Journal Name

Dynamic Article Links ▶

ARTICLE TYPE

Syntheses of Sterically Shielded Stable Carbenes of the 1,2,4-Triazole Series and their Corresponding Palladium Complexes: Efficient Catalysts for Chloroarene Hydrodechlorination

Nataliya V. Glinyanaya[a], Vagiz Sh. Saberov[a], Nikolai I. Korotkikh[a]*, Alan H. Cowley[b], Rachel R. Butorac[b], Daniel A. Evans[b], Tatyana M. Pekhtereva[a], Anatolii F. Popov[a], and Oles P. Shvaika[a]

The new sterically shielded 1,3,4-trisubstituted 1,2,4-triazol-5-ylidenes **8b-d** were synthesized by a three step method starting from 2-phenyl-1,3,4-oxadiazole. The syntheses of palladium complexes **9a-d** and **10a-d** (including the sterically shielded derivatives **9c,d** and **10a-d**) were carried out via the reactions of the stable carbenes **8a-d** with palladium halogenide salts in THF or toluene solution. Complexes **9c,d** and **10a-d** were found to be excellent catalysts for the reductive dechlorination (hydrodechlorination) of *p*-dichlorobenzene. The structures of **8c**, **9a,b**, and **10a** were determined by single-crystal X-ray diffraction.

Introduction

Recently, stable carbenes have proved to be versatile reagents and catalysts for many important organic reactions.[1-3] Heteroaromatic imidazol-2-ylidenes and 1,2,4-triazol-5-ylidenes are particularly well known examples of stable carbenes.[4] The former type has been studied extensively; however, as individual compounds, 1,2,4-triazol-5-ylidenes are relatively little explored. The first stable carbene of this type, namely a 1,3,4-triphenylsubstituted derivative, was prepared and investigated by Enders and co-workers.[5,6] Subsequently, new types of 1-adamantyl- and 1-*tert*-butyl substituted 1,2,4-triazol-5-ylidenes have been described[7,8] along with their transformations upon heating[9] and reaction with a malonic ester.[10] Biscarbenes with enhanced thermal and chemical stability featuring conjugated 3,3'- and 4,4'-bis-1,2,4-triazol-5-ylidenes have been synthesized and used as ligand supports for copper(I) complexes.[11,12] In a series of works 1,2,4-triazol-5-ylidene complexes were prepared *in situ* from the corresponding salts (among the latest see, for example,[13–15]. Furthermore, 1,2,4-triphenyl-1,2,4-triazol-5-ylidene has proved to be not only an effective catalyst for organic reactions (e.g., benzoin and Stetter condensations),[2] but also a ligand for metal catalyzed reactions.[3] To the best of our knowledge, sterically shielded carbenes of this general type have not been synthesized thus far.

However, such compounds could prove to be useful for catalytic applications and the development of new methods for haloarene hydrodehalogenation.

Halogenaromatic compounds (haloarenes) are widely used as e.g. pesticides, pharmaceuticals, and high-temperature fluids. Unfortunately, most of the aforementioned materials are highly toxic. Moreover, these toxic haloarenes have been accumulated in large amounts throughout the world. Several of these haloarene compounds require particular attention, specifically DDT, hexachlorobenzene, dioxins, polychlorodibenzofurans (furans), and polychloro-biphenyls.[16] All of the foregoing compounds were included in the Stockholm Convention of May 22th 2001 in a list of the 12 most hazardous "persistent organic pollutants" (POP). The safe management of these troublesome toxic POPs is a persistent environmental concern.

The most common pathways for haloarene detoxification are as follows: (1) oxidative methods (combustion at high temperatures or oxidation in critical water, etc.), (2) reductive methods such as catalytic reduction with hydrogen, reduction by metals, nanometals, and (3) biodegradation methods.[17] The first group of methods for haloarene detoxification has some disadvantages such as the use of high temperature and/or high pressure conditions, the difficulty in recovering the vaporized polychloroarenes, and the high risk of producing

dioxins. The second group of detoxification methods also presents some unfavorable aspects, particularly those that concern the formation of corrosive hydrohalogenides and the high pressures necessary for hydrogenation and acidic reductions,[18] the use of dangerous or expensive reducing reagents such as alkali metals and metalorganic compounds,[19] microwave techniques,[20] all of which result in low decomposition rates or efficiencies. For example, the promising use of metallic calcium in ethanol for hydrodehalogenation requires large quantities of the metal (10-40 fold excess per 1 Cl) and involves the formation of several by-products of the ring reduction.[21-23] Noble metal nanoparticles permit recycling of the catalyst. However, they require approximately 1 mol % Pd to achieve the necessary activity for detoxification.[24,25] Biodegradation methods with aerobic microbes are only suitable for the reduction of low halogenated arenas and hence they are not useful as a general detoxification method (such organisms are contained in small amounts in the first few mm of soil).[16, 17] Moreover, anaerobic microorganisms are suitable for reductive dechlorination (hydrodechlorination) which results the conversion of more chlorinated hydrocarbons. However, such species only react with *m*- and *p*-substituted compounds and do not activate *o*-substituted haloarenes.

Thus, among the known methods, catalytic reductive dehalogenation (hydrodehalogenation) promises the greatest pontential for success. In the interest of achieving high catalytic activities and cost effectiveness, catalytic reductive dehalogenation could represent the best solution for the neutralization of toxic POPs. Moreover, palladium carbene complexes are well known to be the suitable catalysts for the foregoing reaction. For example, it is known that an *in situ* generated catalyst based on Pd(dba)$_2$ and 1,3-disubstituted imidazolin-2-ylidenes affords high yields of hydrodehalogenation products when carried out in dioxane at 100 °C (TON up to 28–50, TOF up to 28–50 h^{-1}).[26] Compound **1** (Figure 1) provides moderate catalytic efficiencies for the reactions of monochlorobenzenes at room temperature[27] (TON 100, TOF 200 h^{-1}) and complex **2** has been shown to be active for the hydrodehalogenation of *p*-dichlorobenzene at 60 °C (TON 194, TOF 111 h^{-1})[28]. Furthermore, the use of microwave irradiation at 120 °C resulted in the highest rate for this reaction. In this case, a virtually quantitative yield of the product was obtained in only 2 min (TON 4000, TOF 120000 h^{-1} for *p*-chlorotoluene; TON 3800, TOF 114000 h^{-1} for *p*-dichlorobenzene)[28].

The catalytic efficiency of the nickel complex **3** that was prepared via the reaction of Ni(PPh$_3$)$_2$Br$_2$ and with the corresponding carbene[29] is not efficient for the hydrodebromination transformation of *p*-bromofluorobenzene or for the hydrodechlorination of *p*-chlorofluorobenzene (activated haloarenes) (TON 15-22 and TOF 4-44 h^{-1} at 25 °C).
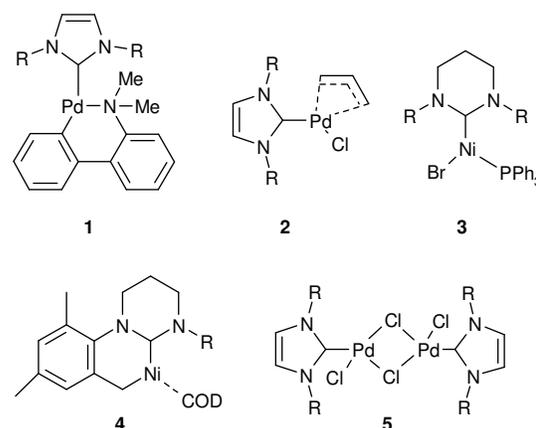

Figure 1 Palladium and nickel catalysts for the hydrodehalogenation reactions (**1,2,5** R = Dipp (2,6-diisopropylphenyl); **3,4** R = Mes (2,4,6-trimethylphenyl).

The nickel(I) complex **4** was used for the hydro-defluorination of fluorobenzenes[30]. It was found that in the presence of Et$_2$CHONa at 100 °C catalysts of the type L$_2$Ni are less efficient for hydrodehalo-genation (TON 12 and TOF 4 h^{-1} for L = IMes) than LNi (TON 18-31 and TOF 6-10 h^{-1}, respectively). Taken collectively, complexes **1-4** exhibit insufficient catalytic activities. However, the highest efficiencies for polyhalogenated arenes were obtained with the dimeric (IPrPdCl$_2$)$_2$ catalyst **5** (R = Dipp)[31] (in the hydrodehalogenation of 1,2,4,5-tetrachlorobenzene in isopropanol at 80 °C TON 19650 and TOF 819 h^{-1} and in the reaction of 2,2′,3,3′-tetrachlorobiphenyl with a TON of 10000 and with a TOF 417 h^{-1}, respectively).

Given the foregoing information, sterically shielded 1,2,4-triazol-5-ylidenes were investigated as ligands for haloarene hydrodehalogenation catalysis. In the present contribution, we describe (i) the syntheses of new sterically shielded carbenes 1-akyl-3,4-diaryl-1,2,4-triazol-5-ylidenes; (ii) the syntheses of mono- and biscarbene palladium halogenide complexes of the 1,2,4-triazol-5-ylidenes; (iii) the X-ray crystal structures of the sterically shielded carbene 1-*tert*-butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-ylidene; three PdI$_2$ and PdCl$_2$ carbene complexes bis-[1-*tert*-butyl-3-phenyl-4-(4-bromophenyl)-1,2,4-triazol-5-yliden]palladium chloride, bis-[1-*tert*-butyl-3-phenyl-4-(4-bromo-phenyl)-1,2,4-triazol-5-yliden]palladium iodide and the sterically shielded [1-*tert*-butyl-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-yliden]palladium chloride; (iv) catalytic efficiencies of the foregoing complexes with respect to the hydrodechlorination of *p*-dichlorobenzene.

