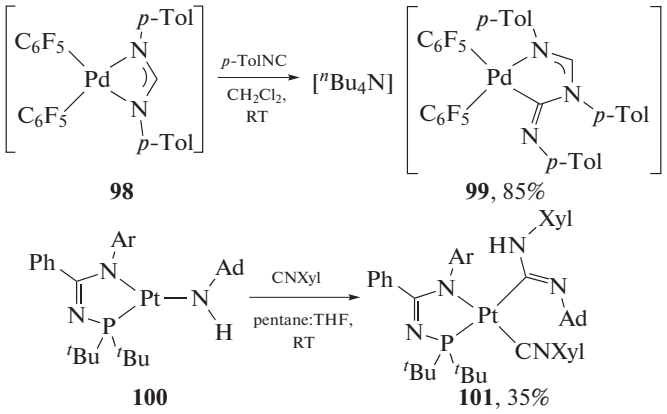
The insertion of isocyanide at the M–N bond leads to the formation of a diaminocarbene fragment; at the same time, classical diaminocarbenes are formed from amino complexes with a formally neutral N-donor ligand, while in the case of amido complexes with a coordinated anionic N-donor centre, the reaction of isocyanide insertion leads to deprotonated diaminocarbenes. It should be noted that among the metal-catalysed and metal-promoted transformations of isocyanides, their insertion into the metal-element bond represents the most common reaction [135, 235]. Isocyanide insertions are important not only in chemistry of transition metal complexes for obtaining libraries of various organometallic compounds but also in organic synthesis, since many metal-catalysed preparation of azaheterocyclic systems or isocyanide polymerisation include the insertion reaction as an intermediate stage [135, 235–240]. The introduction of isocyanides at the M–N bond mainly occurs through the initial coordination of the lone pair of the carbon atom of the isocyanide to the metal centre followed by rapid incorporation into the metal–nitrogen bond [135].

Palladium(II) complexes **92** and **94**, which have an aromatic amine fragment in one of the ligands, interact with isocyanides under mild conditions; the reaction leads to the diaminocarbene complexes **93** and **94** in good yield (Scheme 32) [241]. The binuclear complex **96** obtained by deprotonation of **95** can be oxidised to compound **97**, which is a palladium(III) diaminocarbene complex.



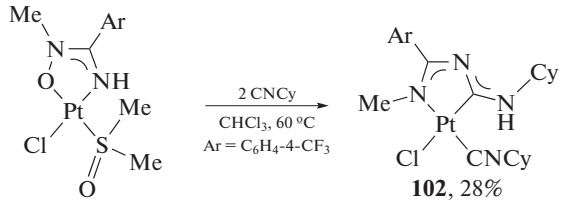
Scheme 32. Insertion of isocyanides into palladium(II) complexes containing aromatic amines.

The deprotonated diaminocarbene complexes of palladium(II) **99** [242] and platinum(II) **101** [243] were synthesised by inserting an isocyanide at the M–N bond into the corresponding amide complexes **98** and **100** (Scheme 33). It should be noted that, despite the fact that the starting compounds contain several N-donor ligands, the insertion reaction proceeds selectively only at one M–N bond.



Scheme 33. Preparation of deprotonated diaminocarbene complexes of palladium(II) and platinum(II) by introducing isocyanide at the M–N bond into the corresponding amide complexes.

The C,N-chelate ADC complex of platinum(II) **102** was synthesised from the aminonitrone complex (Scheme 34) [244]. The reaction proceeds formally through the insertion of isocyanide at the Pt–N bond followed by a deoxygenation step using a second isocyanide molecule. The disadvantage of this method is the use of a two-fold excess of isocyanide and a low preparative yield of the product.



Scheme 34. Synthesis of a C,N-chelated ADC-derivative of platinum(II) from the starting aminonitrone complex.

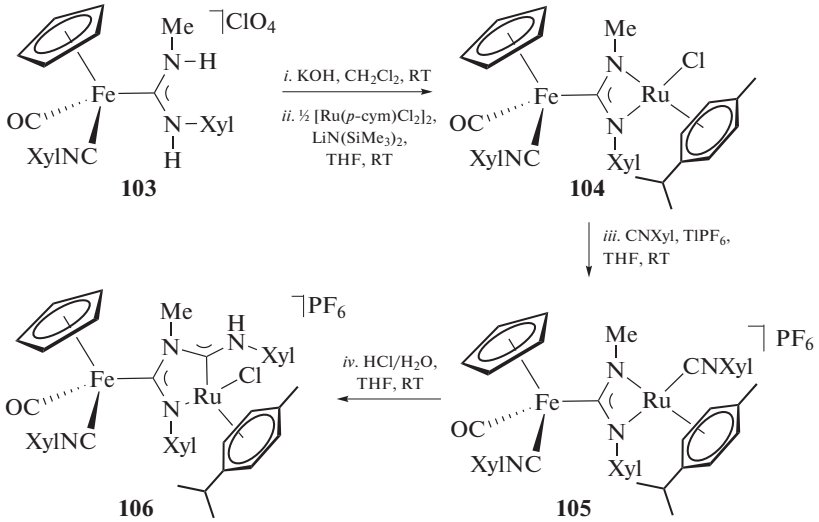
An example of the synthesis of the ADC complex of ruthenium(II) **106** was reported [77] (Scheme 35). The synthetic pathway is based on the N-metalation of the ADC complex of iron(II) **103** with a dimer of ruthenium dichloride followed by the insertion of isocyanide at the Ru–N bond. The heterobimetallic complex contains two diaminocarbene moieties bound to the ruthenium atom; the acyclic diaminocarbene moiety is part of a five-membered metal-N-heterocyclic carbene bound to iron.

APPLICATION OF COMPLEXES OF PLATINUM GROUP METALS WITH ACYCLIC DIAMINOCARBENE LIGANDS

Application in Catalysis of Organic Processes

The first works reporting the use of acyclic diaminocarbene complexes as catalysts were published in 2005 evaluating their application in palladium-catalysed reactions of aryl halides, namely, Suzuki cross-coupling and Heck reaction [131, 195]. These studies clearly demonstrated the similarity of the catalytic properties of complexes with acyclic and heterocyclic diaminocarbene ligands, which led to an avalanche-like growth of research in the field of the catalytic use of acyclic diaminocarbene complexes. While some researchers openly refused to acknowledge the promising nature of complexes with acyclic diaminocarbenes ("There is little hope that acyclic carbenes could find applications as ligands in transition metal catalysts" [245]), others improved catalytic systems. In 2012, two review papers were published simultaneously, which were prepared by the group of Academician RAS V. Yu. Kukushkin [26] and in the group of Prof. L. M. Slaughter [27], which summarised the results of studies of the catalytic activity of acyclic diaminocarbene complexes in the period from 2005 to 2011. The main differences between cyclic and acyclic diaminocarbene complexes important for their catalytic application as suggested by the authors of the above-mentioned reviews are (i) the conformational flexibility of acyclic diaminocarbenes, which allows

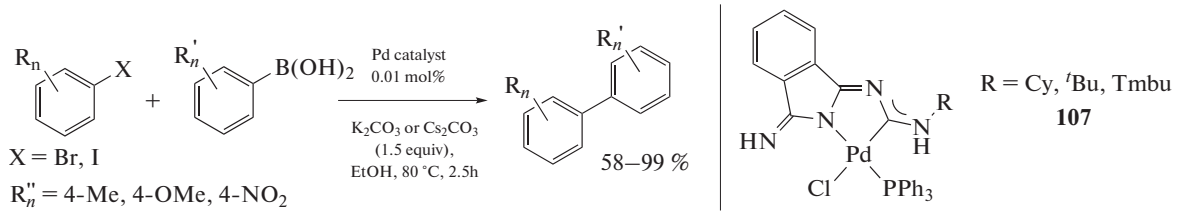
the ligand to adopt several conformations due to rotation around the C–N bonds, and (ii) the modular synthesis method that makes the library of M-ADC complexes synthetically available with a wide range of donor and steric characteristics, as well as functionalised compounds. To prevent repetition, this review considers the catalytic systems published from 2012 to the present.



