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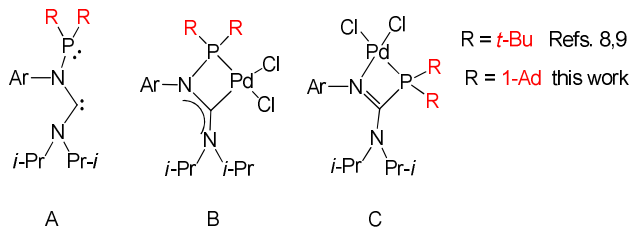
Pd(II) complexes with a novel N-(diadamantylphosphanyl)-diaminocarbene and related ligands: synthesis and catalytic application in intermolecular alkyne hydroaminations

Anatoliy Marchenko,[a] Georgyi Koidan,[a] Anastasiya Hurieva [a] Aleksandr Kostyuk,*[a] Dario Franco,[b] Marco Baron[b] and Andrea Biffis*[b]

Abstract: A novel *N*-diadamantylphosphanyl-diaminocarbene **5** was prepared, isolated and characterised. The carbene appeared to be much more stable compared to previously reported di-*tert*-butyl congeners. The molecular structure of the carbene was determined by X-ray diffraction analysis. A novel (diisopropylamino)(diadamantylphosphanyl)carbene **8** was also prepared in situ but not isolated, since in this case the adamantyl groups do not render the carbene more stable with respect to previously known carbenes with di-*tert*-butyl substitution. Carbene **8** reacted in situ with phenylazide to give iminophosphane **9**, which was accessible also from carbene **5** upon rearrangement under heating. Stable chelate Pd(II) complexes were synthesized using both carbene **5** and iminophosphane **9** as ligand. The complex with ligand **9** displayed a very promising catalytic performance in the intermolecular hydroamination of alkynes with primary arylamines.

Introduction

Strongly electron-donating, sterically encumbered trialkylphosphanes represent a class of compounds that has explosively grown in number and importance in the course of the last decades, mainly in relation to their application as ligands in the preparation of late transition metal complexes exhibiting outstanding performances in many catalytic processes.[1] The most commonly employed ligands of this kind are the parent tricyclohexylphosphane and tri-*tert*-butylphosphane, as well as several related mono- and polytopic ligands featuring di-cyclohexylphosphano or di-*tert*-butylphosphano moieties. The resulting catalytic complexes are usually stable, as such ligands provide good steric protection towards catalyst poisoning and decomposition. In some cases, for even better steric protection the diadamantylphosphano group instead of the di-*tert*-butylphosphano one has been employed.[2–4]
In the course of the last years we[5,6] and others[7] have been interested in novel ditopic ligands of this kind, namely *N*-di-*tert*-butylphosphanyl-N-heterocyclic carbenes; we have reported on their preparation[5] and use as ligands in the synthesis of mono- and dinuclear late transition metal complexes exhibiting promising catalytic properties.[6] Very recently, we have extended these investigations to novel acyclic *N*-di-*tert*-butylphosphanyl-diaminocarbene ligands **A**,[8] their palladium(II) complexes **B** and palladium(II) complexes of related iminophosphanes **C** – a rearrangement product of ligand **A** which invariably occurs in the preparation of type **B** complexes (Scheme 1).[9] We have tested Pd complexes **B** as catalysts in Suzuki coupling reactions and found that they exhibit a higher reactivity towards aryl chlorides compared to acyclic diaminocarbene ligands not bearing the *N*-di-*tert*-butylphosphanyl group,[10] but we have also recorded that such catalytic performance is accompanied by complex decomposition and by the appearance of reaction byproducts deriving from Ullmann-type homocoupling of the aryl chloride, which suggests in situ formation of catalytically competent Pd colloids;[11] isomerized complexes **C** exhibit comparable or lower reactivity, but without formation of the homocoupling product. These observations have been tentatively attributed to the fact that type **B** and **C** complexes feature small bite angle chelating ligands, which produce stable square planar complexes with palladium(II) but which, when the palladium is reduced to palladium(0) in the course of the catalytic cycle, do not fit well in the tetrahedral coordination geometry of palladium(0), leading to ligand dissociation and catalyst decomposition, particularly in the case of the diaminocarbene ligands.