Results and discussion

Synthesis of carbenes and their palladium complexes

In order to obtain the desired carbene complexes, along with the known carbene **8a**[9], a series of new stable carbenes **8b-d** was synthesized in the following three stages: (1) syntheses of sterically hindered 4-substituted 3-phenyl-4-aryl-1,2,4-triazoles **6b,c** via the ring transformation of 2-phenyl-1,3,4-oxadiazole with the appropriate anilines, (2) quaternization of 1,2,4-triazoles **6b,c** using sterically hindered alkyl-halogenides (*tert*-butyl iodide and 1-bromoada-mantane), (3) deprotonation of the aforementioned salts **7b-d** using potassium *tert*-butoxide in a mixture of toluene and isopropanol akin to previously published work from our laboratory[7] (Scheme 1), most of which (**8b-d**) include sterically hindered groups (*t*-Bu, 1-Ad in position 1 with Mes or Dipp in position 4).
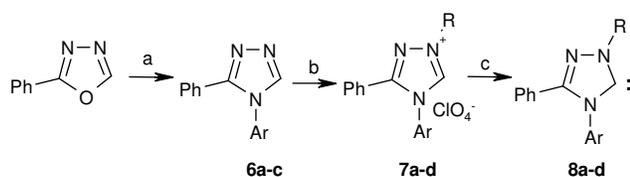
Scheme 1 Synthesis of carbenes **8a-d**. *Reaction conditions*: (a) ArNH₂, TFA, *o*-DCB, 190 °C, 12h; (b) 1. RX, AcOH, 120 °C, 10-18 h; 2. NaClO₄; (c) *t*-BuOK, PhMe, *i*-PrOH, r.t. *Compounds*: **6a** Ar = 4-BrC₆H₄; **6b** Ar = Mes; **6c** Ar = Dipp; **7a, 8a** R = *t*-Bu; Ar = 4-BrC₆H₄; **7b, 8b** R = 1-Ad; Ar = Mes; **7c, 8c** R = *t*-Bu; Ar = Dipp; **7d, 8d** R = 1-Ad; Ar = Dipp; Dipp = 2,6-*i*-Pr₂C₆H₃

The syntheses of the new biscarbene complexes **9a-d** (Figure 2) were carried out via the direct reaction of the free carbenes **8a-d** with palladium halogenides (chloride and iodide) in a molar ratio of 2:1 in THF solution according to the pertinent literature method[32]. An analogous method was used for the syntheses of the monocarbene complexes **10a–d**, using the appropriate molar ratio of 1:1. For the purposes of comparison, the known complex **5** was obtained via the reaction of the appropriate 1,3-diarylimidazol-2-ylidene with Pd(PhCN)₂Cl₂ according to the literature procedure[31].

Compounds **6a-c**, **7a-d**, **8a-d**, **9a-e**, **10a–d** were characterized by ¹H and ¹³C NMR spectroscopy, and their elemental compositions were established on the basis of elemental analysis. The ¹³C NMR spectra of the sparingly soluble complexes **9c,d** and **10b,d** were recorded in the solid state. In the case of the ¹H NMR spectra of triazoles **6b,c** with the exception of the specific signals for the mesityl or dipp groups, the resonances of the *meso*-protons CHN were evident (δ 8.73, 8.88 ppm in DMSO-d₆). In the case of the spectra of the triazolium salts **7a-d** the signals were shifted significantly downfield (δ 10.61–10.91 ppm). It is noteworthy that two forms of the triazole **6c** were detected in CDCl₃ solution. The NMR spectrum of

one of these forms was characterized on the basis of different signals for the methyl groups (δ 0.90, 1.10 ppm) and an upfield signal for the methine CH-groups (δ 2.37 ppm) of the corresponding isopropyl fragments. The other form was evident from the presence of only one signal for the methyl groups (δ 1.19 ppm) and a downfield signal for the methine CH-groups (δ 3.02 ppm).
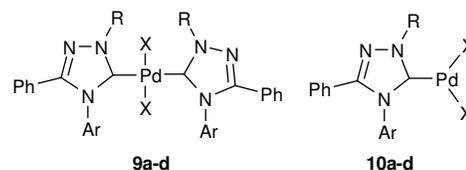
Figure 2 Mono and biscarbene palladium complexes (**9a** X = Cl, R = *t*-Bu, Ar = *p*-BrC₆H₄; **9b** X = I, R = *t*-Bu, Ar = *p*-BrC₆H₄; **9c** X = I, R = Ad, Ar = Mes; **9d** X = I, R = *t*-Bu, Ar = Dipp; **10a** X = Cl, R = *t*-Bu, Ar = Dipp; **10b** X = I, R = *t*-Bu, Ar = Dipp; **10c** X = Cl, R = Ad, Ar = Dipp; **10d** X = I, R = Ad, Ar = Dipp)

The *meso*-proton CHN resonances for these forms were found at 8.10 and 8.30 ppm, respectively. Presumably, the second form relates to a symmetrical structure with a close to 90° angle for the N(4)-aryl group. On the other hand, the alternate form could be a rotational form with a smaller bond angle. In DMSO-d₆ solution the second form converted to the first one (the pertinent signals were located at δ 0.88, 1.09, and 2.24 ppm, respectively). Probably for the same reason, in DMSO-d₆ solution, salt **7c** shows only the first form of the isomers (δ 0.88, 1.09, and 2.24 ppm). However, the NMR spectrum of salt **7d** in CDCl₃, corresponds only to the first form (δ 0.91, 1.21, and 2.24 ppm, respectively). Interestingly, compounds **6b,c** were also obtained recently[33] by the similar method to the one described above. Following purification, only one form of this compound was isolated.

The most useful information, for carbenes **8a-d**, are the ¹³C NMR signals for the carbene carbon atom C(5) (δ 211.1–212.7 ppm). It was found that the NMR signals for complexes **9a-d** and **10a-d** are shifted upfield (δ 153.3–171.9 ppm). Interestingly, two closely spaced resonances were detected for compound **9b** in CDCl₃ solution. These resonances can be assigned to the *trans-trans* and *cis-trans* isomers of **9b** (the first designation relates to the disposition of the rotating triazole rings with respect to each other and the second one relates to the disposition of the halogen atoms at the metal center). The first isomer was isolated in a pure state and subsequently characterized on the basis of a single crystal X-ray diffraction study. The ¹H and ¹³C NMR spectra for complex **10a** in CDCl₃ solution exhibited two forms, presumably due to rotation of the N(4)-aromatic ring. The two different signals for the *tert*-butyl protons confirmed this interpretation (δ 2.18 and 2.29 ppm). However, only one methyl signal was evident in the ¹³C NMR spectrum (δ 31.4 ppm), along

with one signal for the *ipso*-C atom (δ 64.3 ppm). Furthermore, the presence of two groups of methyl and CH-resonances is evident in the ^{1}H NMR spectra (δ 0.54–0.70 ppm and 1.16–1.57 ppm, and 2.50, 2.61 ppm, respectively). These resonances indicate the existence of non-equivalent isopropyl and methyl groups in both isomers. However, only one isomer was detected in the single crystal X-ray structure (see below).

The solid state ^{13}C NMR spectra of complexes **9c,d**, and **10c,d** exhibited only one isomeric form for each compound (single resonances are apparent for the *i*-Pr CH, Ad *ipso*-C, C(3) and C(5)Pd atoms at δ 47.4–49.1, 64.1–65.6, 148.2–156.4, and 154.9–171.9 ppm, respectively). The C(5)Pd signals for the chloride complexes (**10a,c**) were shifted upfield (δ 153.3-154.9 ppm) relative to those for similar resonances (δ 167.0-171.9 ppm) that were observed for the iodide complexes (**9c,d**, **10b,d**). Four resonances were evident for the complex **10b** carbenoid carbon atom and can be explained by the presence of four fixed rotational forms in the solid state. The ^{1}H NMR spectrum for **10b** in DMSO-d_6 solution indicates that only two forms of the complex were present in solution (for *i*-Pr group CH$_3$C δ 0.62, 1.36; CHC 2.94 ppm and CH$_3$C δ 0.83, 1.25; CHC 4.11 ppm and one signal of *t*-Bu CH$_3$C group).

X-ray diffraction studies

The single crystals of compound **8c** were grown from toluene solution and studied subsequently by X-ray diffraction. The structure of **8c** is presented in Figure 3 and the bond lengths (Å), bond orders, bond angles and dihedral angles (degrees) for structure **8c** are presented in Table 1. As can be seen from these data, the planar structure of **8c** is reminiscent of those for the 1,2,4-triazol-5-ylidenes[9, 10, 34]. The bond angle at the carbene carbon atom is approximately 100.5° and the high bond order of 1.718 for the C(1)-N(3) bond implies a substantial ylide contribution to the carbene structure. Moreover, the C(2)-aromatic ring is twisted relative to the plane of the triazole ring by 36.3° (the bond order is 1.284), and furthermore the N(1)-aromatic ring is twisted almost orthogonally with respect to the triazole ring (87.4°) (the bond order is 1.139).