Scheme 35. N-metalation of the ADC-complex of iron(II) **103** with a dimer of ruthenium dichloride followed by the introduction of isocyanide at the Ru–N bond.

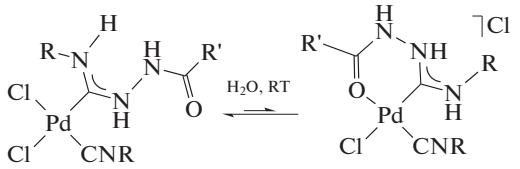
Discovered in the 1970s palladium-catalysed cross-coupling reactions with the participation of organometallic compounds and aryl/alkenyl halides, allowing the creation of C_{sp2}–C_{sp2} and C_{sp2}–C_{sp} bonds, as well as C_{sp2}–X carbon–heteroatom bonds, currently are one of the most used tools of organic synthesis [246–248]. Despite the fact that cross-coupling reactions can be catalysed by a wide range of catalysts, including compounds of less expensive metals such as nickel [249–253], cobalt [254], and iron [255–257], catalysis with palladium catalysts has a number of advantages: milder reaction conditions, high selectivity, the possibility of using deactivated substrates and conducting cooperative catalysis [258, 259].

The Suzuki–Miyaura cross-coupling reaction, which is a combination of arylboronic acids with aryl/alkenyl halides, has established itself as one of the most convenient and simple methods for creating biaryl/arylalkenyl fragments [260, 261]. Organoboron compounds differ from organolithium, organomagnesium, and organozinc compounds by the tolerance of many functional groups and higher stability, while their combination with aryl/vinyl halides usually occurs in high yield. In [222, 224], the catalytic activity in the Suzuki cross-coupling reaction of mixed ligand diaminocarbene/isocyanide complexes **57** and **60** and diaminocarbene/phosphine complexes **107** was studied (Scheme 36). Catalysts **60** and **107** exhibited similarly high catalytic activity. Under optimised conditions (ethanol, K_2CO_3 or Cs_2CO_3, 2–2.5 h, 80°C), the yield of biaryls was 58–99%, with the catalyst turnover numbers reaching 5.8×10^4 for aryl bromides and 9.8×10^4 for substituted aryl iodides. As in the case of other catalytic systems based on Pd-ADCs [206], for systems based on **60** and **107** there are no differences between experiments carried out in a dry solvent and in an inert gas atmosphere, with similar results obtained in air and in undried EtOH. Thus, catalytic systems based on **60** and **107** can be successfully used in air and in an undried solvent that does not require additional degassing and azeotropic drying. It should be noted that diaminocarbene/phosphine derivatives **107** are more efficient catalysts for Suzuki reactions compared to the structurally similar diaminocarbene/isocyanide derivatives **57**, which contain the isocyanide ligand instead of the phosphine ligand; in addition, under the experimental conditions, catalysts **107** are an order of magnitude more active than *cis*-$[PdCl_2(PPh_3)_2]$. Palladium complexes **49** [210], **50** [37], **51** [205], and **63** [31] are also effective catalysts for the Suzuki reaction.



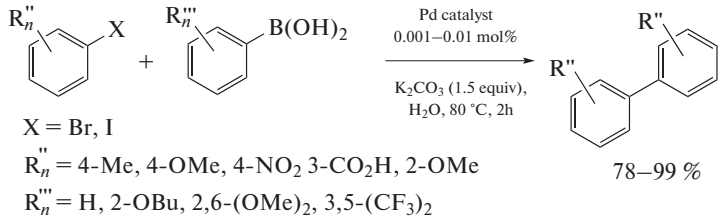
Scheme 36. (a) Suzuki cross-coupling of aryl bromides and aryl iodides with substituted phenylboronic acids; (b) catalytically highly active palladium(II) derivatives containing diaminocarbene/phosphine ligands.

An important modification of the Suzuki reaction is its implementation in an aqueous medium, which is especially important for the modification of biomolecules, and also promising from an economic and environmental point of view [262, 263]. The study [37] describes the use of Pd-ADC-based catalysts for carrying out the Suzuki cross-coupling reaction in an aqueous medium. Compounds **50** and **108** are moderately soluble in water (0.01–0.02 mmol/L) and can be extracted from aqueous solutions unchanged, which attests their hydrolytic stability. One of the possible reasons for the moderate solubility in water for the compounds **50** and **108** is their propensity to intramolecular cyclisation in aqueous solution with the formation of six-membered C,O-chelate ring derivatives (Scheme 37) [264]. Cross-coupling of aryl bromides and aryl iodides with substituted phenylboronic acids occurs when 0.01 mol% palladium catalysts **50** or **108** is used and leads to biaryl derivatives with a yield of up to 98% (Scheme 38). Scope for this catalytic system include a range of bromobenzene derivatives and arylboronic acids, including sterically hindered ones. Activated aryl chlorides can also be converted into diaryl derivatives under similar conditions (100°C, 3 h); at the same time, non-activated aryl chlorides do not enter into the reaction even when the catalyst loading is increased to 1 mol %. It should be noted that at the time of the publication of this work, Pd-ADC catalysts **50** and **108** are the most efficient for carrying out the Suzuki reaction in an aqueous medium [265–268]. These catalysts can be used in an alcohol medium, showing comparable and higher catalytic activity.

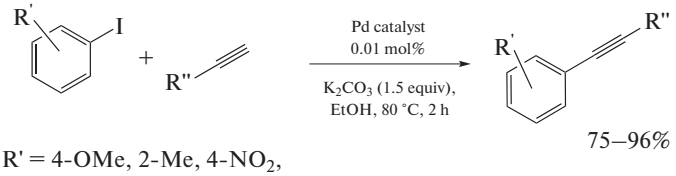


Scheme 37. Aqueous solubility of diaminocarbene derivatives related to the intramolecular cyclisation.

Cross-coupling of terminal acetylenes with aryl/alkenyl halides catalysed by palladium compounds, known as Sonogashira reaction, is a convenient and effective method for the synthesis of internal alkynes and enines [269–271]. The Sonogashira reaction in the classical version is catalysed simultaneously by compounds of two metals, namely palladium and copper; however, the use of such a bimetallic system negatively affects the selectivity of the reaction due to the formation of a byproduct of homocoupling, which is butadiine [26, 27, 272]. Pd-ADC complexes **60** and **108** exhibited high catalytic activity in the Sonogashira reaction in the "copper-free" version (Scheme 39) [29]. The reaction proceeds in undried EtOH in the presence of K_2CO_3 as a base and at a loading of **60** and **108** catalysts being 0.01 mol %. Aryl iodide substrates containing substituents with different electronic and steric properties react with a variety of terminal alkynes to form the corresponding internal alkynes. Thus, the versatility of the catalytic system is demonstrated. Palladium compounds **49** [212], **51** [204], and **63** [227] are also effective catalysts for the Sonogashira reaction under similar conditions.