Scheme 1. Structure of the ligands and complexes investigated by our group.

Consequently, in the frame of the present work, we aimed at directing further investigation on the catalytic potential of complexes of this kind towards reactions that are generally believed to be redox-neutral, such as alkyne hydroaminations, in which we expected our complexes to be more stable and consequently more productive as catalysts. Furthermore, we also aimed at extending our library of complexes to include

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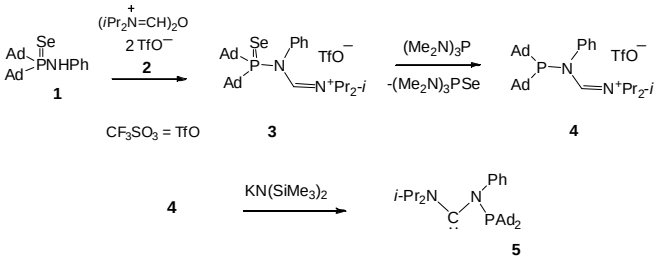
ligands with the diadamantylphosphano group, in order to study whether replacing *tert*-butyl groups with 1-adamantyl ones renders these complexes more productive catalysts.

Results and Discussion

The synthesis of carbene **5** (Scheme 2) was accomplished using the procedure developed by us earlier.[8] Salt **3** was prepared by treatment of P,P-di(adamantan-1-yl)phosphanoselenoic amide **1** with Alder's dimer **2**. It is a hydrolytically stable crystalline substance that was reduced with hexamethylphosphorus triamide to the highly moisture-sensitive P^{III} salt **4**.



Scheme 2. Synthesis of salts **3**, **4** and of carbene **5**.

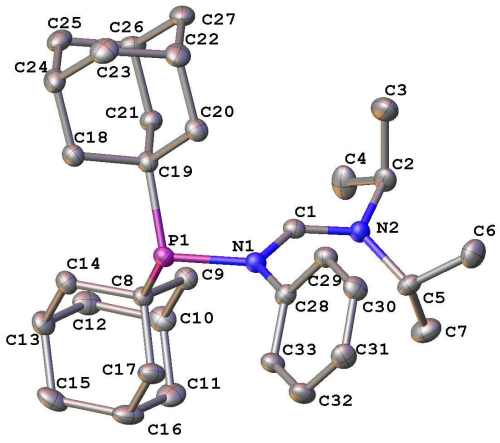


Figure 1. ORTEP view of the molecule **4**, hydrogen atoms and triflate anion are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): N1-P1 1.792(2), N1-C1 1.341(3), N2-C1 1.308(3), N1-C28 1.455(3), N1-C1-N2 132.0(2), C1-N1-P1 120.74(16), C1-N1-C28 121.7(2), P1-N1-C28 116.62(15).

The ^{31}P NMR spectrum of P^V formamidinium salt **3** exhibited two broad signals at δ_p = 139.0 and 142.6 ppm with an integral ratio 3:2 that can be attributed to hindered rotation about the P-N bond. At the same time, the ^{31}P NMR spectrum of P^{III} formamidinium salt **4** exhibited one signal at δ_p = 130.9. Compound **4** was studied by X-Ray analysis (Figure 1). Structural parameters for **4** are very close to those reported by us for the corresponding compound with *tert*-butyl instead of 1-adamantyl substituents at the phosphorous atom.[8] In particular, the distances P1-N1, N1-C1 and C1-N2 are 1.792(2), 1.341(3) and 1.308(3)Å in **4** instead of 1.7950(14), 1.333(2) and 1.305(2). The angles P1-N1-C1 and N1-C1-N2 are 120.74(16) and 132.0(2)° in **4** instead of 122.29(13) and 131.79(18).