The single crystals of the palladium complexes **9a,b** and **10a**, that were used for the X-ray diffraction studies, were grown from acetonitrile. The crystal structures of **9a,b** and **10a** are displayed in Fig. 4-6 and the bond lengths, bond orders, bond angles and dihedral angles are presented in Tables 2-4.

Complexes **9a,b** have predominant *trans-trans* isomeric orientations. The bond orders for N(2)-C(1) in these molecules (*p* 1.770–1.782) closely resemble that of the initial carbene (1.799)[10]. For comparison, similar features were observed for the linear bistriazolylidene complexes of copper(I) chloride[9, 16] and the related bistriazolylidene chelate complex of

copper(I) iodide[11].

The dihedral angles of the aromatic rings in molecules **9a,b** are also close to that of the initial carbene. The C(2)-nucleus is twisted relative to the triazole ring by 36.3° (**9a**) and 12.3° (**9b**), respectively versus 29.9° for the initial carbene.
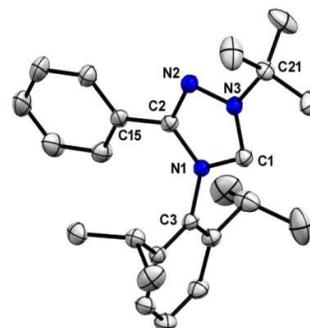
Figure 3 POV-Ray diagrams for 1-*tert*-butyl-3-phenyl-4-(2,6-diiso-propylphenyl)-1,2,4-triazol-5-ylidene **8c** with thermal ellipsoids displayed at 50% probability. All hydrogen atoms have been removed for clarity.

Table 1. Selected bond lengths and angles in carbene **8c**

Bond	Length (Å)	Bond order	Angles	°
C(1)-N(3)	1.3491(14)	1.718	N(3)-C(1)-N(1)	100.53(9)
C(1)-N(1)	1.3843(15)	1.516	N(1)-C(2)-N(2)-N(3)	-0.48(11)
C(2)-N(1)	1.3860(14)	1.506	N(1)-C(1)-N(3)-C(21)	177.70(10)
C(2)-N(3)	1.3134(14)	1.923	N(1)-C(2)-C(9)-C(10)	36.3(6)
C(2)-C(15)	1.4781(15)	1.284	C(1)-N(1)-C(3)-C(4)	87.40(13)
C(3)-N(1)	1.4498(13)	1.139	-	-
N(2)-N(3)	1.3834(13)	1.336	-	-
N(3)-C(21)	1.4917(14)	0.898	-	-

Furthermore, the N(1) nucleus is twisted with respect to the same plane by 69.3° (**9a,b**) versus 51.1° for the initial carbene. The bond orders for C(2)-C(9) and N1-C(3) are 1.31-1.33 and 1.18-1.22 respectively, since the C(2) nucleus is naturally more conjugated with the triazole ring than the N(1)-nucleus.
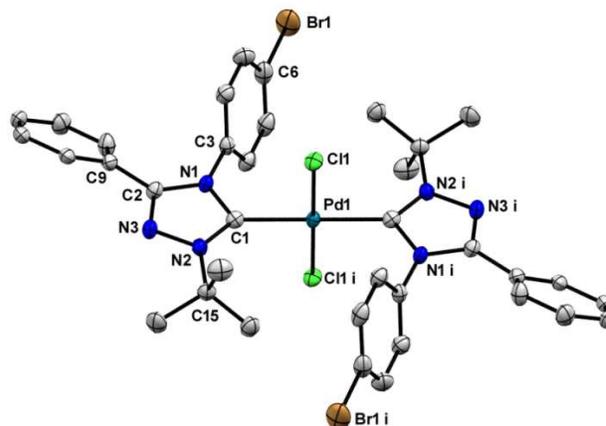
Figure 4 POV-Ray diagrams for bis-(1-*tert*-butyl-3-phenyl-4-bromo-phenyl-1,2,4-triazol-5-yliden)palladium iodide **9b** with thermal ellipsoids displayed at 50% probability. All hydrogen atoms have been removed for clarity.

The bond angles at the carbenoid carbon atom (103°) are significantly larger than those for the carbene (100.3°) and are noticeably smaller than that observed for the salt complex (110°)[7, 34]. Furthermore, the Pd-C bond distances (2.025, 2.034 Å) are notably larger than the sum of the covalent radii for these atoms (1.95 Å) and significantly larger than the sum of covalent radius of the carbon atom and the ionic radius of palladium(II) (1.75 Å) that is indicative of a coordination C-Pd bond in the complexes.

The Pd-Cl bond distances in complex **9a** (2.330 Å) are intermediate in length between those of covalent and ionic bonds (the sum of the covalent radii is 2.19 Å, while the sum of the ionic radii is 2.67 Å). Overall, however it is closer to a covalent bond (the extent of Pd(1)-Cl(1) ionization is approximately 29 %). In the case of complex **9b**, the Pd-I bond (2.60 Å) is also intermediate in character with respect to covalency vs. ionicity (the sum of covalent radii is 2.53 Å and the sum of ionic radii is 3.06 Å). Overall, however, the Pd-I bond more closely resembles a covalent bond (the extent of Pd(1)-I(1) ionization is 13 %). Thus, the complexes **9a,b** have typical structures with coordination C-Pd bonds and shortened Pd-halogen bonds.

Table 2. Selected bond lengths and angles in complex **9a**

Bond	Length Å	Bond order	Angles	°
C(1)-N(2)	1.338(4)	1.782	N(1)-C(1)-N(2)	103.7(3)
C(1)-N(1)	1.368(5)	1.609	C(1)-Pd(1)-Cl(1)	89.70(10)
C(2)-N(3)	1.308(5)	1.954	Cl(1)-Pd(1)-Cl(1a)	180.00(5)
C(2)-N(1)	1.377(4)	1.557	N(3)-C(2)-N(1)-C(1)	-0.2(4)
C(2)-C(9)	1.469(5)	1.330	N(1)-C(1)-N(2)-N(3)	-1.7(4)
C(3)-N(1)	1.443(4)	1.178	N(1)-C(2)-C(9)-C(10)	36.3(6)
N(2)-N(3)	1.386(4)	1.323	C(4)-C(3)-N(1)-C(1)	69.3(5)
N(2)-C(15)	1.500(5)	0.851	Pd(1)-C(1)-N(1)-C(2)	-174.1(2)
C(6)-Br(1)	1.895(4)	-	Pd(1)-C(1)-N(2)-C(15)	-4.4(6)
C(1)-Pd(1)	2.025(4)	-	N(1)-C(1)-Pd(1)-Cl(1)	86.0(3)
Pd(1)-Cl(1)	2.3301(10)	-	N(2)-C(1)-Pd(1)-Cl(1)	92.4(4)
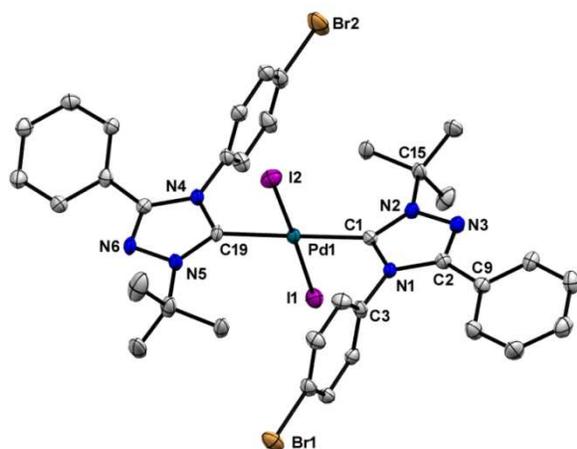
Figure 5 POV-Ray diagrams for bis-(1-*tert*-butyl-3-phenyl-4-bromo-phenyl-1,2,4-triazol-5-yliden)palladium iodide **9b** with thermal ellipsoids displayed at 50% probability. All hydrogen atoms have been removed for clarity.

Compound **10a** is a monocarbene-acetonitrile palladium complex. The bond order of the N(1)-C(1) bond in this molecule (*p* 1.833) is larger than that of the initial carbene (1.718). The Pd-C bond distance (1.963 Å) is close to the sum of the covalent radii of the constituent atoms (1.95 Å) and significantly larger than the sum of the covalent radius of the carbon atom and the ionic radius of palladium(II) (1.75 Å). The latter observation, along with the bond orders, indicates that there is a stronger interaction between the carbene carbon and the palladium atoms than in the case of the biscarbene complexes **9a,b**. Moreover, the Pd-Cl bond in the structure of **10a** (2.308 Å) is intermediate in length between covalent and ionic bonds (the sum of the covalent radii is 2.19 Å and the sum of the ionic radii is 2.67 Å), but, closer to a covalent bond (the extent of Pd(1)-Cl(1) ionization is approximately 25 %).