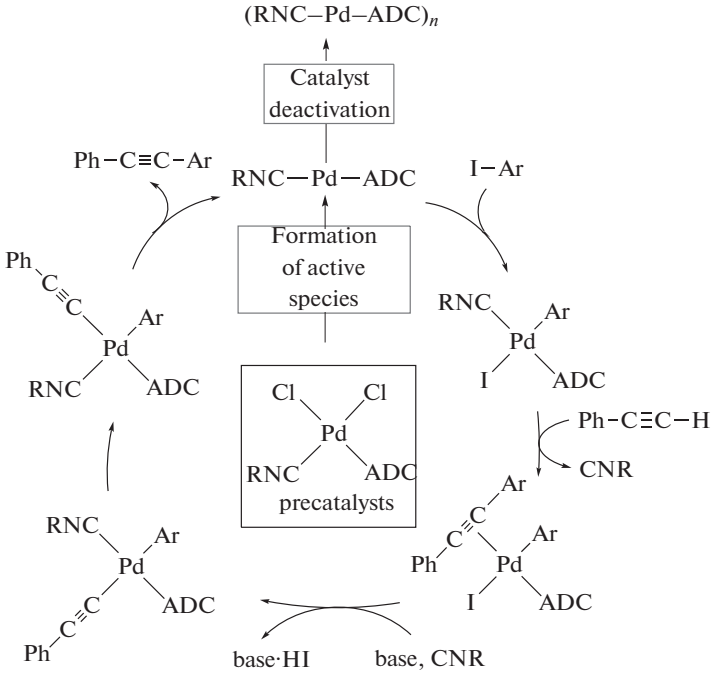
Scheme 38. Suzuki cross-coupling of aryl bromides and aryl iodides with substituted phenylboronic acids, catalysed by water-soluble diaminocarbene complexes of palladium(II).



R' = 4-OMe, 2-Me, 4-NO_2,
2,3-$(OMe)_2$-5-C(O)H;
R'' = Ph, 2-Me, 3-Me, 2-F

Scheme 39. High catalytic activity of Pd-ADC complexes in the copper-free variant of Sonogashira coupling.

The complex used as pre-catalysts in catalytic reactions is a well-defined species; however, in most cases, the real structure of catalytically active particles is unknown [273–275]. The studies of the mechanism of the catalytic process [29] indicate that in a system based on compounds **60** and **108**, the catalytic cycle is based on a molecular mechanism (Scheme 40). The formation of catalytically active particles occurs with the elimination of halogen ligands, while isocyanide and diaminocarbene act as stabilising ligands. The deactivation of catalysts is associated with the formation of catalytically inactive palladium clusters stabilised by diaminocarbene and isocyanide ligands.

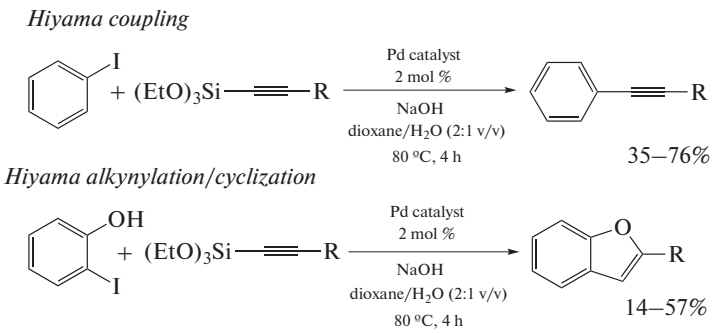


Scheme 40. Proposed mechanism for the catalytic activity of Pd-ADC-complexes in the copper-free variant of Sonogashira coupling.

In [276, 277], the possibility for the in situ preparation of Pd-ADC catalysts by nucleophilic addition of NH-nucleophiles to isocyanide ligands in palladium(II) complexes was studied. Using model Suzuki reaction of 4-iodanisole or 4-bromoanisole and phenylboronic acid, it was demonstrated that Pd-ADC complexes formed in situ by the interaction of 4-nitrophenylhydrazine (complex **49**), benzhydrazide (complex **108a**, R = Cy, R' = Ph), and morpholine (complex **109**) with *cis*-$[PdCl_2(CNCy)_2]$ allow the cross-coupling reaction to be carried out under mild conditions (EtOH, refluxing for 2 h in the presence of K_2CO_3) [277]. The in situ prepared Pd-ADC complexes exhibit similar catalytic activity to the previously isolated compound **109**; morpholine was found to be the best among the studied nucleophiles for the activation of the palladium(II) isocyanide complex in the Suzuki cross-coupling. The same approach has been successfully applied for the Sonogashira cross-coupling using 4-iodanisole and phenylacetylene; in

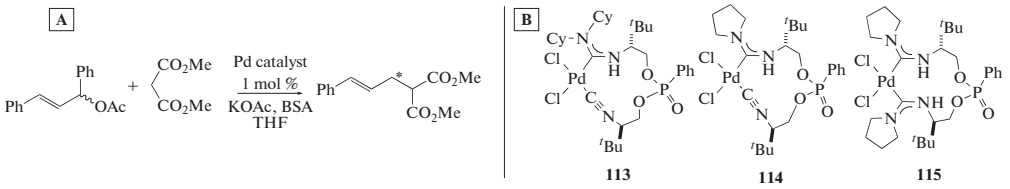
this case, the highest yield of the cross-coupling product was achieved when benzhydrazide was used as an "activator" of the isocyanide complex [276].

The Hiyama cross-coupling reaction is based on the use of organosilicon compounds [278, 279] and is an important approach complementary to the Suzuki and Sonogashira reactions. It was demonstrated [148] that Pd-ADC complexes **110**–**112** can be used as catalysts for the Hiyama cross-coupling reaction. Under optimised conditions, namely, with NaOH as a base and a 1,4-dioxane/water mixture (2 : 1 vol) as a solvent, the catalytic system enables the formation of disubstituted acetylenes from iodobenzene and various triethoxysilylalkines (Scheme 41). Catalysts **110**–**112** can also be used in the tandem Hiyama cross-coupling reaction followed by cyclisation between 2-iodophenol and triethoxysilylalkines, providing a convenient synthetic route to biologically relevant benzofuran derivatives.



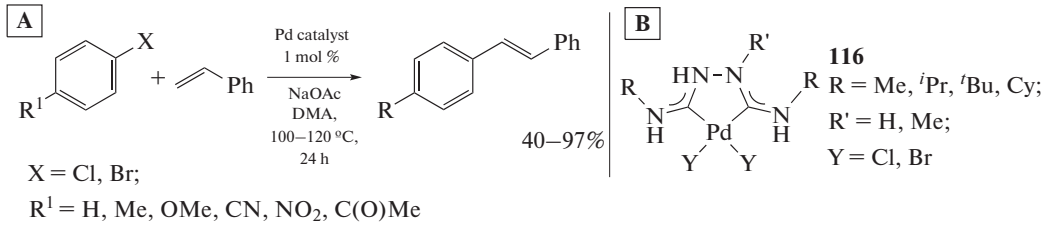
Scheme 41. Application of Pd-ADC-complexes as catalysts for the Hiyama cross-coupling reaction.

