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Structure of Isocyanide Palladium(II) Complexes and Their Reactivity toward Nitrogen Nucleophiles

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Abstract—The review generalizes published data on the chemistry of palladium(II) complexes with isocyanides. The structure and specific features of the reactivity of isocyanide palladium(II) complexes with mono- and polynitrogen nucleophiles, as well as the structure of the products of these transformations, are discussed.

Keywords: palladium complexes, isocyanides, acyclic diaminocarbenes

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1. INTRODUCTION

Interest in reactions of transition metal-coordinated isocyanides with nitrogen nucleophiles has arisen 100 years ago when Chugaev et al. [1] reported for the first time on the reaction of a Pt(II) salt with methyl isocyanide and hydrazine hydrate. Since 1970, extensive studies on reactions of bis(isocyanide) Pd(II) complexes with aromatic amines have been initiated [2–6]. These studies were reviewed in [7]. However, the real boom in studies of isocyanide palladium(II) complexes and their reactivity toward nitrogen nucleophiles was related to the development of multicomponent catalytic reactions involving isocyanides (for reviews, see., e.g., [8–12]) and the discovery of a good catalytic activity of acyclic diaminocarbene complexes with transition metals (primarily palladium; see reviews [13–16]). These data were generalized in the recent review [17] on metal-promoted and metal-catalyzed reactions of isocyanides; but the structure of isocyanide palladium(II) complexes and their reactions with nitrogen nucleophiles were not considered in detail therein.

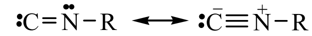
Taking the above stated into account, the present review discusses the structure of isocyanide palladium(II) complexes, specific features of their reactions with nitrogen mono- and polynucleophiles, and the structure of the resulting complexes.

2. STRUCTURE OF ORGANIC ISOCYANIDES AND THEIR COMPLEXES

Isocyanides are organic compounds possessing a C≡N– functionality [18]. They belong to a relatively small group of ligands with a lone electron pair located on a carbon atom. The isocyanide carbon atom is formally divalent. The isocyanide group may be represented as a resonance hybrid of two canonical forms, carbene **1** with the divalent carbon atom and dipolar **2** where the carbon atom is negatively charged (Scheme 1).

Carbene structure **1** [19] explains well chemical properties of isocyanide molecules and their reactivity toward nucleophiles and electrophiles. On the other hand, the isocyano group (like cyano) is linear, and the C≡N bond length therein (0.114 nm) approaches that in nitriles (0.113 nm) [20]. The IR spectral parameters of isocyanides and cyanides are also fairly similar; the C≡N stretching vibration band of free isocyanides is observed at 2165–2110 cm^{-1} [21] against 2260–2210 cm^{-1} for nitriles [22]. Therefore, by analogy with carbon(II) oxide, triple-bonded zwitterionic structure **2** was proposed for isocyanides in the early 1930s [23].

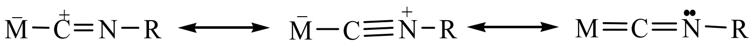
Scheme 1.



$$:C=\ddot{N}-R \longleftrightarrow :\overset{-}{C}\equiv\overset{+}{N}-R$$

1 **2**

Scheme 2.



$$\bar{M}-\overset{+}{C}=N-R \longleftrightarrow \bar{M}-C\equiv\overset{+}{N}-R \longleftrightarrow M=C=\ddot{N}-R$$

3 4 5

Breathing orbital valence bond quantum chemical calculations [24] showed a larger contribution of structure **1**, which accounts for electrophilicity of the carbon atom. Both carbene and zwitterionic structures **1** and **2** are linear, in full agreement with the X-ray diffraction data.

Isocyanide molecule coordinates to a metal ion by donating lone electron pair on the carbon atom to the vacant orbital of the metal (Scheme 2, structures **3** and **4**) [25, 26], thus forming a dative σ-bond. If the metal *d* orbitals (the symmetry of *d* orbitals makes them capable of overlapping vacant antibonding π-orbitals of the ligand) are occupied, the second dative π-bond can be formed (π-back donation; structure **5** in Scheme 2) [25, 26].

The formation of a ligand–metal dative σ-bond is accompanied by reduction of electron density on the ligand, so that its π-acceptor ability increases [27]. On the other hand, electron transfer from the metal to the antibonding orbital of isocyanide makes the latter less electronegative, σ-donor power of the ligand increases, and the M–C bond strengthens.

More information on the structure of isocyanide complexes and nature of bonds therein can be inferred from the IR data. Stretching vibrations of CN bond in isocyanides give rise to an intense IR absorption band in a frequency region convenient for observation, and its frequency is quite sensitive to the population of molecular orbitals of that bond [28]. If only σ-bond is formed in an isocyanide complex, electron density transfer from the carbon atom to acceptor as a result of dative interaction induces displacement of π-electron density from the nitrogen atom to carbon (Scheme 2, structure **4**). Therefore, the order of the carbon–nitrogen bond and hence the ν(CN) frequency increase.

Electron density transfer from the metal to antibonding π*-orbitals of isocyanide leads to reduction of the order, force constant, and stretching vibration frequency of the CN bond (Scheme 2, structure **5**). The degree of such electron density transfer is especially high when the metal ion has a low oxidation number [28]. Thus, increased ν(CN) frequency indicates the lack or very small contribution of metal–ligand dative π-bond, while reduction of ν(CN) suggests a significant contribution of this interaction [25].

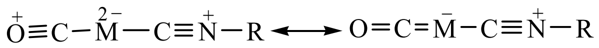
Only σ-bonds are formed by isocyanides with metals belonging to Groups IB and IIB (Cu, Ag, Au, Zn, Cd, Hg) and rare earths, whereas most other transition metals are also capable of forming π-bonds [27].

As we already noted, the contribution of π-bonding is determined by not only metal nature but also its oxidation state. The lower the oxidation number, the larger the reduction of ν(CN) [25]. This is related to more favorable conditions for the formation of dative π-bond. The complexation of isocyanides with zero-valent metals, e.g., Cr^0 or Pd^0, involves significant metal–ligand back donation, and ν(CN) shifts toward lower frequencies: $Cr(CNPh)_6$, ν(CN) 2070, 2012, 1965 cm^{-1}; $Ni(CNPh)_4$, ν(CN) 2050, 1990 cm^{-1} [27, 28]. In the complexation with singly or more highly charged metal ions, the contribution of π-back donation is small or absent at all, and the CN stretching frequency increases: $Fe(CNMe)_6^{2+}$, ν(CN) 2234, 2197 cm^{-1} [27, 28].

Apart from the metal nature and oxidation state, one more factor affecting electron density redistribution upon coordination of isocyanide to a metal, is the presence of other π-acceptor ligands (such as CO or PF_3) in the first coordination sphere. In mixed ligand complexes like $M(CNR)L_n$, the degree of π-bonding of the isocyanide ligand depends on the π-acceptor power of the L ligand [27]. If L = CO which is a much stronger π-acceptor than RNC, the π-bond is formed only with the former, while the isocyano group is linked to the metal through only dative σ-bond. In terms of the valence bond method, the structure of mixed-ligand complex M(CNR)(CO) may be represented by a set of resonance structures (Scheme 3) where the contribution of **7** is larger than that of **6** [27].

Conjugation between the aromatic system and M–CN fragment is possible in metal complexes of aryl isocyanides (Scheme 4, structure **8**) [27]. In particular, *p*-tolyl isocyanide is a stronger π-acceptor than methyl isocyanide, and the complexation with the former is accompanied by stronger reduction of the ν(CN) frequency, e.g., for $[Mn(CNR)_6]I$: R = Me, $\Delta\nu = \nu(CN)_{complex} - \nu(CN)_{ligand} = -13$ cm^{-1}; R = *p*-Tol, $\Delta\nu = -36/-101$ cm^{-1}) [27, 29].

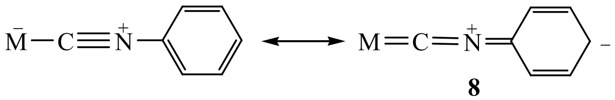
Scheme 3.



$\overset{+}{O}\equiv C-\overset{2-}{M}-C\equiv\overset{+}{N}-R \longleftrightarrow O=C=\overset{-}{M}-C\equiv\overset{+}{N}-R$

6 **7**

Scheme 4.



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Electron-withdrawing substituents in the *para* position of the benzene ring should stabilize structure **8** thus reducing ν(CN), whereas the effect of donor substituents should be the opposite, i.e., ν(CN) should increase. Analysis of the IR spectra qualitatively confirms these theoretical considerations [2, 30]; however, the real change of ν(CN) is smaller than might be expected [29]. This indicates a weak π-conjugation between the benzene ring and NC group in the complexes and a small contribution of canonical structure **8** [29].

Furthermore, planar structure of aryl isocyanide ligand and the possibility of intermolecular π–π interaction make bis(isocyanide) palladium and platinum complexes more prone to intermolecular metallophilic interactions [31].

Structural variations accompanying coordination of isocyanides to a metal center are responsible for the different chemical properties of the free ligand and its complex [27]. Reactions of coordinated isocyanides with electrophiles proceed more readily in complexes with a low oxidation number of the central atom; the contribution of structure **5** in such complexes is larger [25]. This is quite reasonable since reduction of the positive charge on the central atom enhances nucleophilicity of the coordinated ligand. On the other hand, coordination of isocyanides to metals in high oxidation states (that are electron deficient) generally increases the contribution of structures **3** and **4**, so that nucleophilic attack on the carbon atom of coordinated isocyanide becomes possible (the carbon atom in **3** may be regarded as a carbocationic center) [7]. It should be noted that such reactivity is more typical of coordinated isocyanides, whereas the carbon atom in free isocyanide ligands is rather nucleophilic [32].

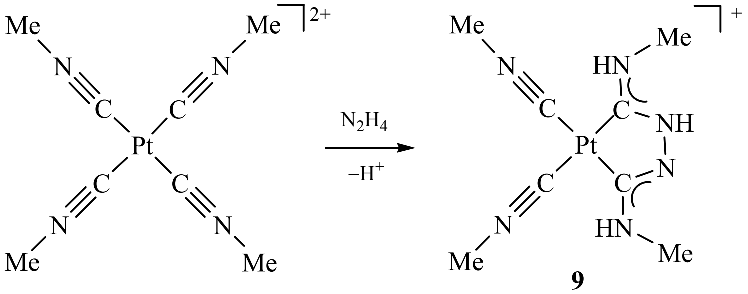
The electrophilicity of an isocyanide ligand (i.e., its ability to undergo nucleophilic attack) in metal complexes may be evaluated by the force constant of C≡N bond vibrations, which correlates with the relative positive charge on the CN carbon atom. The higher the force constant, the larger the positive charge. Therefore, it is believed that nucleophilic attack on an isocyanide complex is possible when $\Delta\nu = \nu(CN)_{coord} - \nu(CN)_{ligand} \geq 40$ cm^{-1} [7].