Table 3. Selected bond lengths and angles in complex **9b**

| Bond	Length (Å)	Bond order	Angles	°
C(1)-N(2)	1.340(7)	1.770	N(1)-C(1)-N(2)	103.4(4)
C(1)-N(1)	1.368(7)	1.609	C(1)-Pd(1)-I(1)	90.02(15)
C(2)-N(3)	1.308(7)	1.954	I(2)-Pd(1)-I(1)	176.59(2)
C(2)-N(1)	1.386(7)	1.506	N(3)-C(2)-N(1)-C(1)	-0.2(6)
C(2)-C(9)	1.474(7)	1.305	N(1)-C(1)-N(2)-N(3)	0.8(6)
C(3)-N(1)	1.435(7)	1.224	N(1)-C(2)-C(9)-C(10)	12.3(10)
N(2)-N(3)	1.376(6)	1.374	C(4)-C(3)-N(1)-C(1)	69.3(5)
N(2)-C(15)	1.491(7)	0.902	Pd(1)-C(1)-N(1)-C(2)	-179.7(4)
C(6)-Br(1)	1.907(5)	-	Pd(1)-C(1)-N(2)-C(15)	-6.3(9)
C(1)-Pd(1)	2.034(5)	-	N(1)-C(1)-Pd(1)-I(1)	85.8(5)
Pd(1)-I(1)	2.6014(7)	-	N(2)-C(1)-Pd(1)-I(1)	-97.6(5)
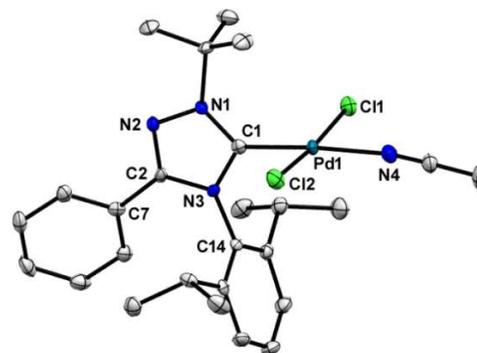
Figure 6 POV-Ray diagrams for 1-*tert*-butyl-3-phenyl-4-(2,6-diiso-propylphenyl)-1,2,4-triazol-5-yliden)palladium chloride **10a** with thermal ellipsoids displayed at 50% probability. All hydrogen atoms and an acetonitrile molecule have been removed for clarity.

The angle of the carbenoid carbon atom (103.4°) is significantly larger than that of the initial carbene (100.5°) although the salt carbenoid angle is larger by comparison (110°)[7, 34]. The C(2) nucleus is twisted relative to that of the triazole ring by 151.0° as opposed to 29.9° for the initial carbene. Furthermore, the N(3)-nucleus is twisted with respect to the triazole ring by 102.1° versus 51.1° for the same carbene. The bond orders for C(2)-C(7) and N(3)-

C(14) are 1.264 and 1.098, respectively. Thus, the complex **10a** adopts a typical structure with a strong C-Pd coordination bond and a shortened bond Pd-Cl.

Table 4. Selected bond lengths and angles in complex **10a**

Bond	Length (Å)	Bond order	Angles	°
C(1)-N(2)	1.329(4)	1.833	N(1)-C(1)-N(3)	104.6(2)
C(1)-N(1)	1.366(4)	1.621	C(1)-Pd(1)-Cl(1)	92.36(8)
C(2)-N(3)	1.384(4)	1.517	Cl(1)-Pd(1)-Cl(2)	173.88(3)
C(2)-N(1)	1.309(4)	2.142	C(1)-N(1)-N(2)-C(2)	0.4(3)
N(1)-N(2)	1.375(3)	1.379	N(3)-C(1)-N(1)-N(2)	0.1(3)
C(2)-C(7)	1.482(4)	1.264	C(19)-C(14)-N(3)-C(1)	102.1(3)
N(3)-C(14)	1.457(4)	1.098	N(3)-C(2)-C(7)-C(8)	151.0(3)
C(3)-N(1)	1.514(4)	0.770	Pd(1)-C(1)-N(3)-C(2)	175.50(19)
C(1)-Pd(1)	1.963(3)	-	Pd(1)-C(1)-N(2)-C(15)	-6.3(9)
Pd(1)-Cl(1)	2.3078(8)	-	N(1)-C(1)-Pd(1)-Cl(1)	-84.3(3)
Pd(1)-N(4)	2.075(3)	-	N(1)-C(1)-Pd(1)-Cl(2)	89.6(3)

Catalytic tests

Test reactions for the hydrodechlorination catalysis were carried out by heating the reaction mixture of the haloarene with potassium or sodium isopropoxides, which had been generated from potassium or sodium *tert*-butoxide or hydroxide, in the presence of a catalyst in isopropanol at 80 °C. Control of the conversion (on 1 chlorine atom) was calculated according to the masses of the sodium or potassium chlorides, which are insoluble in isopropanol. The most efficient catalysis trials were examined on the basis of gas chromatography. The catalytic efficiencies were estimated using the values of TON and TOF.

A summary of the results concerning the study of the catalytic efficiencies of the carbene complexes **5**, **9a-d**, and **10a-d** with respect to the model compound *p*-dichlorobenzene and a variety of bases is presented in Tables 5-7.

Table 5. Catalytic efficiencies of carbene complexes **9a-d**, **10a-d**, **5** for the reaction of *p*-dichlorobenzene with potassium *tert*-butoxide in isopropanol at 80 °C.

Catalyst	Catalyst amount, mol %	Reaction time, h	Conv., %	TON per 1Cl	TOF, h⁻¹
9a	0.1	8	25	500	62
9b	0.1	8	11	220	28
9c	0.1	8	70	1400	175
9d	0.1	8	38	760	95
10a	0.1	8	66	1320	165
10b	0.1	8	58	1160	145
10c	0,1	8	72	1140	180
10c*	0.01	24	40	8000	334
10d	0.01	24	100	20000	840
5	0.01	8	63	12600	1560
5	0.01	24	88	17600	734

*The reagent is potassium *tert*-butoxide to which of 1 mol % lithium *tert*-butoxide has been added.

Examination of Table 5 reveals that the hydrodehalogenation of *p*-dichlorobenzene with potassium *tert*-butoxide proceeds efficiently with most of the carbene catalyst complexes that were tested. The most rapid reaction was observed with the triazolylidene monocarbene complex **10d** (after 24 h of the reaction the maximum TON and TOF values reached 20000 and 840 h⁻¹ respectively). If the efficiency of complex **10c** is relatively low (TON 1140 cycles after 8 h), in the presence of 1 mol % lithium *tert*-butoxide after 24 h the TON is enhanced up to 8000 cycles.

When sodium *tert*-butoxide was used in these hydrodehalogenation reactions (Table 6), a notable increase in the efficiency indices by almost an order of magnitude was observed for the triazolylidene complexes **9d**, **10b,c** (TON 7200 – 15400, TOF 300 – 2230 h⁻¹). In fact, these values exceeded those for the etalon complex **5** (TON 6400, TOF 266 h⁻¹).

Table 6. Catalytic efficiencies of carbene complexes **9d**, **10b,c**, **5** for the reaction of *p*-dichlorobenzene with sodium *tert*-butoxide in isopropanol at 80 °C.

Catalyst	Catalyst amount, mol %	Reaction time, h	Conv., %	TON per 1Cl	TOF, h⁻¹
9d	0.01	24	53	10600	440
10b	0.01	24	36	7200	300
10c	0.01	6	77	15400	2230
5	0.01	24	32	6400	266

The hydrodechlorination reaction in the presence of sodium hydroxide and isopropanol was examined using complexes **5** and **10c,d**. The use of sodium hydroxide is particularly appropriate in view of the possible development of a technology for haloarene (production wastes) neutralization (detoxication) since it is an inexpensive reagent. It was found (Table 7) that the triazolylidene complexes **10c,d** exhibited high efficiencies for the reaction of *p*-dichlorobenzene with sodium hydroxide (TON 2000 – 6800, TOF 176 – 284 h⁻¹) but in fact for **10d** lesser than that with potassium *tert*-butoxide by a 3 fold decrease.

Table 7. Catalytic efficiencies of carbene complexes **9d**, **10a-d** for the reaction of *p*-dichlorobenzene with sodium hydroxide in isopropanol at 80 °C.

Catalyst	Catalyst amount, mol %	Reaction time, h	Conv., %	TON per 1Cl	TOF, h⁻¹
10c	0.1	8	100	2000	250
10c	0.01	24	34	6800	284
10d	0.01	24	21	4200	176
5	0.01	24	96	19200	800

Interestingly, the known complex **5** appeared to

be somewhat more effective for the reaction with sodium hydroxide (TON 19200, TOF 800 h^{-1}), than those with potassium *tert*-butoxide (TON 17600, TOF 734 h^{-1}) and sodium *tert*-butoxide (TON 6400, TOF 266 h^{-1}).

According to gas chromatographic data, noticeable quantities of haloarenes were not observed in the experiments that resulted in quantitative conversion of the initial haloarene.

In summary, it can be concluded that the highest efficiency is apparent for the catalysts with the sterically bulky 1-(1-adamantyl)-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene ligand. The high TON of 20000 cycles (**10d**) with potassium *tert*-butoxide and TON 15400 with sodium *tert*-butoxide exceed the efficiency level of complex **5** (TON 17600 and 6400, respectively). Another factor that contributes to the catalytic efficiency is the presence of iodide as the second ligand, that can enhance the efficiency of the catalyst (TON 20000 cycles for **10d**, TON 8000 cycles for **10c**).