Optically active Pd-ADC complexes **113**–**115** were studied as catalysts for the reaction of asymmetric intermolecular allyl alkylation (Scheme 42) [145]. The use of catalyst **114** allows the catalytic reaction to be carried out in a short time with high yield and moderate enantioselectivity (catalyst **113**: yield 87% (enantiomeric excess ee 6%, S) after 18 h; catalyst **114**: yield 100% (ee 45%, S) after 2 h). The catalytic activity of bis-diaminocarbene complex **115** in both reactions was significantly lower than that of **113** and **114**. Compounds **113** and **114** were also catalytically active in the Suzuki reaction using substituted bromobenzenes (1 mol % catalyst, RT, 20 h, biaryl yield 75–84%).



Scheme 42. (a) Application of palladium(II) daminocarbene complexes as catalysts for the reaction of intermolecular asymmetric allyl alkylation; (b) structure of compounds **113**–**115**.

Palladium-catalysed interaction of aryl and alkenyl halides with alkenes, the Heck reaction, is one of the best and most productive modern methods for the preparation of terminal and internal alkenes [280, 281]. Chugaev-type diaminocarbene palladium(II) complexes were evaluated as catalysts for the Heck reaction (Scheme 43) [32]. Screening of a series of 10 structurally similar catalysts in the model reaction of 4-bromoacetophenone and styrene (1 mol %, AcONa, DMF, 100°C) revealed large variations in catalytic activity depending on the catalyst structure (stilbene yield 16–98%). Palladium dibromide complexes (Y = Br) exhibit significantly higher catalytic activity (36–98%) compared to chloride analogues (Y = Cl, 16–59%), which, in the authors' opinion, is associated with the greater lability of bromide ligands in catalytic conditions. Pd-ADC complex **116a** (R, R' = Me) was found to be the best catalyst (stilbene yield 98%).



Scheme 43. (a) Application of the Chugaev type diaminocarbene palladium(II) complexes as catalysts for the Heck reaction; (b) Pd-ADC species with the highest catalytic activity.

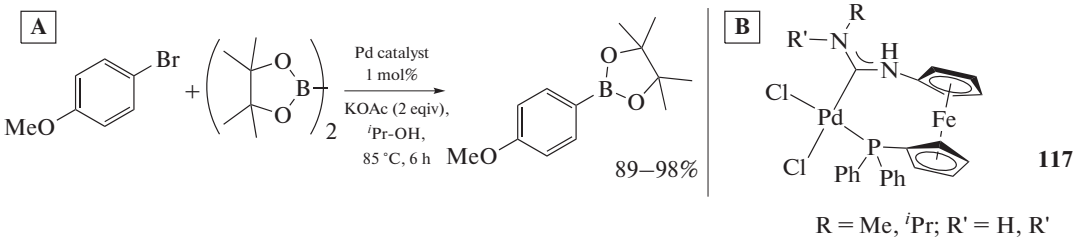
The scope of this catalytic system includes aryl bromides containing both electron-donor and electron-withdrawing substituents, which can be converted to the corresponding stilbenes in good yield. Aryl chlorides (4-nitrochloroaniline) activated by the strong electron-withdrawing substituents can also be converted to corresponding stilbenes. At the same time, aryl chlorides containing less electron-withdrawing substituents lead to the product in low yield or do not react at all.

When the reaction is carried out in an undried and not-degassed solvent, the yield of the target stilbenes is reduced by 34–40% compared to the reactions carried out in a nitrogen atmosphere and in a previously dried solvent. Note that, in contrast to the catalytic system for the Heck reaction, the previously published catalytic system for the Suzuki reaction based on compound **116** is not sensitive to moisture and atmospheric oxygen [197].

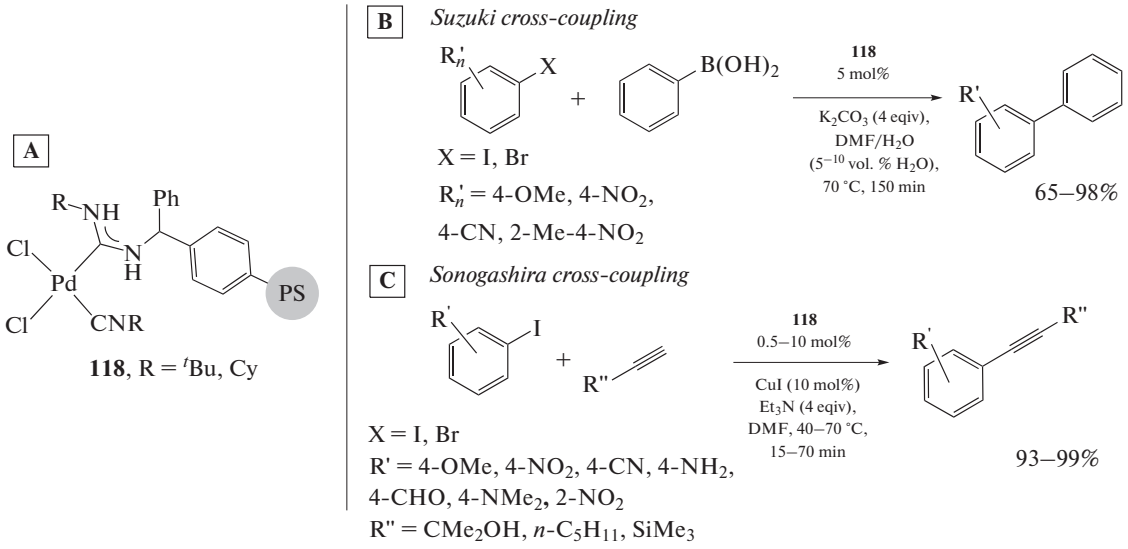
Esters of arylboronic acids are often used in organic synthesis in cross-coupling reactions to form C–C, C–O, C–N, and C–S bonds [282]. The modern most general method for the synthesis of esters of arylboronic acids is a recent approach based on the interaction of aryl halides and diborane derivatives catalysed by palladium complexes (borylation according to Miyaura) [283]. In [33], the possibility of using Pd-ADC complexes **117** as catalysts for the borylation of aryl bromides by the Miyaura method was shown (Scheme 44). The reaction leads to a good yield of the target arylboronic ether with almost complete absence of biaryl homocoupling products. Complexes **117** used as the catalyst outperformed the reference catalyst [$PdCl_2$(dppf)] both in terms of activity and selectivity.

The creation of recoverable and re-usable catalysts by immobilising highly active homogeneous complexes on a suitable support is an urgent line of research in the field of palladium-catalysed cross-coupling reactions [284, 285]. When using an immobilised catalyst, it can be simply removed from the reaction mixture and reused, while the product is not contaminated with transition metal compounds, which is especially important in the development of drugs [286]. Acyclic diaminocarbene complexes of palladium(II) **118** immobilised on a polystyrene support were synthesised [101] by the addition of the NH_2 group of a commercially available benzhydrylamide polystyrene resin to an isocyanide ligand in complexes [$PdCl_2(CNR)_2$] (13% carrier) modification of amino groups. Immobilised **118** were tested as catalysts in the Suzuki cross-coupling reaction using a number of aryl iodides and aryl bromides (Scheme 45). The optimal conditions for cross-coupling using **118** are the DMF–water system (5–10 vol % water) as a solvent and K_2CO_3 as a base. The authors showed the possibility of separating immobilised catalysts by filtration and their repeated use (up to three times) without losing catalytic activity. The study of catalysts by XPS before and after catalytic experiments showed that the oxidation state of palladium is preserved, indirectly evidencing that the structure of the immobilised complex remains unchanged in the course of the reaction.