As noted above, the first example of metal-promoted coupling of isocyanides with nucleophiles was the addition of hydrazine to two isocyanide ligands coordinated to platinum [1] (Scheme 5). However, the product structure was assigned erroneously, though in keeping with the contemporary level of knowledge. Later it was shown that so-called orange Chugaev's salt **9** (Scheme 5) is the product of nucleophilic addition of hydrazine to two coordinated isocyanide ligands located *cis* with respect to each other [33]. Analogous structures were formed by coupling on a palladium center [34].

Saegusa et al. [35–37] found that reactions of compounds like HYR^1 (where Y is a heteroatom such as O, N, P, Si, etc.) with isocyanides may be catalyzed by Group IB and IIB metals (Cu, Ag, Zn, Cd, Hg) in different oxidation to afford compounds **13** (Scheme 6).

Intermediate carbene complexes **11** formed by platinum(II) and palladium(II) are stable, and they can be isolated from the reaction mixture. Reactions of nitrogen nucleophiles with Pd(II)-coordinated iso-

Scheme 5.



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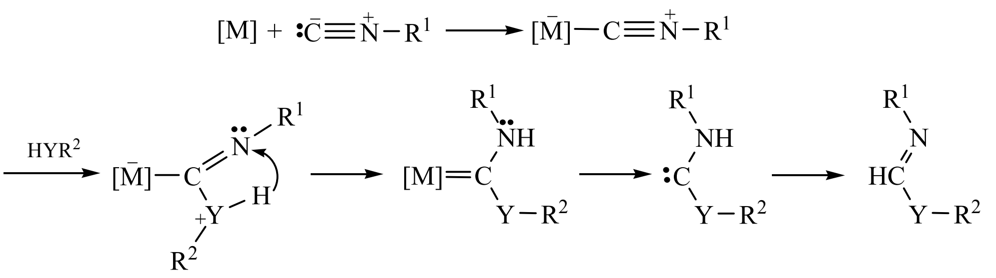
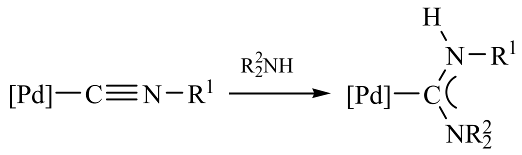
Scheme 6.



10 **11** **12** **13**

Scheme 7.



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cyanides gave acyclic diaminocarbene palladium complexes (Pd-ADC) **14** (Scheme 7). This reaction provides a promising synthetic route to compounds **14** that are often difficult to obtain by other methods [38].

Palladium(II) ion has a d^8 configuration, and it typically forms square–planar complexes. Only in this case, high-energy molecular orbitals remain unoccupied (see figure) [39].

Several methods have been reported for the synthesis of bis(isocyanide) palladium(II) complexes **15**, the most popular of which is based on the replacement of nitrile ligands by isocyanide [2, 40–42] (Scheme 8). The steric structure of bis(isocyanide)dihalopalladium(II) complexes is determined by the halogen nature. Crystalline dichloro complexes have the *cis* structure [31, 43–46], while dibromo [47] and diiodo analogs [48, 49] are *trans* isomers. As shown in [50], the complex $[PdCl_2(CNCy)_2]$ in chloroform solution undergoes *cis–trans* isomerization and exists as a mixture of *cis* and *trans* isomers (Scheme 9).

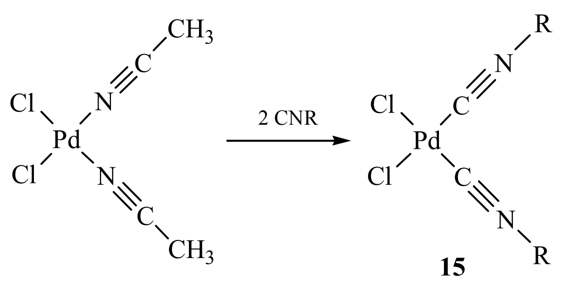
In all cases, coordination of isocyanides to Pd(II) leads to a high-frequency shift of the C≡N stretching vibration band ($\Delta\nu \approx 90$ cm^{-1}) [7], indicating increase of the electrophilicity of the CN carbon atom; this suggests enhanced reactivity of the resulting complex toward nucleophiles [7].

3. REACTIONS OF ISOCYANIDE PALLADIUM COMPLEXES WITH NITROGEN NUCLEOPHILES

Reactions of isocyanide palladium complexes with NH nucleophiles can follow two pathways, ligand substitution (Scheme 10, pathway *a*) and nucleophilic addition to activated isocyanide (pathway *b*).

Crociani et al. [2] were the first to report the synthesis of Pd-ADC complex **16** by coupling of *p*-

Scheme 8.



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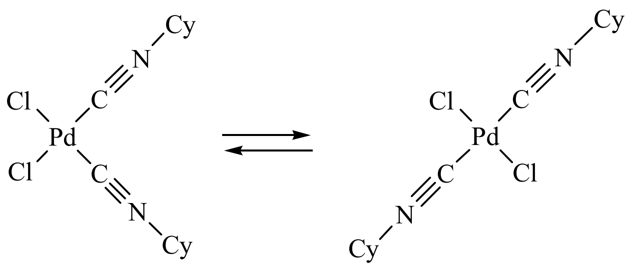
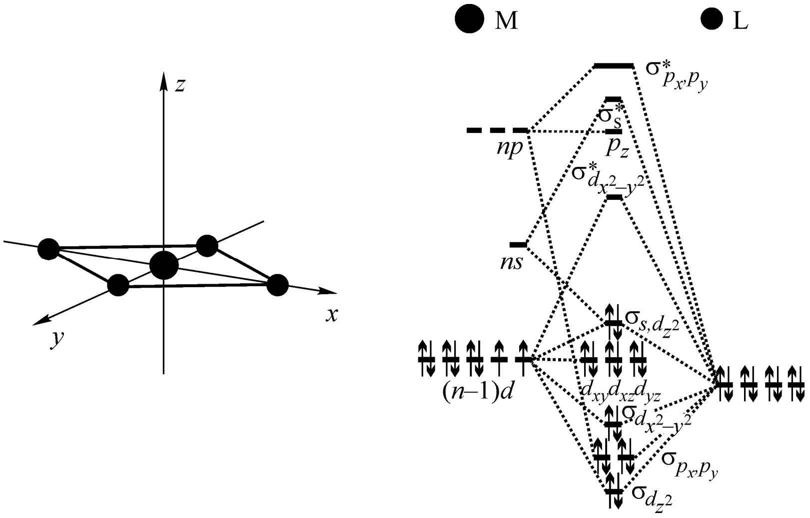
Scheme 9.



cis-**15a** *trans*-**15a**



Molecular orbital diagram of palladium(II) complexes.

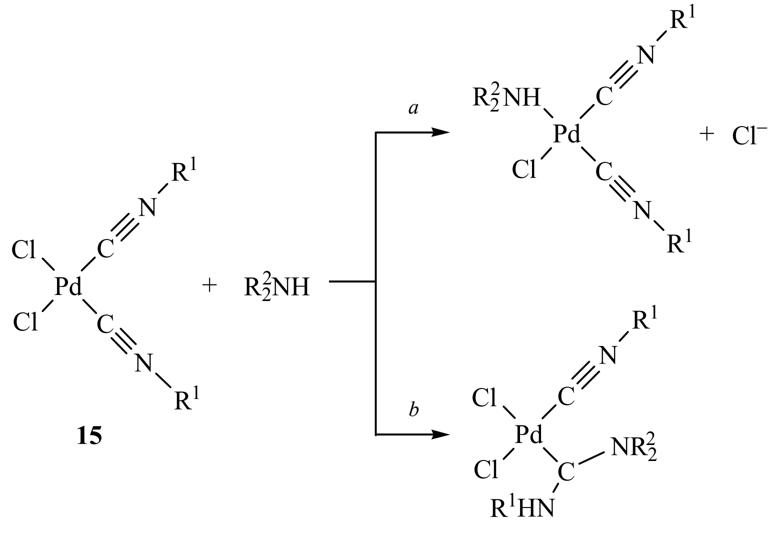
toluidine with palladium(II)-coordinated phenyl isocyanide (Scheme 11) in boiling chloroform 10 min. Provided that the ratio of isocyanide complex **15b** and nucleophile was exactly 1 : 1, additional purification was avoided [2]. This reaction was later extended to various nitrogen nucleophiles, in particular aliphatic [2, 5, 30, 46], aromatic [2, 5, 30, 46, 51], and cyclic amines (aziridine, azetidine) [52, 53], imines [54], hydrazones [55], and ambident nucleophiles (see Section 4).

Rotondo et al. [6] analyzed experimental data on the coupling of Pt(II)- and Pd(II)-coordinated isocyanides with amines and proposed a stepwise mechanism (Scheme 12). The key step is attack by the amine nitrogen atom on the CN carbon atom of the ligand with formation of intermediate **17**. The subsequent proton transfer yields final product **18**.

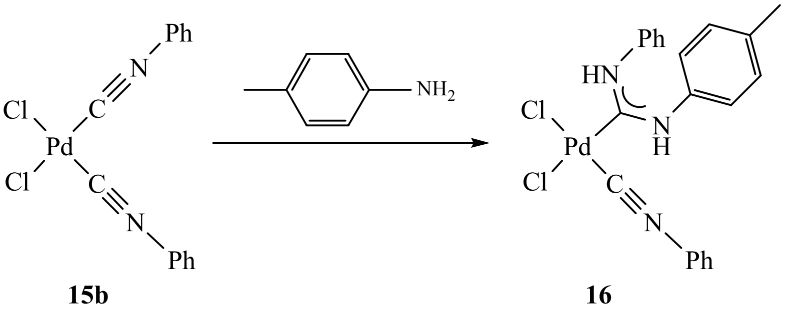
The reaction rate depends on the substituents in the isocyanide ligand and amine. Electron-withdrawing substituents in the isocyanide and/or electron-donating groups in the amine accelerate the reaction [56]. As shown in [25], increase of the solvent polarity strongly slows down the reaction.

It should be noted that diaminocarbene ligand is a better σ-donor and a poorer π-acceptor than its isocyanide precursor [56]. Therefore, the addition of first nucleophile molecule to a bis(isocyanide) com-

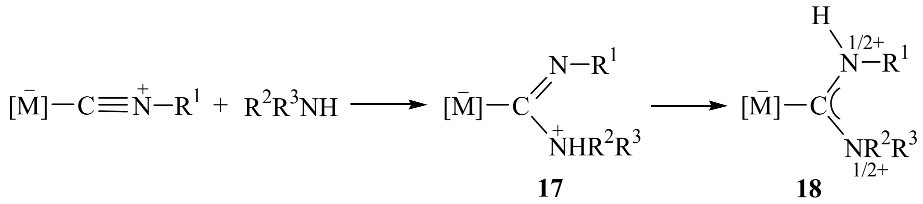
Scheme 10.