As far as known, the mechanism of haloarene (i.e. *p*-dichlorobenzene) hydrodehalogenation,[2, 3] involves the formation of palladium (0) complex (**D**) as the first step via the interaction of palladium (II) complex with metal isopropoxide, followed by reaction with the haloarene **E** thereby affording the product of further addition to palladium (**F**) (Scheme 2).
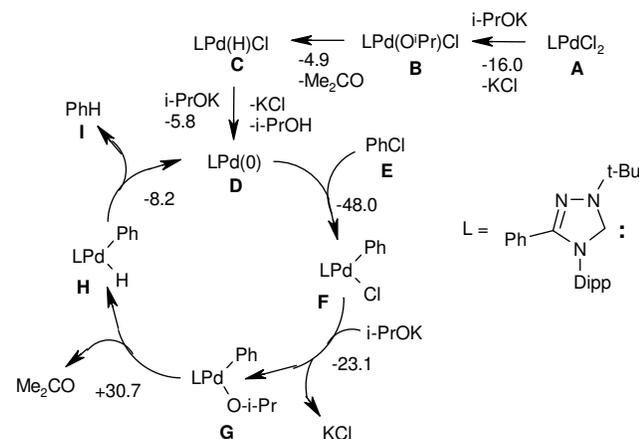
Scheme 2 Mechanism of haloarene hydrodehalogenation

The activated complex **F** reacts subsequently with the metal isopropoxide via the nucleophilic substitution of the halogen, thus forming the adduct of the H-arene with palladium **H** due to decomposition of the previously formed isopropoxide complex **G**. Finally, decomposition of the latter produces H-arene **I** and the palladium (0) complex **D**. The enthalpy changes that take place during chlorobenzene conversion catalyzed by complex **10a** were evaluated on the basis of DFT, B3LYP5, 3-21G calculations (Scheme 2, in kcal/mol). These calculations indicate that a strong exothermic reaction takes place between palladium(0) compound **D** and

chlorobenzene (ΔH -48.0 kcal / mol) and that the conversion of compound **G** to **H** is endothermic (ΔH +30.7 kcal / mol). An important stage in the foregoing process may be the interaction of the initial precatalyst **A** with the metal isopropoxide (ΔH –16.0 kcal / mol), which is the intitial stage in the formation of these molecular complexes. As might be expected, the stabilities of these complexes depend on steric conditions in the molecule.

A possible reason for the increase in catalytic efficiency, for sterically shielded carbene complexes, particularly **10c,d**, is attributable to the increased stability of the intermediate Pd(0) species in the reaction medium.

Conclusions

Along with the syntheses of the new biscarbene palladium complexes **9a,b** from the known carbene **8a**, a series of sterically shielded 1,3,4-trisubstituted 1,2,4-triazol-5-ylidenes **8b-d** and their palladium complexes **9c,d, 10a-d** have been synthesized in the present work. It was found that sterically shielded compounds (**9c,d**; **10a-d**) are effective catalysts for *p*-dichlorobenzene hydrodechlorination. The efficiencies for the monocarbene complexes **10c,d** were shown to be somewhat higher than those for the biscarbene complexes **9c,d**. However, the latter results are strongly dependent on the nature of the reagent.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400 MHz for ^{1}H NMR spectra and 100 MHz for ^{13}C NMR spectra) in DMSO-d[6], C[6]D[6] or CDCl[3] solution or in the solid state. The ^{1}H NMR and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane (TMS) (solution) and sodium 2,2-dimethyl-2-silapentan-5-sulfonate (DSS) (solid state). The X-ray diffraction data were collected on either a Rigaku AFC12 Saturn 724+ CCD diffractometer equipped with a Rigaku XStream low temperature device that operated at 100 K or on a Rigaku SCX-Mini Diffractometer equipped with a Rigaku XStream low temperature device that operated at 100 K, or on a Nonius-Kappa CCD diffractometer with a Oxford cryostream 600 that operated at 153K. All instruments used a graphite-monochromated Mo Kα radiation source (λ = 0.71075 Å). Corrections were applied for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares cycles on F[2] using the Siemens SHELXTL PLUS 5.0 (PC) software package [35] and PLATON [36]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in fixed, calculated positions using a riding model.

Thin-layer chromatography was performed on silica gel with chloroform or a 10:1 mixture of chloroform and methanol as eluent, followed by development with iodine. Elemental analyses were carried out at the Analytical Laboratory of the Litvinenko Institute of Physical Organic and Coal Chemistry. The quantum chemical calculations were performed with the help of Firefly 8.0 program.

3,4-Diaryl-1,2,4-triazoles (**6b,c**) **(general procedure)**. 3,4-Diaryl-1,2,4-triazoles were obtained according to the modified procedure of the work [37] by the ring transformation of 2-phenyl-1,3,4-oxadiazole with the respective anilines in the presence of trifluoroacetic acid at 190 °C. The mixture of aromatic amine (20 mmol) and trifluoroacetic acid (20 mmol) in *o*-dichlorobenzene (1-2 mL) was added to 2-phenyl-1,3,4-oxadiazole (20 mmol) and heated at 190 °C for 12 h. The resulting oil or crystalline product was washed 5 - 6 times with petroleum ether (50 ml). Then 10% aqueous solution of potassium hydroxide was added and the mixture was stirred for 15-20 min. The resulting crystalline precipitate was filtered off, washed with water, then with a mixture of petroleum ether - isopropanol (3:1) and petroleum ether and dried. The obtained products were recrystallized from benzene.

3-Phenyl-4-(2,4,6-trimethylphenyl)-1,2,4-triazole (**6b**). Yield 2.63 g, 50 %, mp 125 – 126°C (benzene). δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 1.86 (s, 6H, *o*-CH$_3$C), 2.31 (s, 3H, *p*-CH$_3$C), 7.09 s (2H, Ar), 7.39 s (5H, Ar), 8.73 s (1H, C^{5}HN). Compound **6b** was identical to the product of the same reaction in ionic liquids isolated by colomn chromatography [33] (mp 125-126 °C).

3-Phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazole (**6c**). Yield 3.05 g, 50 %, mp 98 – 100 °C (benzene). Found: C, 78.7; H, 7.4; N, 13.9. Calc. for C$_{20}$H$_{23}$N$_3$: C, 78.7; H, 7.6; N, 13.8%. δ_H (400 MHz; DMSO-d$_6$; Me$_4$Si): 0.88 (d, 6H, CH$_3$C, *J* 6.8 Hz), 1.09 (d, 6H, CH$_3$C, *J* 6.8 Hz), 2.24 (qr, 2H, CHC, *J* 6.8 Hz), 7.25–7.42 (m, 7H, Ar), 7.58 (m, 1H, Ar), 8.88 (s, 1H, C^{5}HN). δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 1 form: 0.90 (d, 6H, CH$_3$C, *J* 6.8 Hz), 1.10 (d, 6H, CH$_3$C, *J* 6.8 Hz) (*i*-Pr), 2.37 (qr, 2H, CHC, *J* 6.8 Hz), 8.10 (s, 1H, C^{5}HN); 2 form: 1.19 (d, 12H, CH$_3$C, *i*-Pr), 3.02 (qr, 2H, CHC, *J* 6.8 Hz); 8.30 (s, 1H, C^{5}HN); general for both forms: 7.20–7.37 (m, 12H, Ar), 7.45 (d, 3H, Ar, *J* 7.6 Hz), 7.51 (dd, 1H, Ar, *J* 7.6 Hz). The first form of compound **6c** was identical to the product of the same reaction in ionic liquids isolated by colomn chromatography [33] (mp 114–115 °C).

1-Alkyl-3,4-diaryl-1,2,4-triazolium perchlorates (**7b-d**) **(general procedure)**. The mixture of sodium iodide (50 – 60 mmol) and 1.5 fold access of *tert*-butyl chloride in acetic acid (10 mL) was boiled for 1.5 h. One equivalent (to iodide amount) of the respective 3,4-diaryl-1,2,4-triazole **6a,c** was added and boiled for 21 h. Then water (20 mL) and sodium sulfite were added to the obtained mixture to discolor the solution. The mixture was diluted by water (0.5 L) and activated carbon (1 – 3g) was added. The subsequent mixture was heated to boiling and filtered hot. Sodium perchlorate was added in an amount exceeding equivalence by 10 – 20%. The precipitate that formed was filtered off, washed with isopropanol and ether, recrystallized from the respective solvent, and subsequently dried. The salts **7b,d** were obtained similarly using 1-bromoadamantane instead of *tert*-butyl iodide. The heating time was 10-18 h.

1-(1-Adamantyl)-3-phenyl-4-(2,4,6-trimethyl-phenyl)-1,2,4-triazolium perchlorate (**7b**). The heating time was 10 h. Yield 85 %, mp > 300 °C (acetic acid). Found: C, 65.0; H, 6.5; Cl, 7.1; N, 8.5. Calc. for C$_{27}$H$_{32}$ClN$_3$O$_4$: C, 65.1; H, 6.5; Cl, 7.1; N, 8.4%. δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 1.79 (s, 6H, Ad), 2.02 (s, 6H, CH$_3$C), 2.30 (s, 3H, Ad), 2.35 (s, 3H, *p*-CH$_3$C), 2.36 (s, 6H, *o*-CH$_3$C), 7.19 (s, 2H, Ar), 7.44 (dd, 2H, Ar, *J* 7.6 Hz), 7.51 (dd, 2H, Ar, *J* 8.0 Hz), 7.62 (dd, 1H, Ar, *J* 7.2 Hz), 10.59 (s, 1H, C^{5}HN).