Catalysts **118** also demonstrated high catalytic activity in the Sonogashira cross-coupling reaction for a wide range of substrates (65–98%) with the possibility of recycle up to eight times without significant loss of catalytic activity (Scheme 44). In the study of samples **118** by the XPS method, it was found that after the Sonogashira reaction, the oxidation state of palladium immobilised on the support changes from +2 to 0; therefore, compounds **118** in this reaction are more correctly called precatalysts.



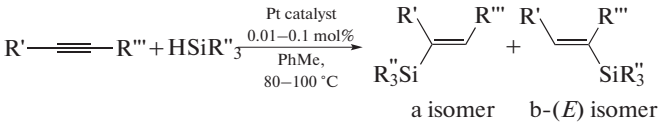
Scheme 44. (a) Reaction of aryl halides and diborane derivatives catalysed by palladium complexes (Miyaura reaction) (a); (b) highly efficient and selective catalyst for the Miyaura reaction containing a diaminocarbene ligand.



Scheme 45. (a) Acyclic diaminocarbene complexes of palladium(II) immobilised on a polystyrene support as catalysts for (b) Suzuki cross-coupling reaction and (c) Sonogashira cross-coupling reaction.

In [119], it was reported on the application of Pd-ADC complexes in the reaction of intermolecular amination of alkynes; the reaction proceeds leads to the low 20% yield of the hydroaminated product with the total alkyne conversion of 77%.

Hydrosilylation of unsaturated compounds is one of the fundamental approaches in the laboratory and industrial preparation of organosilicon compounds [287, 288]. Pt^{II}-ADC complexes **52** and **61** were studied as catalysts for the reaction of hydrosilylation of terminal and internal alkynes with hydrosilanes [34, 35]. The catalytic reaction was carried out at 80–100°C for 3–6 h in toluene (Scheme 46); the highest catalytic activity (yield 96%) was achieved using compound **61a** (R = C_6H_3–2-Cl–6-Me; R'^{n} = 3-Me).



Scheme 46. Reaction of hydrosilylation of terminal and internal alkynes with hydrosilanes catalysed by platinum(II) complexes with ADC ligands.

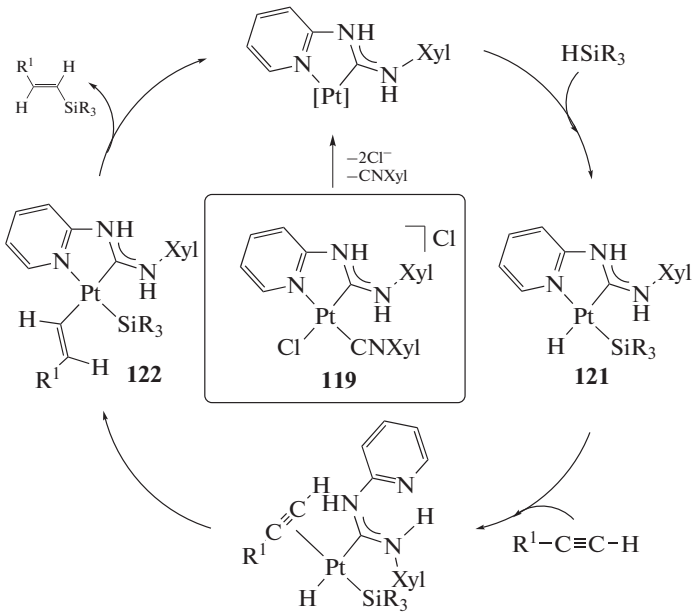
Hydrosilylation of terminal alkynes (PhC≡CH, ^{t}BuC≡CH, and 4-(^{t}Bu)C_6H_4C≡CH) by hydrosilanes (Et_3SiH, Pr_3SiH, $^i Pr_3SiH$, and $PhMe_2SiH$) in all cases proceeds with the formation of a mixture of α/β-isomers of silylated alkenes (α/β ratio from 81 : 19 to 5 : 95) with a total yield of 48–96%. The α/β isomer ratio depends on the substituents in both substrates; for example, the reaction of $^i Pr_3SiH$ with 4-(^{t}Bu)C_6H_4C≡CH gives the α-isomer of the silylated alkene as the main product (81 : 19), while the reaction of $PhMe_2SiH$ with ^{t}BuC≡CH gives β-isomer as the main product (5 : 95). Hydrosilylation of internal alkynes (PhC≡CPh, $Me(CH_2)_2C{\equiv}C(CH_2)_2Me$ and PhC≡CMe)Et_3SiH and $PhMe_2SiH$ leads to the corresponding trisubstituted silylated alkenes in 86–94% yield. Platinum complexes **59** [36] are also effective catalysts for the hydrosilylation of alkynes under similar conditions.

Reactions under the influence of visible light have become a powerful tool in modern organic synthesis. In this context, in recent years, photocatalysis with transition metal compounds is gaining popularity, in which the metal complex catalyst simultaneously serves as both a light-absorbing substance and a catalytic centre [289, 290]. The bond formation/breaking process for these visible light-induced transitions catalysed by transition metal compounds takes place with the direct involvement of the metal centre. The transformations are carried out in a single catalytic cycle, where the transition metal complex performs two functions simultaneously: it absorbs light and acts as a catalytically active particle. Although the advantages

of the latter type of catalytic system are obvious, precise tuning of such systems is currently difficult compared to cooperative systems because of the limited range of known photocatalytically active ligands and complexes, as well as because of the lack of knowledge about the mechanism of their catalytic action.

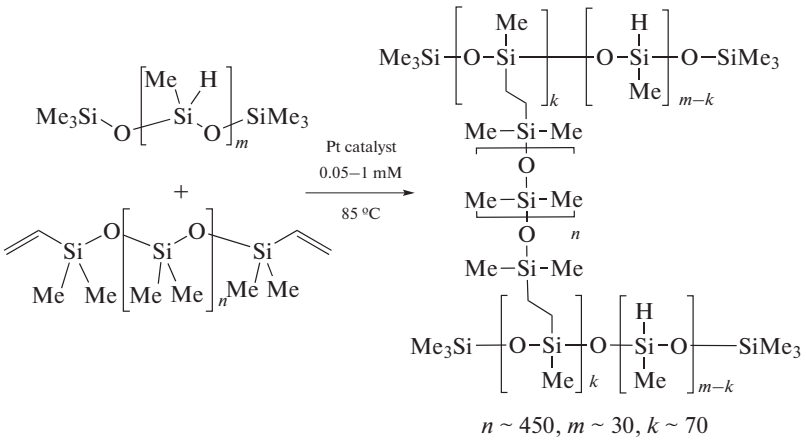
In [38], it was demonstrated for the first time that platinum(II) complexes with acyclic diaminocarbene ligands can be used as photocatalysts (Fig. 10). The hydrosilylation reaction catalysed by photoactive compounds **119** and **120** proceeds upon irradiation with blue light (400–500 nm, 36 W) and leads to silylated alkenes in a good yield (59–96%).