Deprotonation of salt **4** was achieved by treatment with potassium hexamethyldisilazide in THF to give carbene **5**. Carbene **5** appeared indeed to be more stable compared to analogous carbenes featuring *tert*-butyl groups instead of 1-adamantyl ones: its lifetime ($t_{1/2}$) measured in solution at 20 °C is 60 days, that is, more than 4 times longer.

The molecular structure of **5** was determined by single crystal X-ray diffraction (Figure 2). The N1-C1-N2 angle of 116.6(2)° of **5** is significantly smaller than the same angle in a related type **A** carbene with R = *t*-Bu and Ar = 4-methoxy-phenyl[8] (121.1(2)°). The same is true for the dihedral angle P1-N1-C1-N2, which is 157.08(17) in **5** compared to 176.10(15)°. The N1–C1 and N2-C1 bond lengths are instead 1.410(3) and 1.324(3) for **5**, compared to 1.380(3) Å and 1.325(3) Å for the reference compound; it is worth to remark the double bond character of the N2-C1 bond, evidenced by its shorter length. The N1 and N2 atoms of **5** both have a trigonal-planar bond configuration (the sums of the bond angles are 357.2(6)° for N1 and 359.3(6)° for N2).

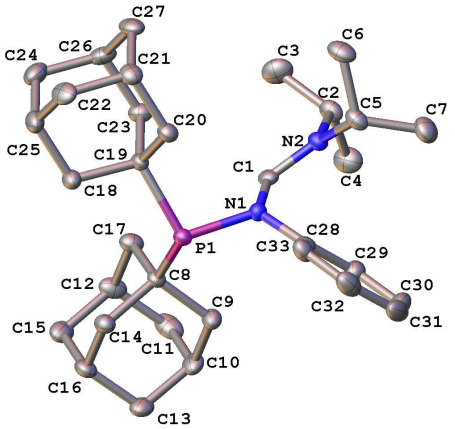
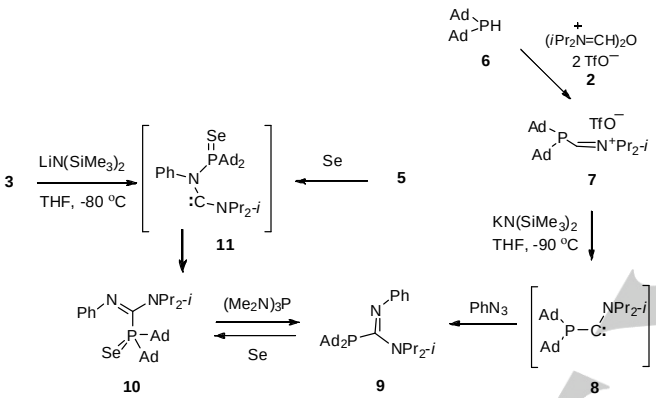


Figure 2. ORTEP view of **5**, hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°):N1-P1 1.742(2), N1-C1 1.410(3), N2-C1 1.324(3), N1-C28 1.445(3), N1-C1-N2 116.6(2), C1-N1-P1 118.10(16), C1-N1-C28 123.7(2), P1-N1-C28 115.45(16).

As substitution of *tert*-butyl groups with 1-adamantyl ones made type **A** carbenes more stable we also expected that the same would be true for closely related (diisopropylamino)(phosphano)-carbenes. In fact, Bertrand has shown that (diisopropylamino)-(phosphano)carbenes can be separated as individual compounds,[12,13] and that their stability depends on the substituents at the phosphorus atom, the most stable compound being (diisopropylamino)(di-*tert*-butylphosphano)carbene. It was also shown that the phosphano group acts as a spectator group and reactions can proceed either at the carbene atom or at phosphorus. We assumed that the introduction of 1-adamantyl groups at phosphorus increases the stability of these carbenes.