1-*tert*-Butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazolium perchlorate (**7c**). Yield 64 %, mp 232 – 234 °C (acetic acid – water, 1:1). Found: C, 62.5; H, 6.9; Cl, 7.6; N, 9.2. Calc. for C$_{24}$H$_{32}$ClN$_3$O$_4$: C, 62.4; H, 7.0; Cl, 7.7; N, 9.1%. δ_H (400 MHz; DMSO-d$_6$; Me$_4$Si): 0.91 (d, 6H, *J* 6.8 Hz), 1.16 (d, 6H, *J* 6.8 Hz) (CH$_3$C, *i*-Pr), 1.81 (s, 9H, CH$_3$C, *t*-Bu), 2.40 (qr, 2H, CHC, *i*-Pr, *J* 6.8 Hz), 7.44 (d, 2H, *J* 7.6 Hz), 7.51 (d, 2H, *J* 7.6 Hz), 7.54 (d, 2H, *J* 7.6 Hz), 7.63 (dd, 1H, *J* 7.6 Hz), 7.73 (dd, 1H, *J* 7.6 Hz) (Ar), 10.91 (s, 1H, C^{5}HN).

1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazolium perchlorate (**7d**). The heating time was 18 h. Yield 59 %, mp 210 – 212 °C (acetic acid–water, 1:1). Found: C, 66.8; H, 7.0; Cl, 6.6; N, 7.7. Calc. for C$_{30}$H$_{38}$ClN$_3$O$_4$: C, 66.7; H, 7.1; Cl, 6.7; N, 7.8%. δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 0.91 (d, 6H, *J* 4.4 Hz), 1.28 (d, 6H, *J* 4.4 Hz) (CH$_3$C, *i*-Pr), 1.87 (m, 6H, Ad), 2.23 (qr, 2H, CHC, *i*-Pr, *J* 4.4 Hz), 2.42 s (3H, Ad), 2.48 (s, 6H, Ad), 7.37 (m, 4H), 7.42 (m, 2H), 7.51 (m, 1H), 7.63 (m, 1H), (Ar), 10.28 (s, 1H, C^{5}HN).

1-Alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes (**8b-d**) **(general procedure)**. A suspension of 1-*tert*-butyl-3,4-diaryl-1,2,4-triazolium perchlorate **7a-d** and potassium *tert*-butoxide (95 % from the calculated amount) was added to the mixture of anhydrous isopropanol and toluene (1:3) or in THF and stirred for 1.5 h. The solvent was evaporated and the oil was obtained. This oil was then stirred with petroleum ether and the subsequent precipitate that was formed was filtered off and dried. Then, anhydrous toluene (10 – 20 mL) was added to the precipitate and stirred for 1 h. The resulting inorganic

salt was filtered off. The mother liquor was evaporated and the resulting product was crystallized by stirring with petroleum ether. The precipitate was filtered off, washed several times with petroleum ether, dried, and recrystallized from toluene.

1-(1-Adamantyl)-3-phenyl-4-(2,4,6-trimethyl-phenyl)-1,2,4-triazol-5-ylidene (8b). Yield 50 %, mp 168 – 169 °C (toluene). Found: C, 81.7; H, 7.8; N, 10.5%. Calc. for $C_{27}H_{31}N_3$: C, 81.6; H, 7.9; N, 10.6%. δ_H (400 MHz; C_6D_6; Me_4Si): 1.64 (m, 3H, Ad), 1.73 (m, 3H, Ad), 1.97 (s, 6H, o-CH_3C), 2.06 (s, 3H, p-CH_3C), 2.13 (m, 3H, Ad), 2.66 (m, 6H, Ad), 6.69 (s, 2H, Ar), 6.94 (s, 3H, Ar), 7.61 (d, 2H, Ar, J 3.6 Hz). δ_C (100 MHz, C_6D_6, Me_4Si): 18.3 (o-CH_3C), 21.0 (p-CH_3C), 30.2 (CHC, Ad), 36.7 (CH_2C, Ad), 44.2 (CH_2C, Ad), 59.4 ($ipso$-C, t-Bu), 127.7, 128.4, 128.6, 129.5, 130.2 (Ar), 135.5, 136.8, 137.9 ($ipso$-C, Ar), 151.1 (C^3), 211.5 (C^5).

1-$tert$-Butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-ylidene (8c). Yield 70 %, mp 112 – 114 °C (toluene). Found: C, 79.8; H, 8.5; N, 11.7. Calc. for $C_{24}H_{31}N_3$: C, 79.7; H, 8.6; N, 11.6%. δ_H (400 MHz; C_6D_6; Me_4Si): 0.85 (d, 6H, J 7.2 Hz), 1.18 (d, 6H, J 7.2 Hz) (CH_3C, i-Pr), 1.83 (s, 9H, CH_3C, t-Bu), 2.74 (qr, 2H, J 7.2 Hz, CHC, i-Pr), 6.90 (m, 3H), 7.10 (d, 2H, J 7.6 Hz), 7.24 (dd, 1H, J 7.6 Hz), 7.61 (m, 2H) (Ar). δ_C (100 MHz; C_6D_6; Me_4Si): 22.5, 24.5 (CH_3C, i-Pr), 29.0 (CH, i-Pr), 30.9 (CH_3C, t-Bu), 59.3 ($ipso$-C, t-Bu), 128.2, 128.5, 129.5, 129.6 (Ar), 124.2, 136.6, 146.1 ($ipso$-C, Ar), 151.8 (C^3), 213.0 (C^5).

1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-ylidene (8d). Yield 68 %, mp 151 – 153 °C (toluene). Found: C, 82.1; H, 8.4; N, 9.6. Calc. for $C_{30}H_{37}N_3$: C, 82.0; H, 8.5; N, 9.6%. δ_H (400 MHz; C_6D_6; Me_4Si): 0.87 (d, 6H, J 6.8 Hz), 1.20 (d, 6H, J 6.8 Hz) (CH_3C, i-Pr), 1.64 (m, 3H), 1.71 (m, 3H), 2.12 (m, 3H), 2.63 (m, 6H) (Ad), 2.76 (qr, 2H, CHC, i-Pr, J 6.8 Hz), 6.94 (m, 3H), 7.12 (d, 2H, J 7.6 Hz), 7.26 (dd, 1H, J 7.6 Hz), 7.62 (m, 2H) (Ar). δ_C (100 MHz, C_6D_6, Me_4Si): 22.5, 24.5 (CH_3C, i-Pr), 29.4 (CH, i-Pr), 30.5 (CHC), 36.6, 44.6 (CH_2C) (Ad), 59.5 ($ipso$-C, Ad), 124.2, 128.1, 128.5, 129.4, 129.5 (Ar), 127.6, 136.8, 146.3 ($ipso$-C, Ar), 151.5 (C^3), 211.8 (C^5N).

$Trans$-$trans$-bis(1-$tert$-butyl-3-phenyl-4-p-bromophenyl-1,2,4-triazol-5-ylidene)palladium chloride (9a). A powder of carbene **8a** [9] (2 g, 0.56 mmol) and anhydrous dimethylsulfoxide (0.03 mL) was added to the suspension of palladium chloride (0.05 g, 0.28 mmol) in THF (5 mL) and stirred for 0.5 h. The suspension of complex **9a** was evaporated to dryness and stirred with petroleum ether. The precipitate was filtered off and dried. Yield 0.25 g (100 %), mp 160 – 163 °C (subl.) (acetonitrile). Found: C, 48.7; H, 4.0; Br, 18.3; Cl, 8.1; N, 9.4. Calc. for $C_{36}H_{36}Br_2Cl_2N_6Pd$: C, 48.6; H, 4.1; Br, 18.0; Cl, 8.0; N, 9.4%. δ_H (400 MHz; $CDCl_3$;

Me_4Si): 1.65 (s, 18H, CH_3C), 7.26 (m, 10H), 7.53 (m, 4H) 7.69 (m, 4H) (Ar). δ_C (100 MHz, $CDCl_3$, Me_4Si): 30.6 (CH_3C), 61.9 (CH_3C), 128.5, 128.6, 130.3, 131.6, 132.9 (Ar), 124.0, 125.1, 136.3 ($ipso$-C), 151.8 (C^3), 171.3 (C^5Pd).

Bis(1-$tert$-butyl-3-phenyl-4-p-bromophenyl-1,2,4-triazol-5-ylidene)palladium iodide (9b). The same procedure that was used for complex **9a** was applied to the synthesis of **9b**. Yield 75 %, mp 119 – 120 °C (acetonitrile). Found: C, 40.4; H, 3.4; Br, 14.8; I, 23.6; N, 7.9. Calc. for $C_{36}H_{36}Br_2I_2N_6Pd$: C, 40.3; H, 3.4; Br, 14.9; I, 23.7; N, 7.8%. The product was a mixture of two isomers $trans$-$trans$- and presumably cis-$trans$-forms:
For $trans$-$trans$-isomer: δ_H (400 MHz, $CDCl_3$, Me_4Si): 1.58 (s, 18H, CH_3C), 7.24 (m, 10H), 7.61 (m, 8H, Ar). δ_C (100 MHz; $CDCl_3$; Me_4Si): 30.9 (CH_3C), 62.2 (CH_3C), 128.6, 128.7, 130.5, 132.4, 132.8 (Ar), 124.0, 125.3, 136.3 ($ipso$-C), 152.5 (C^3), 168.7 (C^5Pd).