Studies of the mechanism have shown that irradiation with visible light is necessary at two stages of the catalytic cycle. First, light irradiation promotes the dissociation of isocyanide ligands from **119** and **120**, making the metal centre reducible with a silane substrate (Scheme 47). Oxidative addition of silane leads to product type **121**. Reversible photodissociation of the pyridine moiety of the C,N-bidentate aminocarbene ligand leads to a change in the coordination mode to C-monodentate, potentially facilitating substrate binding during catalysis. This is followed by the π-coordination of alkyne, its 1,2-migrating insertion at the Pt–H bond, or reductive elimination of the corresponding silylated products. In both **121** and **122**, the platinum centre has an oxidation state of +2, which is consistent with the initial loss of isocyanide and chloride ligands from the original precatalyst **119** and the reduction of the metal centre to platinum(0). The calculated quantum yield for the photocatalytic process is 0.2, which excludes the possibility of a radical chain path.



Scheme 47. Proposed mechanism of the photocatalytic action of platinum(II) complexes with acyclic diaminocarbene ligands in the hydrosilylation of alkynes.

Elastic organosilicon polymers, the so-called silicone elastomers, have found widespread use both in industry and in high-precision applications in recent decades due to the fact that cured silicone coatings are highly resistant to thermal, corrosion, and frictional effects. Conventional silicone coating preparation involves metal catalysed hydrosilylative crosslinking of vinyl and hydrogen-functional polydimethylsiloxanes. Ideally, the coating composition remains liquid at room temperature, but hardens quickly above 100°C, which allows the coated article to be used for further processing without refrigeration. In [36], platinum(II) complexes **59** were proposed as effective catalysts for the vulcanisation of siloxane elastomers; crosslinking occurs at a temperature of 85°C in the presence of 5×10^{-5}–1×10^{-3} M catalyst for 8–15 h (Scheme 48). The platinum(II) derivative **59a** (R; Ar = C_6H_4-4-OMe) has the highest catalytic activity, which is probably due to the presence of an electron-donor methoxy substituent. In addition, silicone materials obtained using catalysts **59** exhibit luminescent properties.



Scheme 48. Vulcanisation of siloxane elastomers using platinum(II) complexes.

Luminescent Systems

Coordination compounds of platinum group metals with organic ligands exhibit bright and efficient fluorescence, phosphorescence, and thermally activated delayed fluorescence. The emergence of these properties makes these compounds attractive objects for use in various fields of optoelectronics, including the creation of efficient OLEDs (for relevant reviews on this topic, see [291–299]). Despite the fact that the luminescent properties of acyclic diaminocarbene complexes were discussed in detail in the recently study [300], we believe that this review will be incomplete without the current chapter, therefore, we present key points in brief.

While organic phosphors are predominantly fluorescent (the resulting triplet excitons are deactivated by thermal processes), the strong spin-orbit interaction in transition metal complexes allows transition from the singlet to the triplet state followed by phosphorescent relaxation. A triplet excited state can be efficiently generated due to the spin-orbit interaction induced by heavy atoms; therefore, organometallic compounds can be used to create phosphorescent OLEDs (PHOLEDs) that produce light from both triplet and singlet excitons [301–303]. Among the complexes of transition metals, the phosphorescent compounds of iridium [304–306] and platinum [307] are the most effective because of the high population of triplet excited states that undergo radiative decay.

The colour of the emission, as well as its efficiency, is largely determined by the nature of the organic ligand bound to the metal atom. However, for some types of triplet phosphors, harmful photodegradation processes can occur as a result of dissociation of the ligand after thermal population of metal-centred excited states located in energy above the emission level. The problem is most significant for blue phosphors, in which the indicated states have similar energies. The introduction of strong σ-donor ligands, in particular diaminocarbenes, into a luminophore molecule based on a transition metal complex, leads to an increase in the splitting of the energy of *d*-orbitals by the ligand field and makes it possible to obtain phosphorescent phosphors with a high quantum yield.

The photophysical properties of diaminocarbene complexes are determined not only by the choice of a suitable metal centre but also by the balance between the donor properties of cyclometalated and auxiliary carbene ligands. For each field of application of a light-emitting device, luminophores with a different set of parameters (properties) are required, which are selected, as a rule, empirically. The strategies for the preparation of acyclic diaminocarbene complexes described herein proved to be successful in the development of organometallic luminophores based on platinum(II) and iridium(III) light-emitting systems where fine tuning of photophysical parameters is required. Representative examples of luminescent complexes of platinum(II) [43, 47, 214, 308, 309] and iridium(III) [39–42, 121, 178, 199] and their main characteristics are shown in Figs. 11.

Sensors

Some of the most sensitive methods of quantitative chemical analysis are those based on the measurement of luminescence [310–314]. The high sensitivity of luminescent analytical methods defines their special role in the quantitative determination of trace impurities in high-purity substances, in toxicological studies and in the analysis of pharmaceuticals. In the context of the development of chemosensor materials, organometallic phosphorescent emitters have unique advantages, such as (i) high quantum yield of luminescence due to strong spin-orbital interaction because of the "heavy atom effect," (ii) long lifetime of the excited state of phosphorescence, which makes it possible to distinguish the emission of chemosensors from

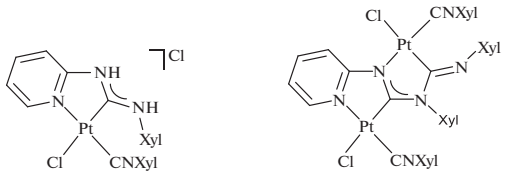
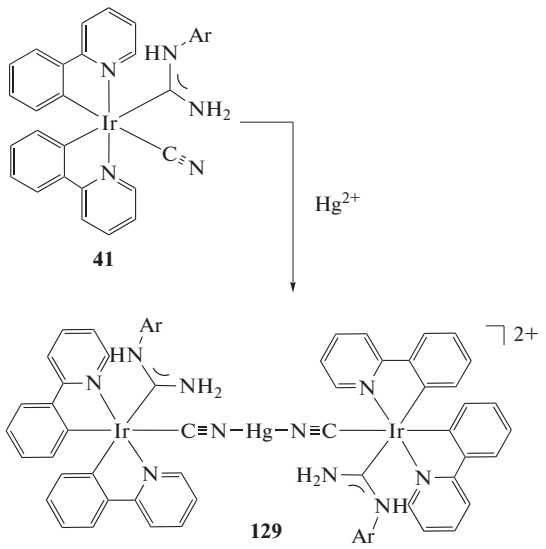


Fig. 10. Structures of compounds **119** and **120**.

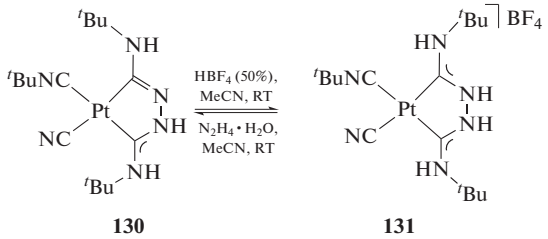
background fluorescence of the sample, and (iii) large Stokes shift required for the effective discrimination of the excitation and emission wavelengths.

In [39], a new class of organometallic chemosensors was proposed for the quantitative determination of mercury based on acyclic diaminocarbene complexes of iridium. Complexes **41** have effective phosphorescence in solution ($\Phi = 0.45$), the intensity of which decreases linearly with the addition of mercury(II) cations up to the ratio **41**: $Hg^{2+} = 1 : 2$, after which further addition of mercury(II) cations shows no effect on the emission. The detection limit for mercury is ~0.04 mg/L (2.63×10^{-7} M), the presence of cations of other heavy metals (copper, zinc, lead, cadmium, silver, and others) does not affect the detection of mercury cations. Mechanistic studies have shown that the quenching of phosphorescence upon the addition of a mercury(II) cation occurs due to the formation of binuclear complexes of iridium(III) **129** with a bridging dicyanomercury fragment (Scheme 49, Fig. 12).