Scheme 11.



Scheme 12.



plex deactivates the second isocyanide group, and only monocarbene complexes with the second isocyanide ligand remaining unchanged were formed in reactions of bis(isocyanide)dichloropalladium(II) complexes with *p*-toluidine [2], other amines [3–6], and benzophenone hydrazone [55].

On the other hand, the number of added saturated N-heterocycles, aziridine (**19**) [52] and azetidine (**20**) [53], depended on the isocyanide ligand nature (Scheme 13). In the reaction with bis(4-methoxyphenyl isocyanide) complex, both isocyanide ligands were successively involved to give mono- and bis-adducts **21** and **23**, whereas only monoadducts **22** and **24** were formed in the coupling reaction of azetidine (**20**) with bis(*tert*-butyl isocyanide) palladium(II) complex where the more donor and larger *tert*-butyl group hindered nucleophile addition to the N≡C bond. Compound **23** was assigned *trans* configuration; however, no reasonable explanation was given to the *cis–trans* isomerization [53].

The coupling products of aziridine and azetidine with isocyanide complexes of palladium(II) are also interesting compounds. Azetidine reacts like common aliphatic amines, yielding complexes **23** and **24** [53], while the coupling of aziridine with coordinated isocyanides gives cyclic diaminocarbene complexes **21** and **22** [52]. Presumably, the attack by the aziridine nitrogen atom on the NC carbon atom is followed by opening of the three-membered ring and closure of imidazolidine ring as shown in Scheme 14 [52].

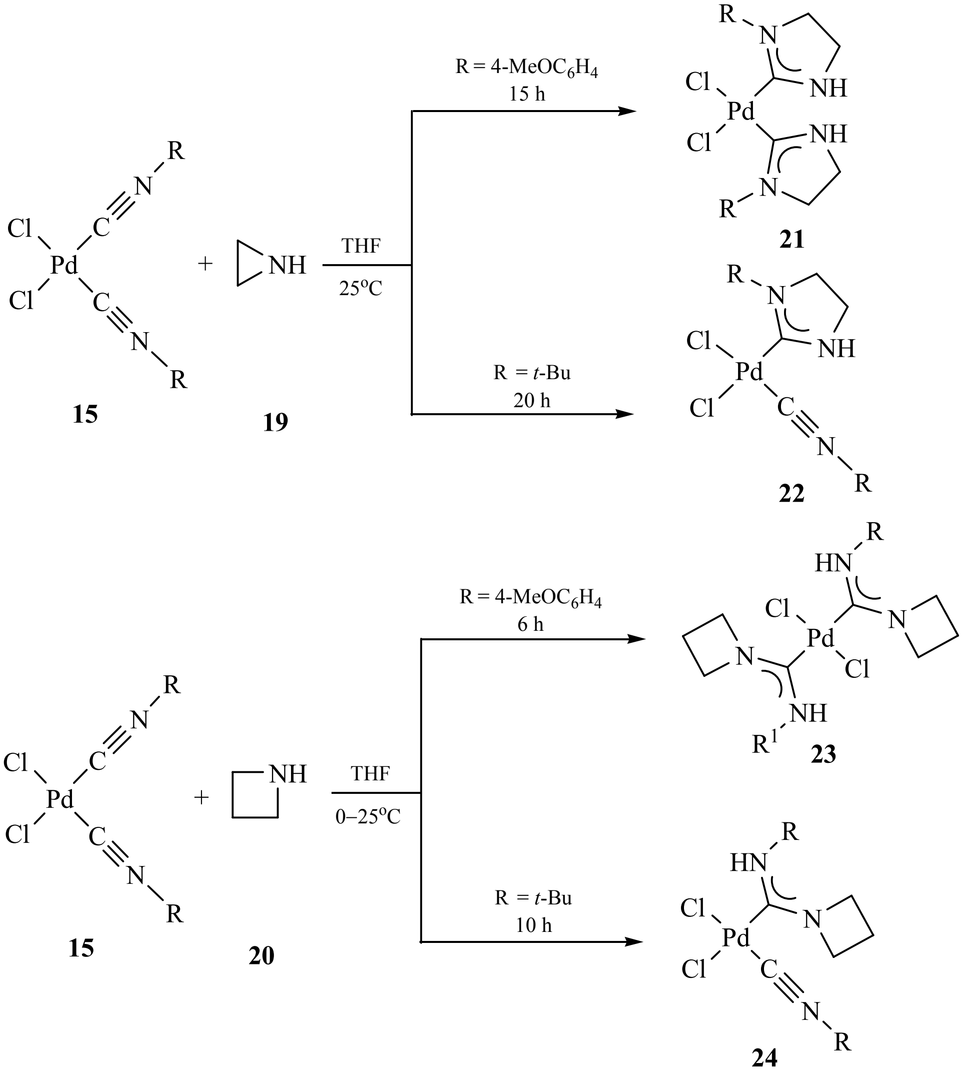
This synthetic approach to cyclic diaminocarbene palladium(II) complexes, i.e., metal-promoted reaction of isocyanides with nitrogen nucleophiles possessing an electrophilic carbon atom in the α- or β-position, has recently been extended (Scheme 15). 2- and 3-Chloroalkylamines **26** (or their salts in the presence of a weak base) [46, 57, 58], *N*-cyclohexylglycine methyl ester (**27**) [59], and 2-aminoacetals **28** [60] were used as nucleophiles. The results were generalized in [61]; it was shown that the developed strategy for the synthesis of unsymmetrical Pd-NHC complexes **29**–**31** ensures facile preparation of a large number of various cross-coupling catalysts whose activity is comparable to the activity of widely known PEPPSI complexes.

Anisimova et al. [62] studied reactions of isocyanide palladium complexes with other amino acid esters **33** (Scheme 16) and found that palladium-promoted coupling of α-amino acids with bis(isocyanide)dichloro- (**15**) and -diiodopalladium(II) complexes (**32**) leads to the formation of optically active acyclic diaminocarbene complexes **34** and **35**.

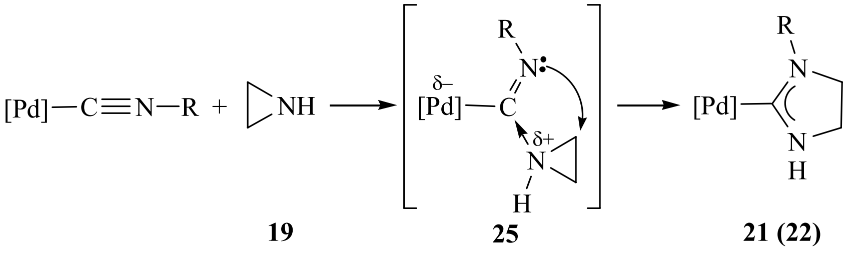
4. REACTIONS OF ISOCYANIDE PALLADIUM COMPLEXES WITH POLYFUNCTIONAL NUCLEOPHILES

If a nitrogen nucleophile possesses an additional N-nucleophilic center, further reaction is possible with formation of more complex structures. In particular, at least two pathways may be proposed for subsequent transformation of ADC complexes **36**. The first of

Scheme 13.

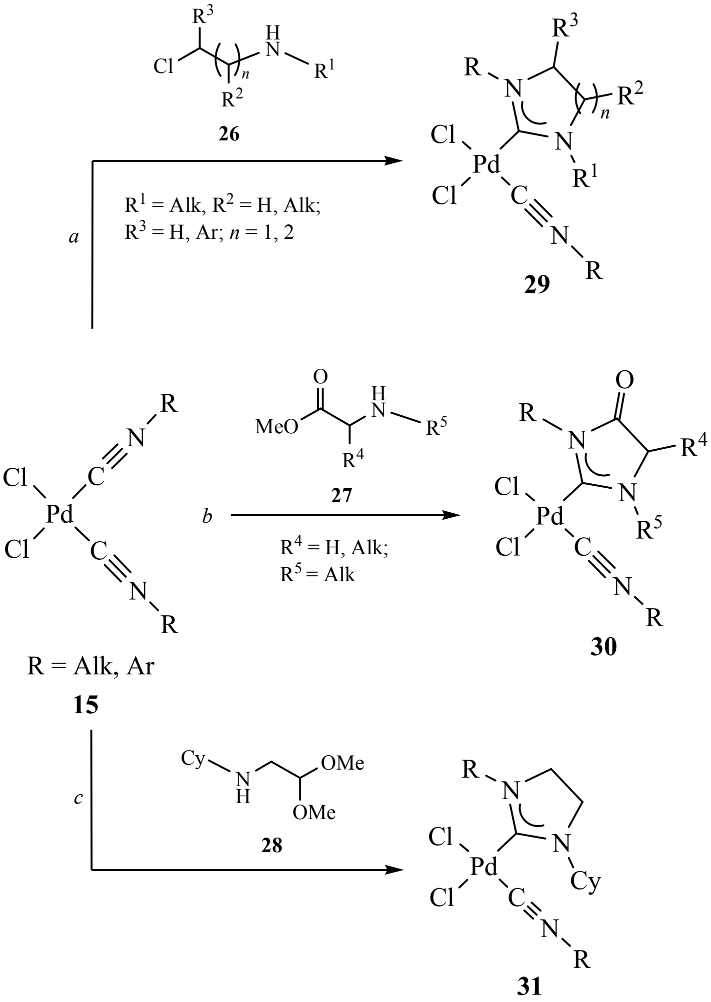


Scheme 14.