For cis-$trans$-isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si): 2.11 (s, 18H, CH_3C), 7.01 (m, 4H), 7.33 (m, 14H); δ_C (100 MHz; $CDCl_3$; Me_4Si): 31.9 (CH_3C), 63.0 (CH_3C), 128.5, 128.6, 130.3, 131.4, 132.0 (Ar), 123.4, 125.5, 136.1 ($ipso$-C), 152.8 (C^3), 167.7 (C^5Pd).

The $trans$-$trans$-isomer was isolated from the mixture by additional recrystallization from acetonitrile and identified by X-ray diffraction study.

Bis-[1-(1-adamantyl)-3-phenyl-4-(2,4,6-tri-methylphenyl)-1,2,4-triazol-5-ylidene]palladium iodide (9c). The powder carbene **8b** (0.4 g, 1 mmol) was added to a solution of palladium iodide (0.18 g, 0.5 mmol) in THF (4 mL), the mixture was stirred for 30 h and boiled for 2 h. The precipitate formed was filtered off and dried. Yield 0.42 g (72 %), mp > 300 °C (dimethylformamide). Found: C 56.3, H 5.3, I 21.9, N 7.4%. Calc. for $C_{54}H_{62}I_2N_6Pd$: C 56.1, H 5.4, I 22.0, N 7.3%. δ_C (100 MHz; solid state; DSS): 21.3, 23.7 (o-CH_3C), 24.6 (p-CH_3C), 30.9 (CHC, Ad), 37.8, 45.2 (CH_2C, Ad), 64.1 ($ipso$-C, Ad), 127.7, 130.0, 131.2, 133.3, 135.6, 139.8, 140.7 (Ar), 154.8 (C^3), 168.2 (C^5Pd).

Bis[1-$tert$-butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-ylidene]palladium iodide (9d). The powder palladium iodide (0.12 g, 0.34 mmol) and dimethylsulfoxide (0.04 mL) were added to a solution of carbene **8c** (0.25 g, 0.68 mmol) in toluene (5 mL), stirred at room temperature for 8 h and boiled for 2 h. The precipitate that formed was filtered off, washed with petroleum ether, and dried. Yield 0.29 g (78 %), mp 260 – 261 °C (acetonitrile). Found: C, 53.3; H, 5.8; I, 23.3; N, 7.7%. Calc. for $C_{48}H_{62}I_2N_6Pd$: C, 53.2; H, 5.8; I, 23.4; N, 7.8%. δ_C (100 MHz; solid state; DSS): 25.5, 27.1, 27.8 (CH_3C, i-Pr), 31.6 (CH_3C, t-Bu), 47.4, 48.1 (CHC, i-Pr), 64.3 (CH_3C, t-Bu), 126.4, 127.2, 128.9, 130.1, 132.1, 132.8 (Ar), 134.0, 146.7, 147.4 ($ipso$-C), 154.9

(C^3), 171.9 (C^5Pd).

[1-*tert*-Butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-yliden]palladium chloride (10a). A mixture of carbene **8c** (0.25 g, 0.68 mmol) and palladium chloride (0.12 g, 0,68 mmol) in anhydrous dimethylsulfoxide (2.5 mL) was stirred for 3 days. The precipitate that formed was filtered off, washed by petroleum ether, and dried. Dichloromethane (5 mL) and water (5 mL) were added to the mother liquour and stirred. The phases that formed were then subsequently separated. The dichloromethane phase was then dried by anhydrous sodium sulfate. The solvent was evaporated; the oil that formed was stirred with petroleum ether. The precipitate that formed was filtered off and dried. Yield 0.15 g (41 %), mp 196 – 198 °C (acetonitrile). Found: C, 53.4; H, 5.9; Cl, 13.2; N, 7.7%. Calc. for $C_{24}H_{31}Cl_2N_3Pd$: C, 53.5; H, 5.8; Cl, 13.2; N, 7.8%. δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 1 form: 0.54 d, 0.63 d, 1.15 d, 1.30 d (12H, CH$_3$C, J 4.8 Hz, i-Pr), 2.29 (9H, t-Bu), 2.50 (m, 2H, CHC, i-Pr); 2 form: 0.57 d, 0.71 d, 1.38 d, 1.53 d (12H, CH$_3$C, J 4.8 Hz, i-Pr), 2.18 (9H, t-Bu), 2.61 (m, 2H, CHC, i-Pr); a general part of two forms: 7.17 (m, 4H), 7.26–7.48 (m, 3H), 7.26 (m, 1H) (Ar). δ_C (100 MHz, CDCl$_3$, Me$_4$Si): 25.1, 25.4, 28.4, 28.6, 28.7 (CH$_3$C, i-Pr), 31.0 (CH$_3$C, t-Bu), 24.3, 24.5 (CH, i-Pr), 64.3 (CH$_3$C, t-Bu), 125.3, 125.7, 127.9, 128.4, 130.9, (Ar), 131.3, 132.1, 146.8, 147.2 (*ipso*-C, Ar), 149.1 (C^3), 153.3 (C^5Pd).

[1-*tert*-Butyl-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-yliden]palladium iodide (10b). A solution of carbene **8c** (0.25 g, 0.68 mmol) and anhydrous dimethylsulfoxide (0.03 mL) in anhydrous toluene (1 mL) was added to a mixture of palladium iodide (0.246 g, 0.68 mmol) in toluene (5 mL) and stirred for 8 h. Then the mixture was boiled for 2.5 h. The precipitate that formed was filtered off, washed with petroleum ether, and dried. Yield 0.40 g (81 %), mp 254 – 255 °C (acetonitrile). Found: C, 40.0; H, 4.2; I, 35.1; N, 5.9%. Calc. for $C_{24}H_{31}I_2N_3Pd$: C, 39.9; H, 4.3; I, 35.2; N, 5.8%. δ_H (400 MHz; CDCl$_3$; Me$_4$Si): 1 form: 0.62 d, 1.36 d (12H, CH$_3$C, J 4.8 Hz, i-Pr), 2.94 (m, 2H, CHC, i-Pr); 2 form: 0.83 d, 1.25 s (12H, CH$_3$C, J 4.8 Hz, i-Pr), 4.11 (s, 2H, CHC, i-Pr); a general part of two forms: 2.09 (s, 9H, t-Bu), 7.19 (m, 2H), 7.30 (m, 2H), 7.39 (m, 3H), 7.60 (m, 1H) (Ar). δ_C (100 MHz; solid state; DSS): 23.7, 25.8, 26.5, 27.2, 29.6 (CH$_3$C, i-Pr), 31.7, 32.3 (CH$_3$C, t-Bu), 47.3 (CHC, i-Pr), 64.5 (CH$_3$C, t-Bu), 126.0, 127.7, 128.6, 131.0, 131.5, 132.7, 134.2, 136.3, 137.3 (Ar), 146.6, 147.2, 149.2, 154.2 (*ipso*-C), 156.1, 157.6 (C^3), 167.0, 169.2, 170.0, 171.3 (C^5Pd).

[1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-ylidene]palladium chloride (10c). A solution of carbene **8d** (0.2 g, 0.455 mmol) in toluene (1 mL) and anhydrous dimethylsulfoxide (0.03 mL) was added to a suspension of palladium

chloride (0.08 g, 0.455 mmol) in anhydrous toluene (4 mL) for 10 min, and the mixture was stirred for 8 h. The precipitate that formed was filtered off, washed by petroleum ether, and dried. Yield 0.19 g (68 %), mp 146 °C (dec.) (acetonitrile). Found: C, 58.3; H, 6.1; Cl, 11.5; N, 6.9. Calc. for $C_{30}H_{37}Cl_2N_3Pd$: C, 58.4; H, 6.0; Cl, 11.5; N, 6.8%. δ_H (400 MHz, CDCl$_3$, Me$_4$Si): 0.65 s, 13.8 s (12H, CH$_3$C, i-Pr), 2.25 (m, 9H, Ad), 2.62 (m, 6H, Ad; 2H, CHC, i-Pr), 7.19 – 7.60 (m, 8H, Ar). δ_C (100 MHz; CDCl$_3$; Me$_4$Si): 24.0 (CH$_3$C, i-Pr), 24.4 (CH, i-Pr), 28.5 (CH, Ad), 31.3, 41.0 (CH$_2$, Ad), 64.2 (*ipso*-C, Ad), 125.4, 125.6, 127.9, 128.5, 130.9 (Ar), 131.4, 132.1, 147.0 (*ipso*-C), 149.1 (C^3), 153.3 (C^5Pd). δ_C (100 MHz; solid state; DSS): 26.2, 27.1, 29.6, 31.0 (CH$_3$C, i-Pr), 31.0, 36.6, 44.5 (CH$_2$, Ad), 41.8, 48.6 (CH, i-Pr), 65.6 (*ipso*-C, Ad), 126.0, 127.2, 130.5, 131.9, 133.2 (*ipso*-C, Ar), 148.2 (C^3), 154.9 (C^5Pd).