With this aim in mind, phosphanoiminium salt **7** was prepared (Scheme 3). Previously, iminium salts of type **7** were prepared starting from stannylphosphanes.[14] We propose here a new approach, i.e. treatment of diadamantylphosphane with Alder's dimer. Deprotonation of phosphanoiminium salt **7** was carried out with potassium hexamethyldisilazide in THF. Formation of carbene **8** was recorded by ^{31}P NMR spectroscopy (δ_p = 5 ppm). Contrary to our expectation, though, its lifetime ($t_{1/2}$) in solution at 22 °C appeared to be only 30 min. An analogous carbene featuring *tert*-butyl groups instead of 1-adamantyl was reported to have a half-life of 12 h at room temperature.[8] The reaction of **8** with phenylazide proceeded at the carbene carbon atom leaving intact the phosphane center. The moderate yield (50 %) of phosphane **9** was attributed to facile decomposition of the intermediate carbene.



Scheme 3. Attempted syntheses of carbenes **8** and **11**.

We also attempted the synthesis of P^V carbene **11** using two approaches (Scheme 3). At first we deprotonated salt **3** with lithium hexamethyldisilazide in THF at –90 °C. In the second approach, P^{III} carbene **5** was oxidized with selenium. We assume that in both cases the reaction indeed results in the transient P^V carbene **11**, that however spontaneously undergoes 1,2-P migration to afford phosphaneselenide **10**. The latter was reduced to phosphane **9**, whose structure was also proved by X-ray diffraction study (Figure 3).

The structure of **9** represents the first example of structure of a phosphane obtained by 1,2-P migration form the corresponding carbene. In the structure of **9** the distances N1-C1 and N2-C1 are 1.279(3) and 1.386(3) Å, respectively. The distance N1-C1 is shorter than in **5**, and this indicates a higher double bond character; conversely, the distance N2-C1 is longer than in **5**. The N1-C1-N2 angle is wider in **9** (127.1(2)°) than in **5** (116.6(2)°); the same trend is observed for the C1- N1-C28 angle, 127.1(2)° in **9** and 123.7(2)° in **5**.

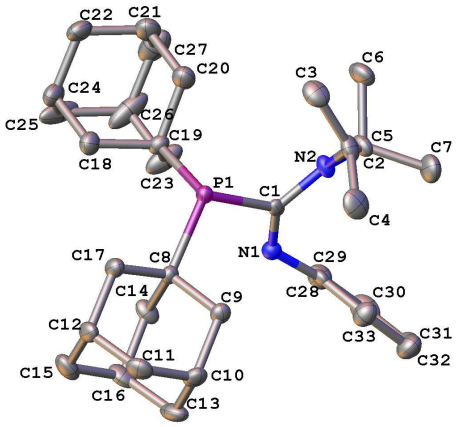
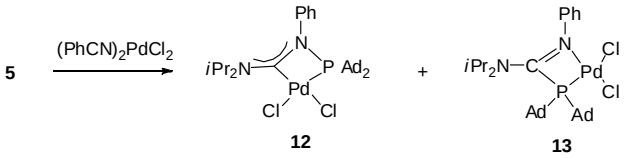


Figure 3. ORTEP view of **9**, hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°):P1-C1 1.879(3), N1-C1 1.279(3), N2-C1 1. 386(3), N1-C28 1.401(3), N1-C1-N2 127.1(2), N1-C1-P1 115.41(19), N2-C1-P1 117.17(19), C1-N1-C28 127.1(2).

Synthesis of palladium(II) complexes starting from carbene **5** resulted in a mixture of the expected palladium complex **12** and palladium complex of phosphane **9** – compound **13** (Scheme 4). Partial ligand isomerisation upon 1,2-shift of the phosphanyl group in the course of complex formation reactions has been previously observed by us also with di-*tert*-butylphosphanyl substituted acyclic diaminocarbene ligands.[9] In order to prepare carbene complex **12**, it is more convenient to generate carbene **5** in situ just before addition of the palladium source; conversely, complex **13** is best prepared starting directly from iminophosphane **9**. Both palladium complexes could be obtained as pure compounds and their molecular structures were proved by X-ray diffraction study (Figures 4 and 5).