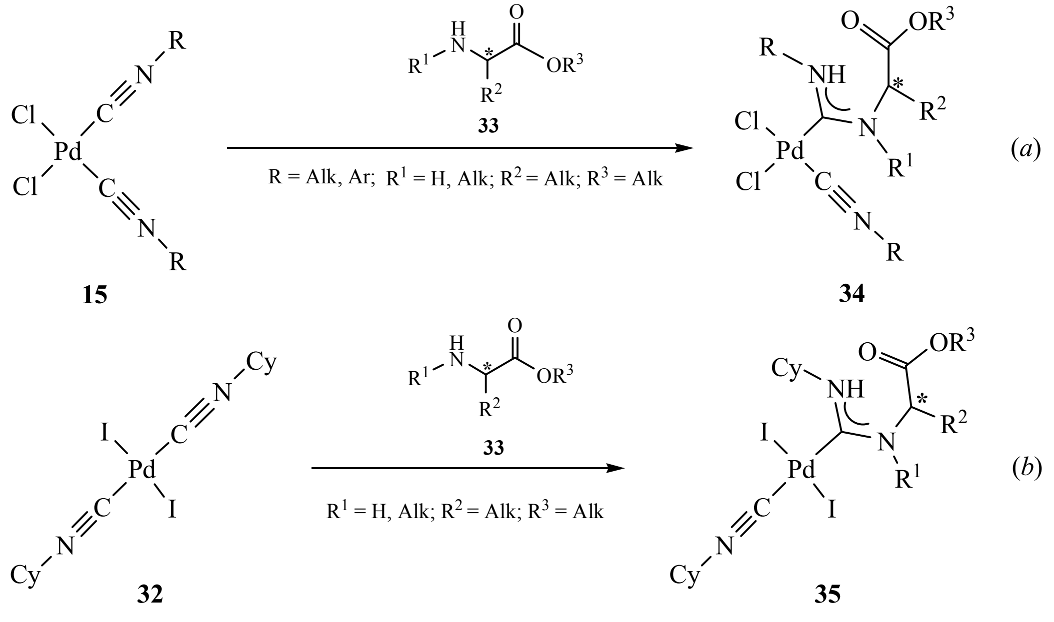


these involves substitution of one halide ligand by the second nucleophilic group with formation of C,N-chelate **37** (Scheme 17, pathway *a*); alternatively, the second nucleophilic group can add to the second isocyanide ligand, yielding bis(carbene) structure **38** (Scheme 17, pathway *b*).

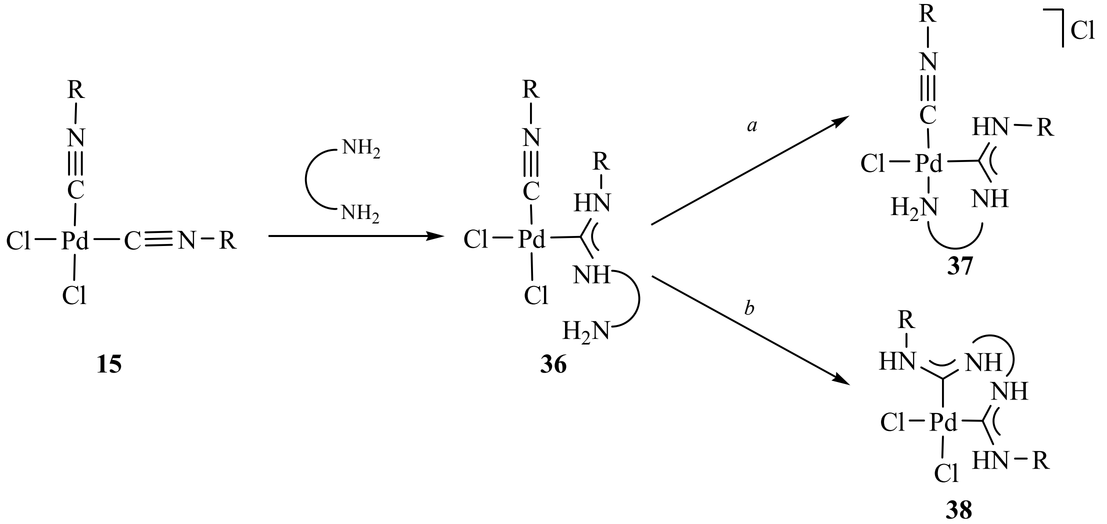
Scheme 15.



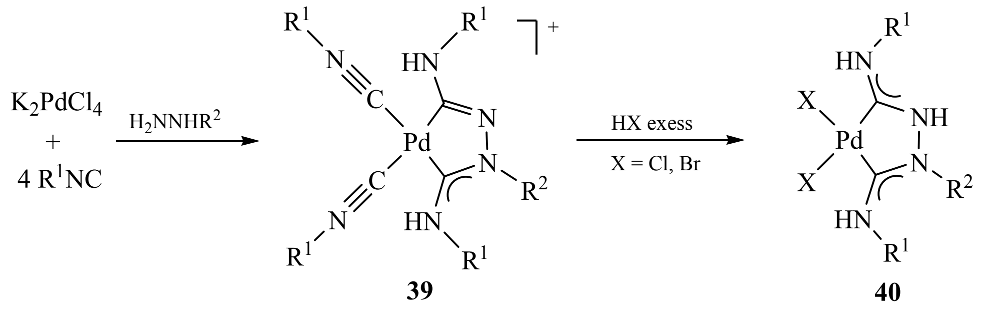
Scheme 16.



Scheme 17.



Scheme 18.



R^1 = Me, *i*-Pr, *t*-Bu, Cy; R^2 = H, Me, Ph.

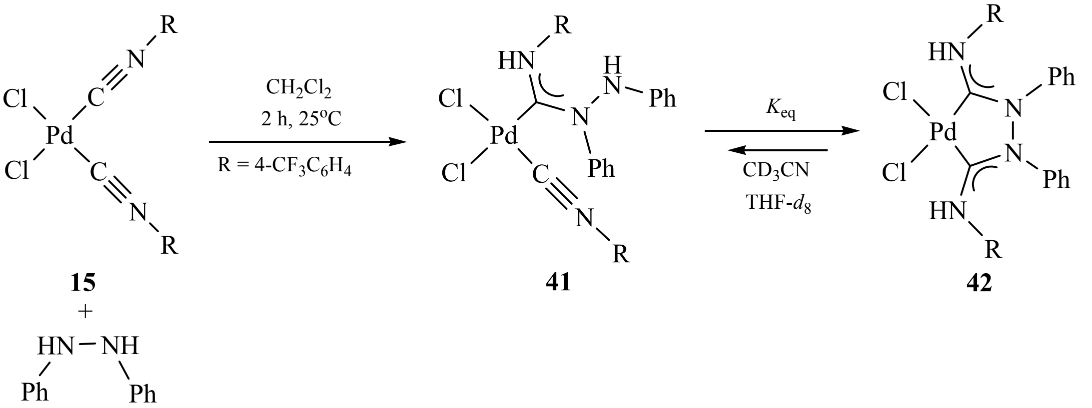
Up to now, some experimental data on the coupling of isocyanide palladium complexes with various nitrogen-centered polynucleophiles have been accumulated; these data are systemized below.

4.1. Addition of hydrazine and its derivatives. Dicarbene palladium complexes (Chugaev's complexes) were synthesized in 1970 by reaction of hydrazine with palladium-coordinated methyl isocyanide (Scheme 18, R^1 = Me, R^2 = H) [63]. The formation of C,C-chelating bis(carbene) ligand implies the addition of hydrazine by both amino groups to two *cis*-positioned isocyanide ligands.

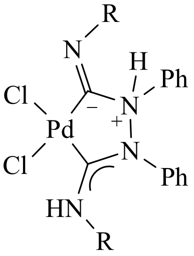
As we noted above, the addition of one N-nucleophile molecule usually prevents coupling with the second isocyanide ligand. The facile formation of C,C-chelate in the reaction with hydrazine may be rationalized as follows. First, hydrazine is a stronger nucleophile than amines and ammonia due to the α-effect [64, 65]. Second, the coupling with the second isocyanide group is an intramolecular process which is easier to occur. Furthermore, the positive charge on the complex ion favors nucleophilic attack on the isocyanide ligand [25].

In 2005–2006 Slaughter and co-workers [66–69] showed that the above reactions can be extended to other isocyanides and substituted hydrazines (Scheme 18). Wanniarachchi and Slaughter [70] studied the reaction of 1,2-diphenylhydrazine with complex **15** (Scheme 19). The reaction was carried out in me-thylene chloride for 2 h, and the product was complex **41** containing one unidentate amino(hydrazino)carbene ligand and unchanged aryl isocyanide ligand. Heating of a solution of **41** in acetonitrile for 2 h gave 67% of bis-(carbene) C,C-chelate **42**. Complex **42** was much better soluble than **41** in weakly polar solvents like methylene chloride or THF, which is most likely due to higher polarity of the latter. This difference made it possible to separate isomeric complexes **41** and **42**.

Scheme 19.



^{1}H NMR study of solutions of **41** and **42** in CD$_3$CN and THF-d_8 revealed equilibrium between these species. The equilibrium in solutions of **41** in CD$_3$CN (ε = 37.5 [71]) and THF-d_8 (ε = 7.4 [71]) established in several days (Scheme 19; K_{eq} = 2.6 and 10, respectively). As the solvent polarity increases, the equilibrium shifts toward monocarbene complex **41**, which indicates its higher polarity. A solution of **42** in CD$_3$CN equilibrated in 24 h, whereas more than 5 days was necessary to achieve equilibrium in THF-d_8. These finding were rationalized [70] assuming that polar solvents stabilize better polar transition state leading to postulated intermediate **43**. Steric interactions between the bulky aryl groups in **42** destabilize the C,C-chelate structure, thus favoring formation of an appreciable amount of complex **41** in the equilibrium mixture [70].



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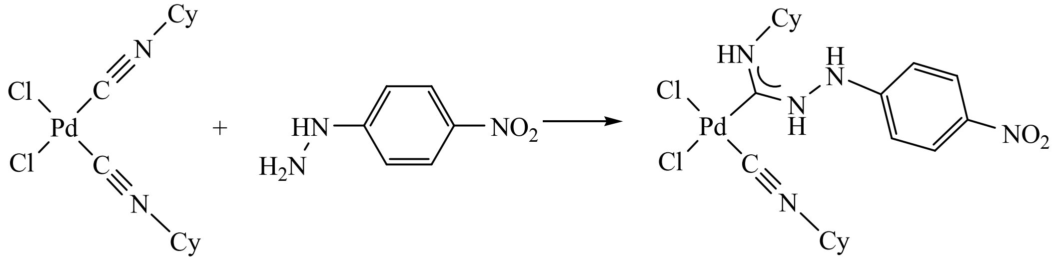
R = 4-CF$_3$C$_6$H$_4$.

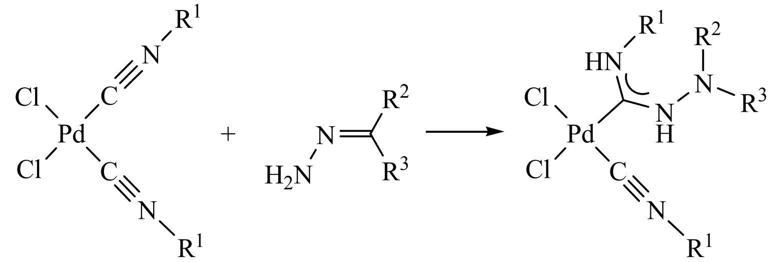
Introduction of an electron-withdrawing nitro group into the *para* position of phenylhydrazine molecule sharply reduces the nucleophilicity of the NH nitrogen atom, and the reaction with **15a** involves only the amino group [72–74] (Scheme 20). Likewise, the NH$_2$ group of hydrazones was solely reactive. Reactions of isocyanide palladium complexes **15** with hydrazones **45** were studied in [55, 75] (Scheme 21). Hydrazones derived from various aromatic ketones and salicylaldehyde turned out to react equally readily, yielding 80–90% of diaminocarbene complexes. The other nitrogen atom of hydrazones showed no nucleophilic properties.