[1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropyl-phenyl)-1,2,4-triazol-5-yliden]palladium iodide (10d). A mixture of carbene **8d** (0.25 g, 0.55 mmol), palladium iodide (0.19 g, 0.55 mmol) and anhydrous dimethylsulfoxide (0.3 mL) in anhydrous toluene (5 mL) was stirred for 4 h, then the mixture was boiled for 3 h. The precipitate that formed was filtered off, washed by petroleum ether, and dried. Yield 0.37 g (84 %), mp > 310 °C (dimethylformamide). Found: C, 45.0; H, 4.8; I, 31.6; N, 5.2%. Calc. for $C_{30}H_{37}I_2N_3Pd$: C, 45.1; H, 4.7; I, 31.7; N, 5.3%. δ_C (100 MHz; solid state; DSS): 26.9, 27.6, 29.0, 29.9 (CH$_3$C, i-Pr), 31.6, 37.5, 43.3 (CH$_2$, Ad), 47.5, 49.1 (CH, i-Pr), 66.2 (*ipso*-C, Ad), 125.7, 128.0, 129.0, 130.5, 130.9, 132.0, 133.2 (Ar), 136.3, 146.9, 148.6 (*ipso*-C, Ar), 156.4 (C^3), 169.5 (C^5Pd).

Notes and references

[a] The L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian Academy of Sciences, 70, R. Luxemburg, Donetsk, 83114, Ukraine; Fax: (38+062)311-68-30; Tel: (38+062)311-68-35; E-mail: nkorotkikh@ua.fm
[b] Department of Chemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165; Tel: (512)471-74-84; E-mail: acowley@cm.utexas.edu

† Electronic Supplementary Information (ESI) available: X-ray crystallographic data for **8c, 9a,b, 10c**; NMR spectra; CIF files for **8c, 9a,b, 10c** CCDC 1000720 (**8c**), 1000718 (**9a**), 1000719 (**9b**), 1000721 (**10a**).

1. Y. Cheng, O. Meth-Cohn, *Chem. Rev.*, 2004, **104**, 2507.
2. D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.*, 2007, **107**, 5606; (b) *N-Heterocyclic Carbenes in Synthesis*, ed. by S. P. Nolan, Wiley VCH Verlag GmbH & Co KgaA, Weinheim, 2006, p. 68; (c) J. Izquierdo, G. E. Hutson, D. T. Cohen, K. A. Scheidt, *Angew. Chem. Int. Ed.* 2012, **51**, 11686. (d) M. J. Fuchter, *Chem. Eur. J.*, 2010, **16**, 12286; (e) P.-C. Chiang, J.Y W. Bode in *RSC Catalysis Series №. 6: N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient*

Synthetic Tools, ed. by Silvia Diez-Gonzalez, Royal Society of Chemistry, 2013, Ch. 14, p. 399.

3. N.I. Korotkikh, O.P. Shvaika, Carbene and carbene complex catalysis of organic reactions, DonNU, Donetsk, 2013, 372 p (ukr.).

4. (a) D. Bourissou, O. Guerret, F. P. Gabbaı, G. Bertrand, *Chem. Rev.,* 2000, **100**, 39; (b) M. C. Jahnke, F. E. Hahn, in *RSC Catalysis Series № 6: N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, ed. S. Dıez-Gonzalez / RSC, 2013, Ch. 1, p. 1; (c) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics,* 2011, **30**, 5304; (d) W. Kirmse, *Angew. Chem. Int. Ed.*, 2010, **49**, 8798.

5. D. Enders, K. Breuer, G. Raabe, J. Runsink, J.H. Teles, J.P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 9, 1021.

6. D. Enders, K. Breuer, J. Runsink, J.H. Teles, *Lieb. Ann. Chem.*, 1996, 2019.

7. N. I. Korotkikh, G. F. Rayenko, O. P. Shvaika, T. M. Pekhtereva, A. H. Cowley, J. N. Jones, C. L. B. Macdonald, *J. Org. Chem.*, 2003, **68**, 14, 5762.

8. N. I. Korotkikh, O. P. Shvaika, G. F. Rayenko, A. V. Kiselyov, A. V. Knishevitsky, A. H. Cowley, J. N. Jones, C. L. B. Macdonald, *ARKIVOC*, 2005, **8**, 10.

9. N.I. Korotkikh, N. V. Glinyanaya, A. H. Cowley, J. A. Moore, A. V. Knishevitsky, T. M. Pekhtereva, O. P. Shvaika, *ARKIVOC*, 2007, **16**, 156.

10. N.I. Korotkikh, A.H. Cowley, J.A. Moore, N. V. Glinyanaya, I.S. Panov, G.F. Rayenko, T.M. Pekhtereva, O.P. Shvaika, *Org. Biomol. Chem.*, 2008, **1**, 195.

11. A.V. Knishevitsky, N.I. Korotkikh, A.H. Cowley, J.A. Moore, T.M. Pekhtereva, O.P. Shvaika, G. Reeske *J. Organomet. Chem.*, 2008, **693**, 1405.

12. A.V. Kiselyov, N.I. Korotkikh, A.H. Cowley, J.A. Moore, T.M. Pekhtereva, O.P. Shvaika *ARKIVOC*, 2008, **15**, 329.

13. C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Dalton Trans.*, 2010, **39,** 2515.

14. V. Hornillos, J. Guerra, A. de Crozar, P. Prieto, S. Merino, M. A. Maestro, E. Dıez-Barra, J. Tejeda, *Dalton Trans.*, 2011, **40**, 4095.

15. J. Turek, I. Panov, M. Horáček, Z. Černošek, Z. Padělková, A. Růžička, *Organometallics*, 2013, **32**, 7234.

16. T.I. Gorbunov, V.I. Saloutin, O.N. Chupakhin, *Rus. Chem. Rev.*, 2010, **79**, 6, 565.

17. C. L. Geiger, K. Carvalho-Knighton, S. Novaes-Card, P. Maloney, R. DeVor, In Environmental Applications of Nanoscale and Microscale Reactive Metal Particles, ACS Symposium Series, American Chemical Society, Washington, DC, 2010, p. 1–20.

18. V. Dichiarante, M. Fagnoni. A. Albini, *Green Chem.*, 2009, **11**, 942.

19. K. A. Cannon, M. E. Geuther, C. K. Kelly, S. Lin, A. H. R. MacArthur, *Organometallics,* 2011, **30**, 4067.

20. W. M. Czaplik, S. Grupe, M. Mayer, A. J. von Wangelin, *Chem. Commun.,* 2010, **46**, 6350.

21 Y. Mitoma, T. Uda , N. Egashira, *Environ. Sci. Technol.*, 2004, **38**, 1216.

22 Y. Mitoma, M. Kakeda, A.M. Simion, N. Egashira, C. Simion, *Environ. Sci. Technol.,* 2009, **43**, 5952.

23. A. M. Simion, H. Miyata, M. Kakeda, N. Egashira, Y. Mitoma, C. Simion, *Separ. Purif. Technol.*, 2013, **103**, 267.

24. Y. Huang, S. Liu, Z. Lin, W. Li, X. Li, R. Cao, *J. Catal.*, 2012, **292**, 111.

25. P. Selvam, S. U. Sonavane, S. K. Mohapatra, R. V. Jayaram, *Tetrahedron Lett.*, 2004, **45**, 3071.

26. M. S. Viciu, G. A. Grasa, S. P. Nolan, *Organometallics*, 2001, **20**, 16, 3607.

27. O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, *J. Org. Chem.*, 2004, **69,** 9, 3173.

28. O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly, S. P. Nolan, *J. Org. Chem.*, 2006, **71**, 2, 685.

29. C. J. E. Davies, M. J. Page, C. E. Ellul, M. F. Mahon, M. K. Whittlesey, *Chem. Commun.*, 2010, **46**, 5151.

30. S. Kuhl, R. Schneider, Y. Fort, *Adv. Synth. Catal.,* 2003, **345**, 3, 341.

31. S. Akzinnay, F. Bisaro, C. S. J. Cazin, *Chem. Commun.*, 2009, **45**, 5752.

32. N.I. Korotkikh, V.Sh. Saberov, A.V. Kiselev, N.V. Glinyanaya, K.A. Marichev, T.M. Pekhtereva, G.V. Dudarenko, N.A. Bumagin, O.P. Shvaika, *Chem. Heter. Comp.*, 2012, **47**, 12, 1551.

33. X. Chen, R. Liu, Y. Xu, G. Zou, *Tetrahedron*, 2012, **68**, 4813.

34. N.I. Korotkikh, G.F. Raenko, T.M. Pekhtereva, O.P. Shvaika, A.H. Cowley, J.N. Jones, *Rus. J. Org. Chem.*, 2006, **42**, 12, 1822.

35. (a) G. M. Sheldrick, *SHELXTL-PC*, version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, 1994, WI. See also, (b) G. M. Sheldrick, *Acta Cryst.* **2008**, *A 64*, 112.

36. A. L. Spek. PLATON, *A Multipurpose Crystallographic Tool*, Utretcht University, The Netherlands, 1998.

37. N. I. Korotkikh, A. V. Kiselyov, A.V. Knishevitsky, G. F. Rayenko, T. M. Pekhtereva, O. P. Shvaika, *Chem. Heterocycl. Comp*. (Latvia), 2005, **7**, 1026.

Sterically Shielded 1,2,4-Triazol-5-ylidenes and their Palladium
Complexes: Efficient Catalysts for Chloroarene Hydrodechlorination