Scheme 4. Synthsis of the palladium(II) complexes **12** and **13**.

In both the complexes the Pd(II) centers are in a distorted square planar coordination environment. The bite angle of the P-C donor ligand in **12** is slightly smaller than the bite angle of the P-N donor ligand in **13** with P1-Pd1-C1 and P1-Pd1-N1 angles being 68.71(18) and 70.44(6)° respectively. The four membered metallacycle present in both structures deviates from planarity and is slightly folded with a fold angle between the P1-Pd1-C1 and P1-N1-C1 planes of 10.6(4)° in **12** and a fold angle between the P1-Pd1-N1 and P1-C1-N1 planes of 6.40(16)° in **13**. In **12** a hydrogen bond is present between the isopropyl C*H* proton (C5)

and the chlorine Cl1, the distance C5-Cl1 is 3.266(7) Å. The presence of this interaction is confirmed also in the ^{1}H NMR spectrum of **12**. The two isopropyl groups give two set of signals in the ^{1}H and ^{13}C NMR spectra, as for the free carbene **5**. Moreover, in the ^{1}H NMR spectrum, two CH proton signals are found at 4.25 and 6.16 ppm, the proton at lower fields is the one involved in the hydrogen bond interaction. In **13**, due to the different connectivity of the ligand the two isopropyl CH protons are found both at 3.92 ppm. In a recent work from our group, we have reported the structure of complexes of type **B** (R = *tert*-butyl and Ar = 4-X-phenyl (X = H, CH_3, OMe and CF_3)) and **C** (R = *tert*-butyl and Ar = 4-OMe-phenyl).[9] Bond distances and angles of **12** and **13** are fully consistent with those previously reported for the other complexes of type **B** and **C**.

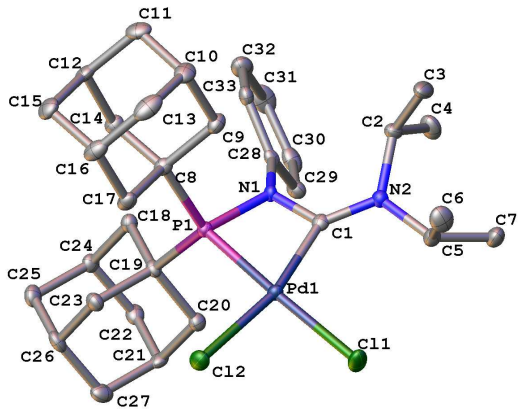


Figure 4. ORTEP view of complex **12**, hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°):Pd1-Cl1 2.3733(9), Pd1-Cl2 2.3552(8) , Pd1-C1 2.038(3), Pd1-P1 2.2060(9), P1-N1 1.730(3), N1-C1 1.387(4), N2-C1 1.323(8), Cl2-Pd1-Cl1 87.38(3), P1-Pd1-Cl2 97.06(3), P1-Pd1-Cl1 173.92(3), C1-Pd1-Cl2 165.75(9).

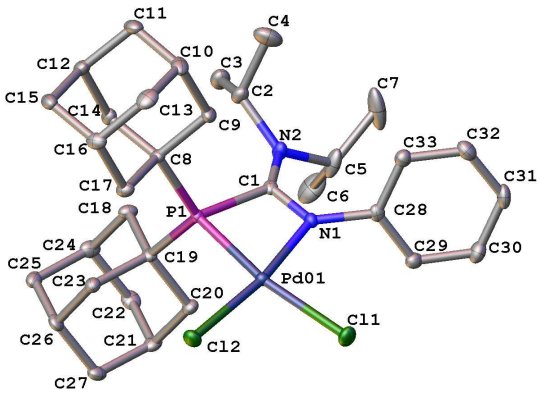
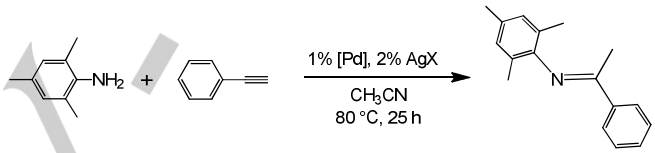
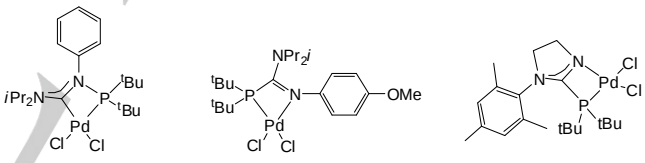