The reaction of (butane-2,3-diylidene)dihydrazine (**48**) with tetrakis(methyl isocyanide)palladium(II) (**47**) generated *in situ* afforded complex **49** with both cyclic and acyclic diaminocarbene fragments [76] (Scheme 22). The reaction was presumed to begin with metal-promoted coupling of isocyanide with the hydrazone to give intermediate **50** which underwent intramolecular cyclization via attack by the nitrogen atom of the second hydrazone group on the carbon atom of the neighboring isocyanide ligand. Intermediate **51** thus formed loses a proton and N$_2$H$_2$ molecule, yielding complex **49**.

Scheme 20.

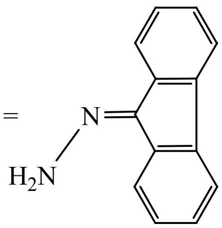


Scheme 21.

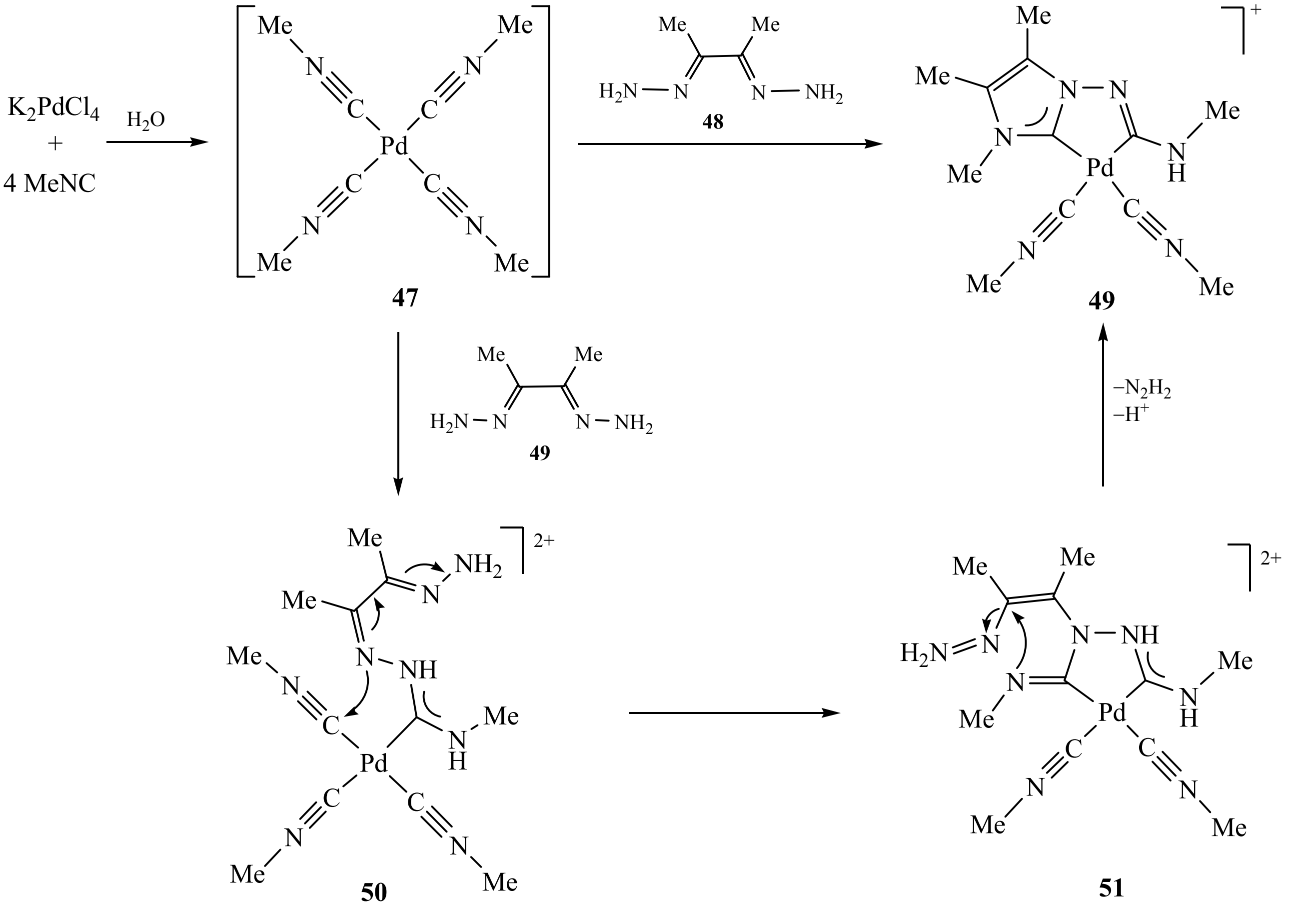


15 **45** **46**

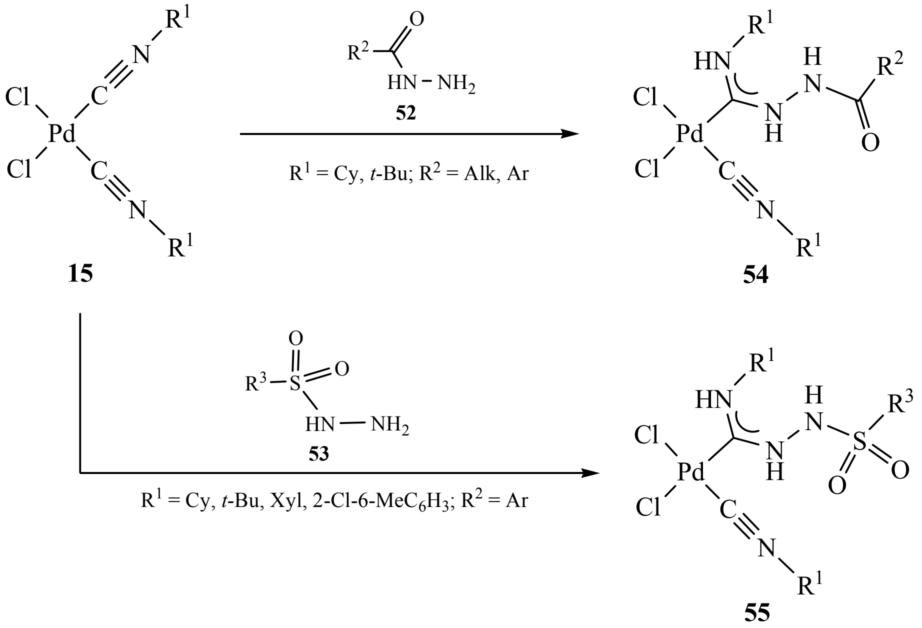
R^1 = Cy, *t*-Bu, Xyl, 2-Cl-6-MeC_6H_3, C_6H_4{2-OC(O)C_6H_4(4-OMe)}; R^2 = H, R^3 = 2-OHC_6H_5 (**45a**); R^2 = R^3 = Ph (**45b**);

R^2 = R^3 = 4-OMeC_6H_5 (**45c**); R^2, R^3 =  (**45d**).

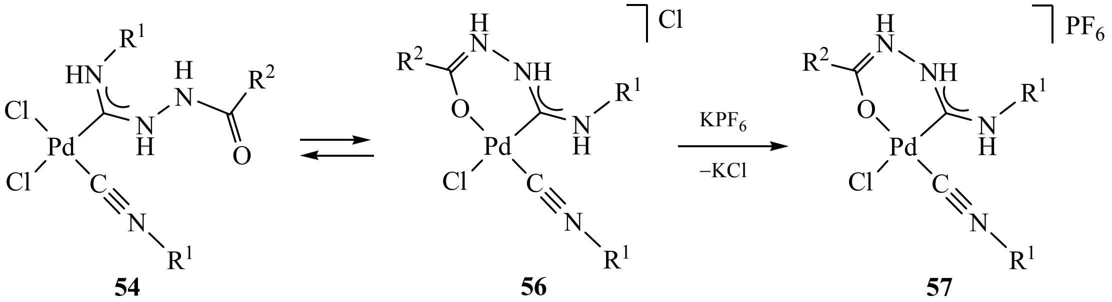
Scheme 22.



Scheme 23.



Scheme 24.

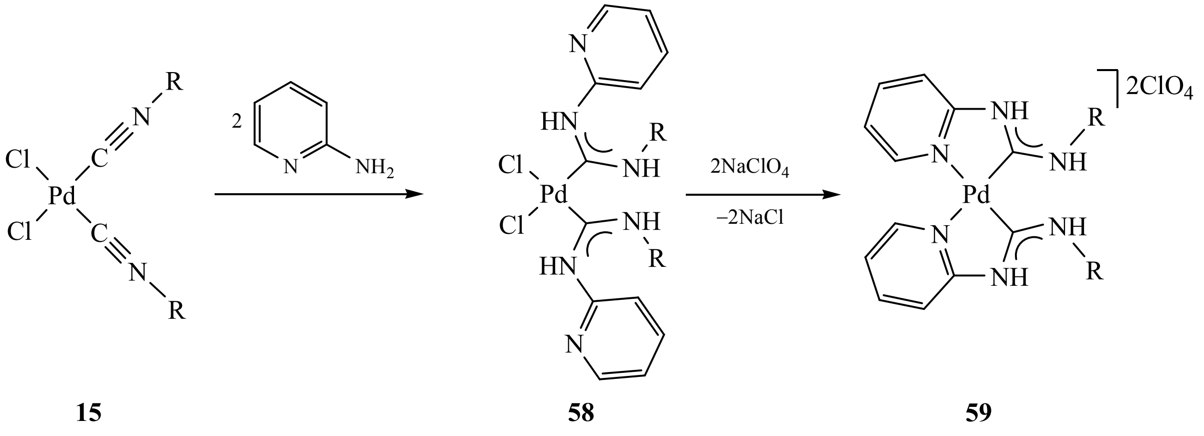


Reactions of isocyanide complexes **15** with carboxylic and sulfonic acid hydrazides **52** and **53** were described in [77, 78] (Scheme 23). The reactants were heated for 4 h in boiling chloroform, and the resulting ADC complexes **54** and **55** were isolated in 60–96%. Complounds **54** and **55** are poorly soluble in water (0.015–0.02 mmol/L) and are stable to hydrolysis and oxidation with atmospheric oxygen. Furthermore, complexes **54** and **55** are stable in protic solvents in the presence of bases. Therefore, they can be used to catalyze cross-coupling reactions under experimentally convenient conditions (in alcohols or water without degassing). As in the above described reactions with other nucleophiles, the addition of hydrazides **52** and **53** to the triple C≡N bond of isocyanides is promoted by the metal [77, 78]. Complexes **54** are capable of undergoing intramolecular cyclization to give six-membered C,O-chelates **56** and **57** [79] (Scheme 24).