Scheme 49. Quenching of phosphorescence upon the addition of a mercury(II) cation, which occurs due to the formation of binuclear complexes of iridium(III) **41** carrying bridging dicyanomercury fragment.

Examples of the phosphorescent pH sensors are diaminocarbene complexes of the Chugaev type. The platinum(II) complex **130** containing a monodeprotonated C,C-chelate bis-diaminocarbene ligand exhibits low-intensity phosphorescence in solution (MeCN, $\lambda_{max} = 490$ nm, $\Phi < 5 \times 10^{-4}$) [43]. With an increase in the acidity of the medium, protonation of the diaminocarbene fragment occurs (Scheme 50), leading to an increase in the donor properties of the latter, which is accompanied by a change in its photophysical properties, namely, an increase in the emission intensity by 12 times with a simultaneous short-wavelength shift of the phosphorescence band ($\Delta\lambda_{max} =$ 48 nm). The change in the photophysical properties is reversible, and the addition of a base to **131** leads to the regeneration of compound **130**. The pH-dependent phosphorescence is also characteristic for other Chugaev-type complexes, namely, platinum(II) **125** [43] and iridium(III) **127** [199].



Scheme 50. Example of phosphorescent pH-sensors based on diaminocarbene complexes of the Chugaev type.

Antitumor Drugs

The development of drugs based on transition metal complexes for clinical cancer therapy began with the discovery of the cytotoxic action of platinum compounds [315], namely, the Peyrone's salt—*cis*-diamminedichloroplatinum(II), by the American chemist Barnett Rosenberg in 1969. Preparations based on compounds of platinum metals are considered one of the most effective of those used for the treatment of oncological diseases; however, treatment with known preparations of platinum is always accompanied (in addition to the development of internal or acquired resistance) with severe side effects due to non-selectivity of action and high general toxicity [316, 317]. Therefore, it is promising to develop new strategies improving the targeting of the tumor (and, consequently, reduce the side effects) of platinum preparations, as well as their analogs based on other transition metals.

Stability under physiological conditions is a critical parameter for the product being developed. Stability under physiological conditions is especially important for organometallic drugs, since they may be prone to ligand exchange reactions with biomolecules. In this respect, complexes with diaminocarbene ligands are promising for the creation of organometallic antican-

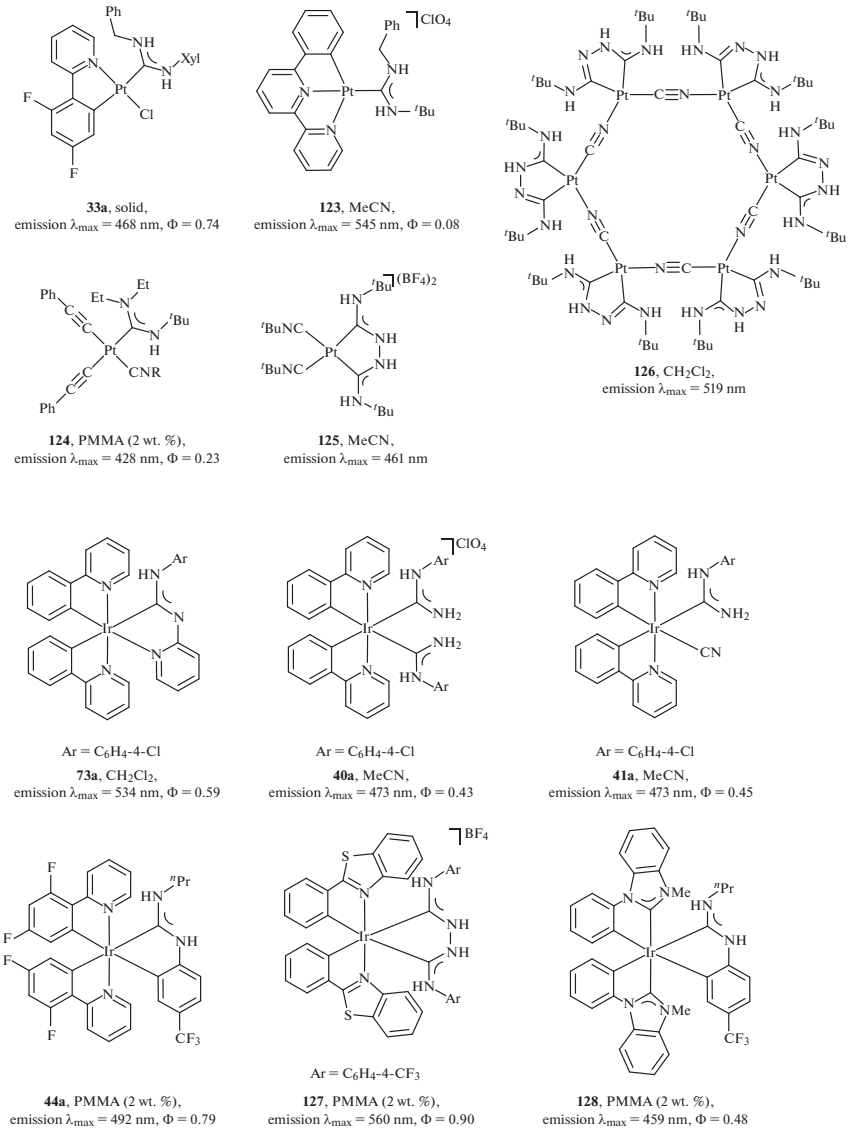


Fig. 11. Representative luminescent complexes of platinum(II) and iridium(III) showing main characteristics.

cer drugs due to the strong metal – carbene bond [318, 319]. Although NHC complexes have been actively studied for about two decades as potential antibacterial and anticancer drugs (relevant reviews [20–22, 24, 320–322]), ADC complexes have been studied to a much lesser extent. Only a few examples of potential therapeutic agents based on ADC complexes of platinum(II) [36, 45–47], palladium(II) [46], and gold (I/III) [323–325] are known.

The authors [45] studied the antitumor activity of the Chugaev-type platinum(II) ADC complex. Compound **132** (Fig. 13a) has a cytotoxic activity similar to cisplatin towards adenocarcinoma cells of the human mammary gland ducts (MCF7, IC_{50} = 4.5 mM; IC_{50} = 4.9 mM for cisplatin), but its activity is 5 times lower than that of cisplatin, in the case of a cell line with a multidrug resistance phenotype (MCF7R, IC_{50} = 14.6 mM for **132**; IC_{50} = 3.1 mM for cisplatin). Based on experiments on the interaction of complex **132** with guanidine and DNA, the authors suggested that the initial binding with biomolecules occurs via the formation of hydrogen bonds between the biomolecule and diaminocarbene (NH) hydrogen atoms, after which the labile chloride ligands are replaced by thiol fragments of proteins.

The antitumor potential of palladium(II) **76** and platinum(II) **77** complexes was studied against three human cancer cell lines (HT-29, MDA-MB-231, and MCF-7) [46]. All tested compounds were found to be cytotoxic towards tumor cells with the xylyl-substituted complexes **76a** (R = Xyl, R' = H) and **77a** (R = Xyl, R' = H) showing the highest cytotoxic activity (IC_{50} = 10 μM for the cell line MCF-7) in relation to all studied cell lines.