Figure 5. ORTEP view of complex **13**, hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°):Pd1-Cl1 2.3657(6), Pd1-Cl2 2.3027(6), Pd1-N1 2.0368(18), Pd1-P1 2.2244(6), P1-C1 1.888(2), N1-C1 1.319(3), N2-C1 1.351(3), Cl2-Pd1-Cl1 92.00(2), P1-Pd1-Cl2 99.46(2), P1-Pd1-Cl1 168.47(2), N1-Pd1-Cl2 169.81(5).

The performance of Pd complexes **12** and **13**, as well as of other complexes of type **B** and **C** bearing di-*tert*-butylphosphano moieties, has been screened in the catalysis of a technologically relevant, redox neutral synthetic reaction such as the intermolecular catalytic hydroamination of alkynes.[15] which is a synthetically useful reaction that can be catalyzed by palladium(II) species,[16] including NHC complexes of Pd.[16e-g] as well as Pd complexes with iminophosphanes.[16d] Catalytic tests were run on the hydroamination of phenylacetylene with an aromatic primary amine such as mesitylamine (Scheme 5), which is notoriously a rather difficult amine substrate for hydroamination reactions.[16f] Two equivalents with respect to Pd of a silver salt were employed as cocatalyst, which removes the halide ligands thereupon activating the Pd center for reaction.[15b,16]



Scheme 5. The employed standard hydroamination reaction.



14 **15** **16**

Scheme 6. Other catalysts employed in the hydroamination reactions.

The catalytic performance of compounds **12** and **13** in the hydroamination reaction was compared with that of related complexes (Scheme 6), namely complexes **14** and **15**, similar to **12** and **13**, respectively, but bearing *tert*-butyl substituents at phosphorus instead of 1-adamantyl substituents,[9] and complex **16** with an N-heterocyclic 1,3-iminophosphane ligand.[17] The results are reported in Table 1. Blank tests were performed before starting the investigation, in order to ascertain whether the Ag salt cocatalyst could promote the reaction by itself, since there have been reports in the literature that hydroamination can be also catalyzed by Ag salts.[18] Under the reaction conditions employed herein, though, the Ag salts $AgPF_6$ and AgOTf displayed only low catalytic efficiency towards hydroamination and produced mostly alkyne hydration and/or alkyne oligo- and polymerization products (Table 1, first two entries); the higher incidence of alkyne hydration in the test with $AgPF_6$ can be explained in terms of the much higher hygroscopicity.of this salt compared to AgOTf (see also below).

The results indicate that complexes based on iminophosphane ligands **13** and **15** perform much better than complexes with N-phosphanyl diaminocarbene ligands **12** and **14**, allowing to reach greater conversions of phenylacetylene and higher yields in hydroamination products. We believe that this is due to the lower stability of the carbene complexes under the reaction conditions, leading to catalyst decomposition and formation of Pd black in the course of the reaction. Furthermore, complex **16** with an iminophosphane ligand derived from an N-heterocyclic moiety is much less efficient compared to acyclic ligands of the same kind. We were able to determine a low quality crystal structure of **16** (Supporting Information, Figure S1), which reveals a rather distorted square planar geometry for this complex: both Pd-N1 and Pd-P bond distances are significantly longer than in complexes **13** and **15** (Pd-N 2.09 vs 2.04 Å; Pd-P 2.25 vs. 2.22 Å) and the two angles N1-C1-P1 and N2-C1-P1, which should ideally have similar amplitude, are instead widely different (103.82° and 140.44°, respectively). Thus , it appears that the more rigid N-heterocyclic structure of the ligand in complex **16** negatively impacts on the stability of the complex and consequently on its catalytic performance. Finally, slightly better results were indeed obtained as expected with the more sterically protecting adamantyl-substituted ligand compared to the *tert*-butyl substituted one.