4.2. Addition of N=C–N nucleophiles. Another group of polynucleophiles whose coupling reactions with isocyanide palladium complexes have been reported includes compounds containing an N=C–N fragment, in particular α-amino azaheterocycles, 3-imino-2,3-dihydro-1*H*-isoindol-1-one, 1*H*-isoindole-1,3(2*H*)-diimine, and amidines.

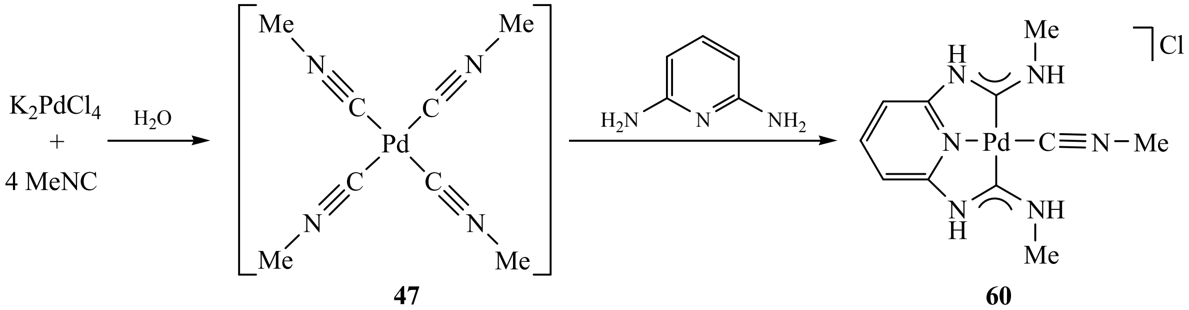
α-Amino azaheterocycles. The reaction of complexes **15** with excess 2-aminopyridine involved both isocyanide ligands [4] (Scheme 25). According to the IR data, the resulting bis(carbene) complex **58** has *cis* configuration. Treatment of **58** with $NaClO_4$ led to the replacement of two chloride ligands in the palladium coordination sphere by pyridine nitrogen atoms with formation of two five-membered C,N-chelate rings (complex **59**) [4].

Scheme 25.



R= Ph, 4-MeC_6H_4.

Scheme 26.



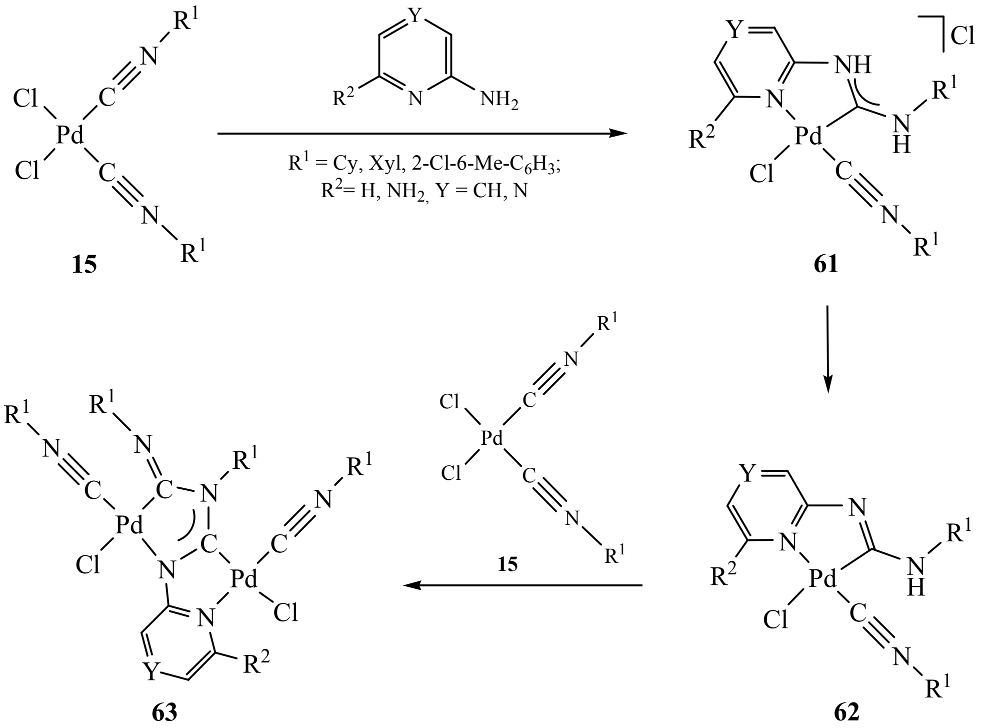
2,6-Diaminopyridine reacted with tetrakis(methyl isocyanide)palladium(II) (**47**) generated *in situ* to afford complex **60** with a pincer-like bis(carbene) ligand as a result of addition of both amino groups of the nucleophile to two isocyanide groups and replacement of one isocyanide ligand [76] (Scheme 26).

Monocarbene complexes **61** were synthesized by coupling of isocyanide complexes **15** with 2-amino- and 2,6-diaminopyridines [42] and 2-aminopyrazine [80] (Scheme 27). Deprotonation of **61** gave intermediate **62** which reacted with the second molecule **15**, yielding dinuclear complex **63** [42]. In the reactions with aminopyridines, the presence of an equimolar amount of potassium carbonate was necessary to convert complex **61** into **63** [42], whereas the corresponding dinuclear complex **63** was formed in the reaction with 2-aminopyrazine without addition of a base [80]. 3-Amino-4-acetyl-5-methylpyrazole (**64**) in which the amino group is involved in intramolecular hydrogen bond reacted with complex **15c** to afford only mononuclear bis-C,N-chelate **65** [80] (Scheme 28).

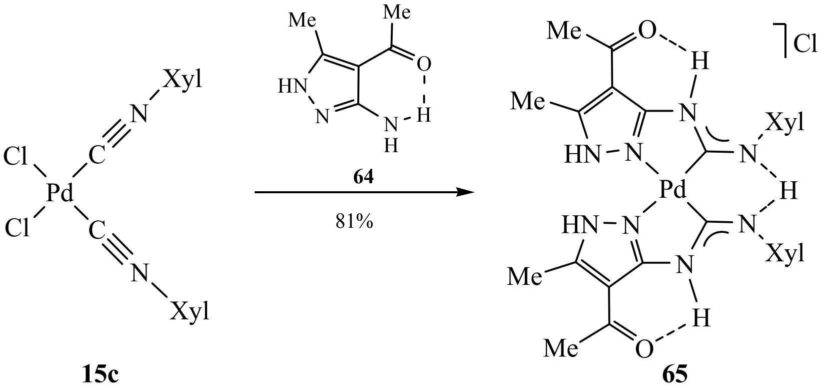
3-Imino-2,3-dihydro-1H-isoindol-1-one and 1H-isoindole-1,3(2H)-diimine. The coupling of 3-imino-2,3-dihydro-1*H*-isoindol-1-one and its substituted derivatives **66** with isocyanide complexes **15** was studied in [81, 82] (Scheme 29). It was shown [81] that the reaction involves intermediate formation of complexes **67** which are converted into carbene chelates **68** (yield 80–85%) via inner-sphere nucleophilic attack on one isocyanide ligand. The best yields of coupling products **68** were obtained using equimolar amounts of the reactants. Excess nucleophile (1:2 or 1:3) affected neither reaction direction nor the yield, but the product was contaminated with 3-imino-2,3-dihydro-1*H*-isoindol-1-one hydrochloride.

The coupling of 1*H*-isoindole-1,3(2*H*)-diimine (**69**) with complexes **15** was sensitive to the isocyanide ligand nature [83] (Scheme 30). Monocarbene complexes **70** structurally similar to **68** were obtained in 78−84% yield from palladium complexes **15** with *tert*-butyl, xylyl, and 2,4,4-trimethylpent-2-yl isocyanides, regardless of the reactant ratio. The reaction

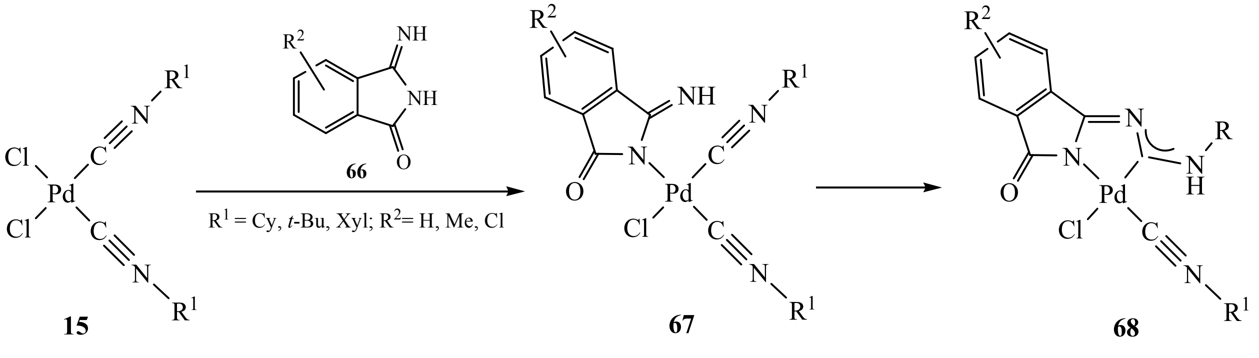
Scheme 27.