Mechanistic studies have shown that complexes **76a** and **77a** interact with DNA predominantly via the formation of monofunctional adducts in the major groove of the macromolecule. The interaction proceeds through a combination of non-covalent and covalent bonding. Non-covalent interaction of ADC complexes with DNA occurs via the non-covalent binding with phosphate groups, known as "phosphate clamp" (Fig. 13b) [326] and previously described for square-planar complexes of tetraammineplatinum(II) [327]. One O=P fragment of the phosphate group of DNA acts as an acceptor of two hydrogen bonds formed with the participation of hydrogen atoms (one from each of two *cis*-oriented diaminocarbene ligands) [328]. Compounds **76a** and **77a** are also capable of forming intercoil crosslinks. Covalent binding of complexes **76a** and **77a** with DNA occurs due to nucleophilic substitution of labile NH_2 groups by DNA nitrogenous bases, weakened by strong *trans*-influence of ADC ligands. As confirmed by the results of the DNA protonation study, the coordination of the metal centre occurs at the N7 atom of guanine. Compound **76a** interacts with DNA much faster than **77a**, which can be explained by the faster exchange of ligands with compound **76a**.

The antiproliferative effect of C,N-cyclometalated platinum(II) complexes **33** and **134** with an acyclic diaminocarbene ligand was studied [47]. The complexes exhibit cytotoxic activity comparable to that of cisplatin towards lung (A549) and cervical (HeLa) carcinoma cell lines. Compounds with a benzyl substituent **33b** (Fig. 11, R = CH_2Ph) and **134b** (Fig. 11) demonstrate better cytotoxic activity compared to compounds **33a** and **134a** containing a propyl substituent. It is interesting to note that presence of the cyclometalated ligand does not affect the cytotoxic activity. The best values were observed for compounds **134b** (IC_{50} = 4.47 μM (A549), 4.44 μM (HeLa)), which were found to be more cytotoxic than cisplatin (IC_{50} = 6.45 μM (A549), 13.60 μM (HeLa)). Electrophoretic studies indicate that complexes **33a**, **33b**, and **134a** can improve the tertiary stability of DNA. In contrast, the addition of **134b** to DNA does not induce conformational changes in DNA. This suggests that the cytotoxic effect of this complex is not based on DNA binding.

The cytotoxic properties of diaminocarbene complexes of platinum(II) **59** were studied in vitro [36]. The compounds are cytotoxic towards the cell lines of ovarian teratocarcinoma (CH1/PA-1), colon carcinoma (SW480), and adenocarcinoma of human alveolar basal epithelial cells (A549), but their effectiveness was several times lower than that of cisplatin.

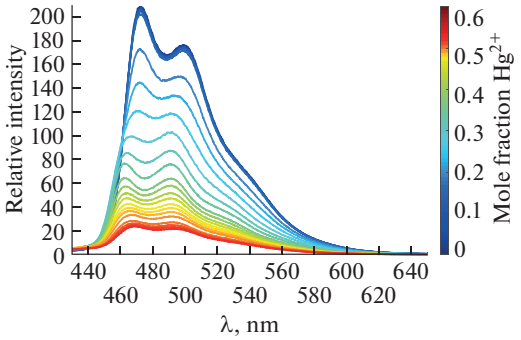


Fig. 12. Change in luminescence intensity upon addition of mercury(II) ions to the solution of diaminocarbene complex of iridium(III) **41**. Reproduced with permission from [39]. Copyright (2020) American Chemical Society.

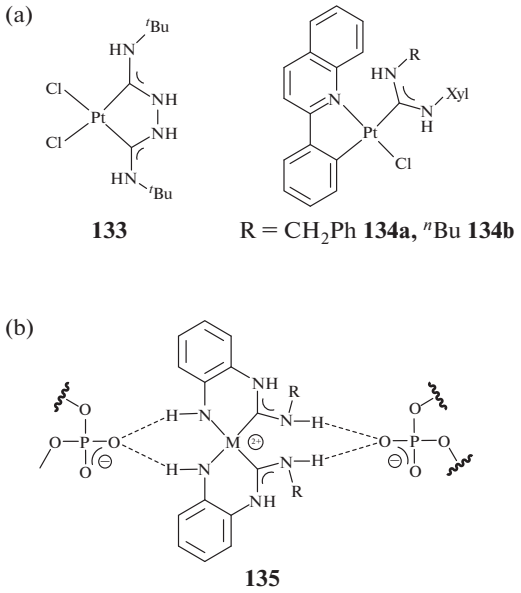


Fig. 13. (a) ADC-complexes of platinum(II), exhibiting cytotoxic activity; (b) non-covalent interaction of ADC complexes with DNA.

CONCLUSIONS

In this review, we have attempted to systematise the published literature data on the preparation and evaluation of the properties of complexes of platinum group metals with acyclic diaminocarbene ligands. The unique σ-donor properties of aminocarbenes

(ADC and NHC) result in strong metal–ligand bond manifesting in high stability of respective metal complexes. At the same time, the absence of a covalent fragment connecting both nitrogen atoms in ADC, as in the case of NHC, allows the rotation of substituents around the $C_{carbene}$–N bonds, causing the unique steric properties of these ligands.

Free acyclic diaminocarbenes (ADCs) can be synthesised in the laboratory and used for direct coordination to metal centres to the same extent as their heterocyclic counterparts (NHC). At the same time, the most widespread approach is based on the metal-mediated nucleophilic addition to coordinated isocyanides that leads to the generation of diaminocarbene metal complexes bypassing free carbene stage. Atom-efficient addition of N-nucleophiles to coordinated isocyanides allows to obtain a wide range of diaminocarbene complexes, including monodentate, chelate, and pincer derivatives, depending on the number of donor centres and their mutual arrangement in the structure of starting nucleophile.

This approach has found the greatest application in the synthesis of complexes of late transition metals, in particular of platinum group; in many cases this is justified by the subsequent application of these compounds. Palladium complexes with diaminocarbene ligands have proven to be highly active catalysts in cross-coupling and Heck reactions; the functionalisation of the diaminocarbene ligand led to the water-soluble ADC derivatives while maintaining their high catalytic activity. The significant kinetic stability of platinum complexes with diaminocarbene ligands made it possible to use them as a convenient model for studying catalytic processes, including metal-catalysed organic processes involving isocyanides and nitrogen-centred nucleophiles, many of which proceed through the formation of an acyclic diaminocarbene fragment. The unique ability of platinum to interact with π-systems of unsaturated compounds, in particular alkenes and alkynes, made Pt-ADC complexes promising catalysts for hydrosilylation of multiple bonds, including under visible light photocatalytic conditions.

Despite the variety of complexes of platinum group metals with acyclic diaminocarbene ligands, their potential biological activity has been studied to a lesser extent. Nevertheless, the known examples have shown that the complexes of palladium(II) and platinum(II) are active as antineoplastic drugs; an acyclic diaminocarbene fragment acts as a binding centre for organometallic compounds with biomolecules. In this direction, more systematic studies are required in order to establish the structure-property correlation that in turn can lead to new pharmaceutical formulations.

The chemistry of acyclic diaminocarbene metal complexes is a dynamically developing area, and there is no doubt that even more impressive examples of their use both in the fundamental applied fields of science will appear in the coming years. In this regard, the authors hope that the presented review will be useful to researchers working in the fields of organometallic chemistry, metal complex catalysis, and bioinorganic chemistry.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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