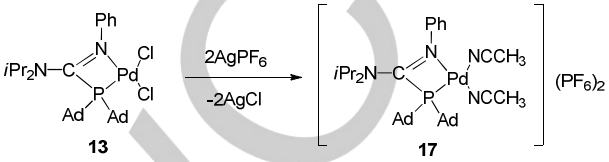
Table 1. Catalyst screening for the hydroamination reaction

Catalyst	Cocatalyst	Alkyne conversion (%)	Hydroamination yield (%)	Hydration yield (%)
-	$AgPF_6$	20	4	10
-	AgOTf	39	4	1
12	$AgPF_6$	77	20	20
13	$AgPF_6$	100	59	27
14	$AgPF_6$	73	15	32
15	$AgPF_6$	96	55	34
16	$AgPF_6$	64	16	16

Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 1 mol% Pd catalyst, 2 mol% silver salt cocatalyst, 1mL acetonitrile, 80℃, 25h.

During the screening of the various complexes it emerged that the yields in hydroamination product was limited by at least two side reactions, namely alkyne polymerization and hydration by traces of water adventitiously introduced in the system. Concerning hydration, we soon realized that the main source of adventitious water was the employed $AgPF_6$ salt, which is rather hygroscopic. We tried to overcome this problem by separately preparing and employing the dicationic complex **17** (Scheme 7).

Complex **17** was isolated as an analytically pure, air-stable solid upon removal of the chloride ligands with $AgPF_6$. Crystals of the compound were also obtained, but they were not of sufficient quality to allow the calculation of a reliable structure, though the results of the diffraction experiment confirmed the postulated connectivity of the complex. Use of **17** as preformed catalyst without $AgPF_6$ addition caused as expected a drastic decrease of the hydration product, but not a corresponding increase in hydroamination product, since alkyne polymerization was promoted as well (Table 2, entry 2).



Scheme 7. Preparation of complex **17**.

Luckily, the extent of alkyne polymerization could be limited by running the reaction under neat conditions: the hydroamination yield with catalyst **17** increased in this case from 51 to 87% (Table 2, entry 3). Furthermore, under these conditions it was no longer necessary to employ a preformed dicationic catalyst for high chemoselectivity: use of the parent catalyst **13** together with less hygroscopic AgOTf and a slight excess (2 equivalents) of the alkyne as both reagent and reaction solvent turned into an almost quantitative hydroamination yield with respect to the amine (Table 2, entry 5). Finally, higher yields with respect to acetonitrile as solvent (but lower than under neat conditions) could also be obtained using as solvent a relatively hydrophobic ionic liquid such as 1-butyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide (Table 2, entry 4). The reason for this remarkable dependence of the reaction chemoselectivity on the nature of the solvent is still unclear and is currently being investigated by tracing it back to the mechanistic differences between the various reactions that can take place.

Table 2. Screening of the reaction conditions for the hydroamination reaction

Entry	Catalyst/ Cocatalyst	Solvent	Alkyne conversion (%)	Hydro-amination yield (%)	Hydration yield (%)
1	**13**/$AgPF_6$	CH_3CN	100	59	27
2	**17**/-	CH_3CN	100	51	1
3	**17**/-	neat	100	87	0.5
4	**13**/AgOTf	IL[b]	94	74	6
5[a]	**13**/AgOTf	neat	63	96	4

Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 1 mol% Pd catalyst, 2 mol% silver salt cocatalyst, 1mL solvent, 80℃, 25h. [a] Reaction performed with 2 equivalents of the alkyne reagent; [b] IL= 1-butyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Basing on the neat conditions, a substrate screening was performed to determine the applicability of this catalytic system. The results are reported in Table 3. It is apparent that on the one hand the reaction is not limited to phenylacetylene but can be extended to other terminal and internal alkynes as substrates; on the other hand, primary aromatic amines appear the only competent nucleophiles among those tested, and moderate to good yields can be obtained irrespective of the nature of the substituents on the aromatic amine. Furthermore, the reaction time is unoptimised and can probably be reduced in several instances without significantly affecting the yield. These results compare favorably with those obtained with other Pd-based catalytic systems previously reported in the literature, which generally require higher Pd loadings, higher reaction temperatures, a larger excess of alkyne or the addition of an acid cocatalyst.[16]

Table 3. Substrate screening for the hydroamination reaction with catalyst **13**

Amine	Alkyne	Amine conversion (%)	Hydroamination yield (%)
mesitylamine	phenylacetylene	96	96
mesitylamine	1-phenylpropyne	63	63[a]
mesitylamine	1-octyne	59	59
4-chloroaniline	phenylacetylene	91	85
4-anisidine	phenylacetylene	75	60
4-toluidine	phenylacetylene	90	65
N-methylaniline	phenylacetylene	20	0
morpholine	phenylacetylene	0	0
cyclohexylamine	phenylacetylene	0	0

Reaction conditions: 1 mmol amine, 2 mmol alkyne, 1 mol% **13**, 2 mol% AgOTf, 80°C, 25h; [a] The reaction yielded 57% benzyl methylketimine and 6% phenyl ethylketimine.

Conclusions

A novel N-phosphanyl acyclic diaminocarbene and its corresponding iminophosphane ligand bearing 1-adamantyl substituents at phosphorus have been prepared for the first time. The compounds are stable and easily form chelate 1:1 complexes with palladium(II), which have been structurally characterized. The Pd complex with the iminophosphane ligand displays a good catalytic performance in the intermolecular hydroamination of terminal alkynes with primary arylamines. It is remarkable that particularly good results can be obtained with mesitylamine, which is a sterically encumbered amine known to be comparably unreactive. Work is currently in progress to further optimize the catalytic system, to understand its mechanistic features and to extend its application to other alkyne hydrofunctionalization reactions.

Experimental Section

Details on the preparation of the various compounds and on their characterization are reported in the Supporting Information.

General procedure for catalytic hydroaminations

In a Schlenk tube equipped with a magnetic stirring bar were placed under an inert atmosphere 10 µmol Pd complex and 20 µmol silver salt cocatalyst. The tube was degassed and put under an inert atmosphere. 1.00 mmol aniline, 1.00-2.00 mmol alkyne and optionally 1 mL dry solvent were then injected into the Schlenk tube. The flask was immediately placed in an oil bath preheated at 80 °C and the reaction mixture was vigorously stirred for 25 hours. Conversions and yields were determined by ^{1}H NMR on a sample of the reaction mixture diluted in $CDCl_3$, after addition of 1,4-bis-trimethylsilylbenzene as an internal standard.

Keywords: N-heterocyclic carbenes • acyclic diaminocarbenes • palladium • hydroamination • alkyne

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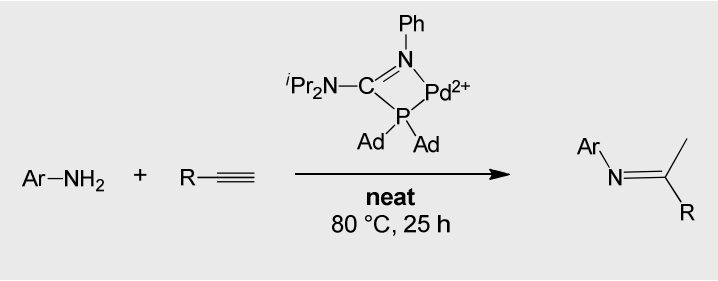

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Title

Text for Table of Contents Pd complexes with novel di-1-adamantylphosphanyl carbene and imino ligands have been prepared and employed as catalysts for the efficient intermolecular hydroamination of alkynes with arylamines.