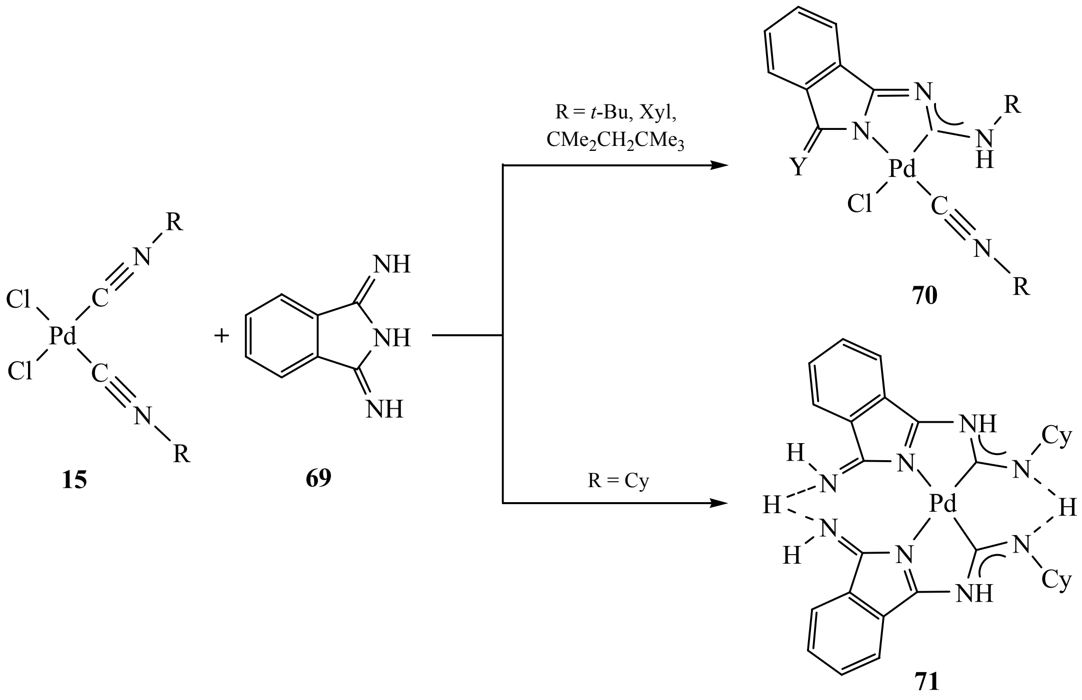
Scheme 28.



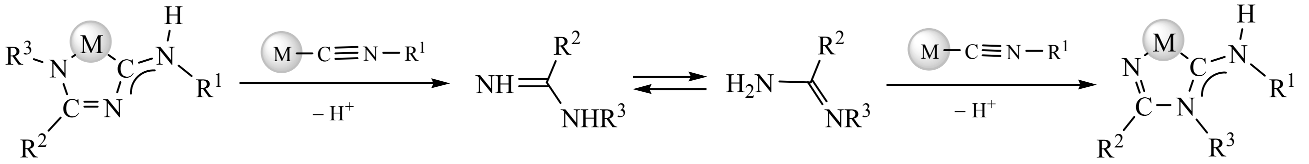
Scheme 29.



Scheme 30.



Scheme 31.

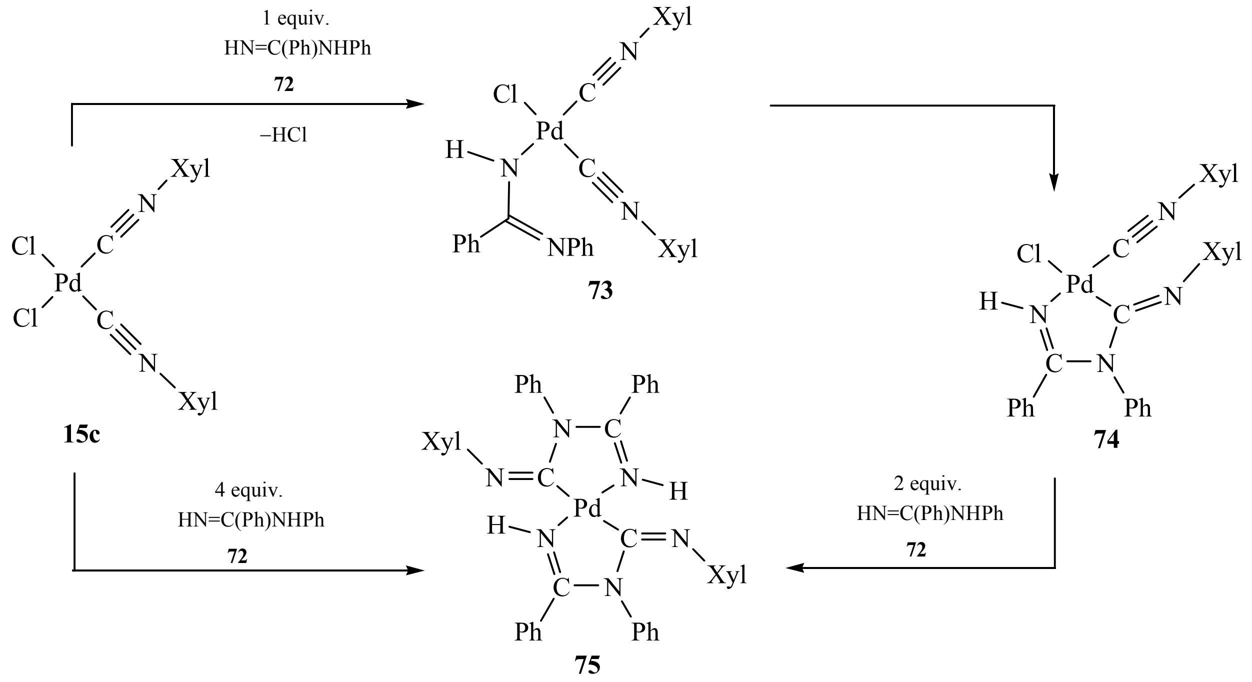


of *cis*-[$PdCl_2(CNCy)_2$] with 2 equiv of **69** afforded 82% of bis(carbene) complex **71**. The yield of the latter decreased to 40% when an equimolar amount of the nucleophile was used, and the reaction mixture contained ~33% of unreacted complex **15a**, while no other coupling products were detected.

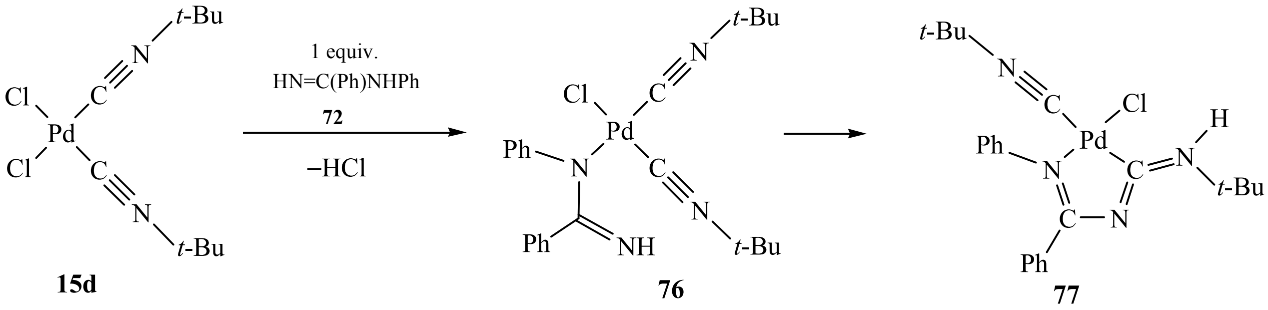
N-Phenylbenzenecarboximidamide. *N*-Substituted amidines are capable of adding to metal-coordinated isocyanides by either of the two NH nitrogen atoms, while the other donor center coordinates to the metal thus forming C,N-chelate (Scheme 31). Complexes **74**, **75**, **77**, and **80–83** with C,N-chelating aminocarbene ligands were synthesized by coupling of *N*-phenylbenzenecarboximidamide (**67**) with one or two isocyanide ligands in *cis*-[$PdCl_2(CNR)_2$] (**15a**, **15c**, **15d**) [84] (Schemes 32–34). As with 3-imino-2,3-dihydro-1*H*-isoindol-1-ones, the reaction is likely to include two steps. Initially, *N*-phenylbenzenecarboximidamide (**72**) replaces one chloride ligand in the metal coordination sphere, and then intramolecular nucleophilic attack on the isocyanide ligand closes five-membered C,N-chelate ring. The coupling mode of *N*-phenylbenzimidamide with CNR isocyanides depends on the R substituent. If R = Xyl, the amidine coordinates to the metal by the HN=C nitrogen atom, whereas the NHPh nitrogen atom acts as nucleophile in the cyclization step (Scheme 32).

Addition of amidine **72** to a suspension of **15c** in chloroform at room temperature afforded complex **73** as the only product (yield 95% according to the NMR data; isolated yield 85%) as a result of substitution of one chloride ligand. Heating of **73** in boiling chloroform for 4 h gave ~85% of C,N-chelate **74**. The rate of formation of complex **73** did not increase to an appreciable extent in the presence of 2 equiv of **72** at 25°C, nor were other carbene complexes formed. However, bis-C,N-chelate **75** was formed in ~65% yield when the complex *cis*-[$PdCl_2(CNXyl)_2$] (**15c**) was heated for 8 h in boiling chloroform with 4 equiv of **72**. The reaction was accompanied by separation of

Scheme 32.



Scheme 33.



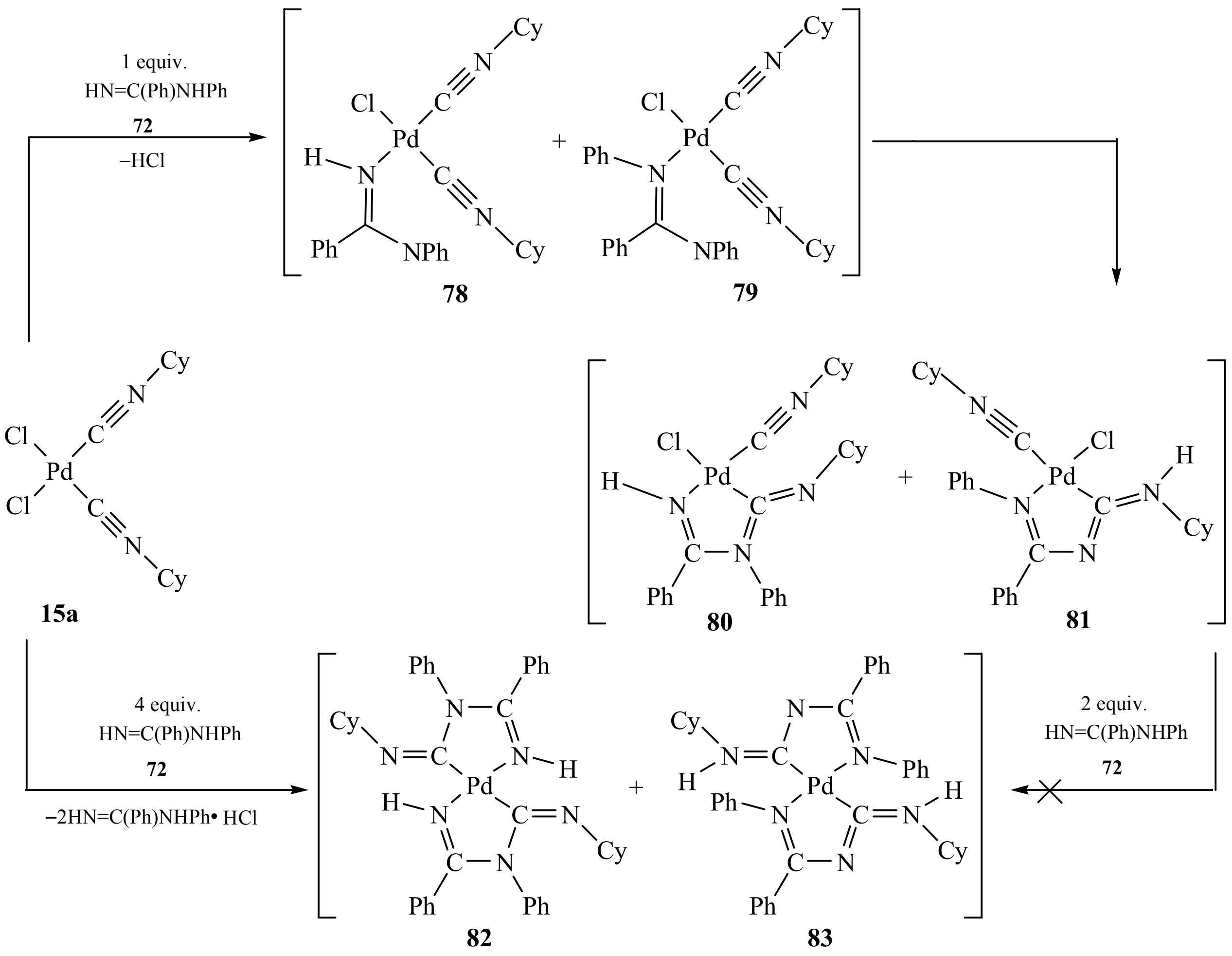
colorless *N*-phenylbenzenecarboximidamide hydrochloride. The same product was also obtained by heating complex **74** with 2 equiv of **72**.

A different pattern was observed in the reaction with *tert*-butyl cyanide complex **15d**. In this case, the amidine coordinates through the NHPh nitrogen atom, while the C=HN nucleophilic center adds to the isocyanide ligand (Scheme 33). The coupling with **15d** was considerably slower than with **15c**. The reaction of **15d** with an equimolar amount of **72** in chloroform resulted in substitution of one chloride ligand by amidine to give 95% (NMR) of complex **76** which was isolated in 85% yield. Subsequent heating of **76** in boiling chloroform for 4 h afforded 85% of C,N-chelate **77**. The use of 2 or 4 equiv of **72** did not change the reaction rate. Attempts to obtain a bis-C,N-chelate analogous to **75** were unsuccessful.

The reactivity of cyclohexyl isocyanide complex **15a** (R = Cy) toward amidine **72** may be regarded as intermediate between **15c** and **15d**. The reaction mixture contained two isomeric carbene complexes **80** and **81** (Scheme 34) which were formed from **78** and **79**, the latter resulting from amidine coordination by different nucleophilic centers. In the reaction of **15a** with 4 equiv of **72** a mixture of isomeric bis(carbene) complexes **82** and **83** was obtained.

Complex **77** obtained from aliphatic isocyanide complex **15d** is characterized by electron density

Scheme 34.



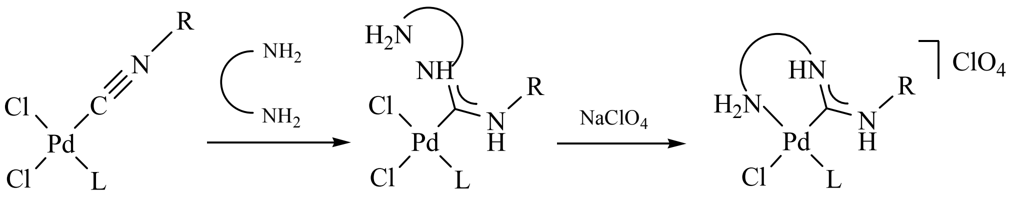
delocalization in the $PdCN_2$ fragment, and the carbene ligand may be regarded as a classical diaminocarbene [84]. The corresponding fragment in analogous compounds **74** and **75** derived from **15c** with aromatic isocyanide ligands contains localized bonds, and these compounds are examples of complexes with carbenoid ligands.

4.3. Addition of 1,2 and 1,3-diamines. Nucleophilic centers in 1,2- and 1,3-diamine molecules are located at different carbon atoms. On the one hand, separation of nucleophilic centers by carbon atoms reduces their effect on each other. On the other hand, their molecules are more flexible, which could give rise to increased number of possible transformations.

Reactions of *cis*-[$PdCl_2$(CNR)L] (**84**) with ethylenediamine and *o*-phenylenediamine were studied in [4]. On the basis of elemental analyses and IR spectral data, the products were assigned the structure of carbene complexes **85** formed via addition of one amino group to the isocyanide ligand, while the second amino group remained uncoordinated (Scheme 35). Coordination of that amino group to palladium with closure of six-membered chelate ring (complex **86**) was achieved by the action of $NaClO_4$ or $AgBF_4$. It was noted that only one isocyanide ligand of the *cis*-[$PdCl_2(CNPh)_2$] complex was involved in the reaction and that no Chugaev type complexes (structurally related to **87**–**89**) were detected.

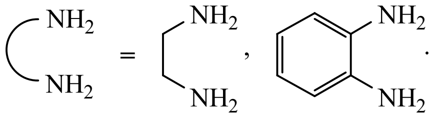
Participation of the second isocyanide ligand in the intramolecular reaction was possible under more severe conditions. Slaughter and co-workers reported a one-step synthesis of chiral bis(carbene) palladium complexes) by coupling of isocyanide complex **15e** with chiral 1,2- [30, 85] and 1,3-diamines [86] (Scheme 36). Complex **15e** containing two *p*-trifluoromethylphenyl isocyanide ligands was selected taking

Scheme 35.

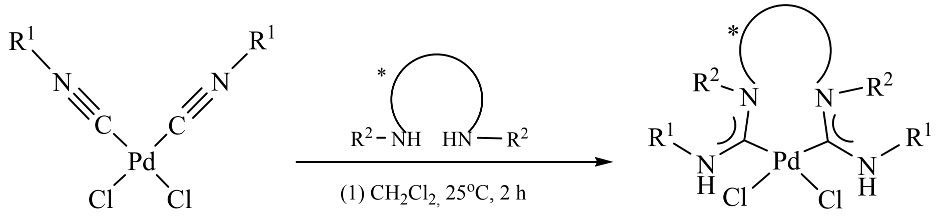


84 **85** **86**

R = Ph, 4-MeOC$_6$H$_4$; L = CNPh, PPh$_3$;

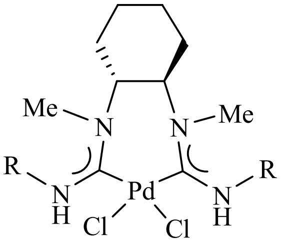


Scheme 36.

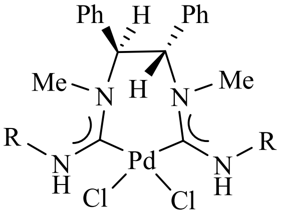


15e **87–89**

R^1 = 4-CF$_3$C$_6$H$_4$.



87



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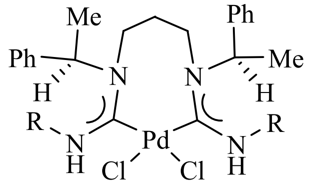
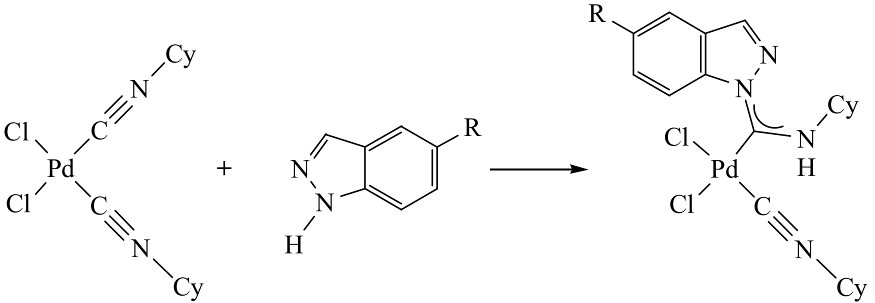


89

into account that electron-withdrawing groups (e.g., CF$_3$) in aryl isocyanides enhance electrophilicity of the N≡C carbon atom, which should favor nucleophilic attack by an amine. Unlike hydrazines, the coupling of 1,2- and 1,3-diamines with isocyanide palladium complexes requires more severe conditions (elevated temperature, long reaction time) to obtain Chugaev type complexes.

4.4. Addition of other polynucleophiles. The addition to the triple C≡N bond of coordinated isocyanides has been well studied for heterocycles containing an NH group not included in the aromatic system (amino heterocycles). However, only one publication is available on reactions of palladium-coordinated isocyanides with NH nucleophiles with the nucleophilic center constituting a part of an aromatic system; in particular, the couplings of *cis*-[PdCl$_2$(CNCy)$_2$] (**15a**) with indazole (**90**) and 5-methylindazole (**91**) were reported [87] to produce aminocarbene complexes **92** and **93** in 72 and 83% yield, respectively (Scheme 37). The structure of **92** and **93** is analogous to that of arylaminocarbene complexes, and the carbene ligand is stabilized due to partial rupture of aromatic system in the heteroaryl fragment [87].

Scheme 37.



15a **90**, **91** **92**, **93**

R = H (**90**, **92**), Me (**91**, **93**).

CONCLUSIONS

The available data indicate essential change of the chemical properties of organic isocyanides due to their coordination to palladium(II). Though isocyanides as free species are nucleophilic, their coordination to Pd(II) endows them with pronounced electrophilic properties. If two isocyanide ligands are present in a Pd(II) complex, they additionally activate each other toward nucleophilic attack. As a result, bis(isocyanide) palladium complexes very readily react with nitrogen nucleophiles even at room or slightly elevated temperature to afford various acyclic diaminocarbene palladium(II) complexes (including chiral ones), which attract interest as promising cross-coupling catalysts. The reactions with nitrogen nucleophiles possessing an electrophilic carbon atom in the α- or β-position with respect to the nucleophilic center may be used to synthesize cyclic diaminocarbene complexes that are excellent catalysts of organic reactions as well.

Furthermore, acyclic diaminocarbene palladium(II) complexes obtained by reactions of bis(isocyanide) palladium complexes with nitrogen nucleophiles are themselves quite reactive compounds capable of acting as both electrophiles (toward excess N-nucleophile) and nucleophiles (after deprotonation of the carbene fragment). This ability can be utilized in reactions with polyfunctional nucleophiles to obtain palladium complexes with various structures, such as mononuclear, dinuclear, bis(carbene), cationic, neutral, etc., which suggests broad prospects in the application of bis (isocyanide) palladium(II) in coordination chemistry.

ACKNOWLEDGMENTS

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