Platinum complexes with chelating acyclic aminocarbene ligands work as catalysts for the hydrosilylation of alkynes

Rogério S. Chay,a Bruno G. M. Rocha,a Armando J. L. Pombeiro,\*a,b Vadim Yu. Kukushkin,b and Konstantin V. Luzyanin\*b,c

*a*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon,   
Portugal, e-mail: pombeiro@ist.utl.pt

*b*Saint Petersburg State University, 7/9 Universitetskaya Nab., Saint Petersburg 199034, Russian Federation.

*c*Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom,

e-mail: konstantin.luzyanin@liverpool.ac.uk

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ABSTRACT: This work describes the preparation of a series of platinum-aminocarbene complexes [PtCl{C(N=C*a*(C6R2R3R4R5CON*b*))=N(H)R1}(CNR1)]*a*–*b* (**8**–**19**, 65–75% isolated yield) via the reaction of *cis*-[PtCl2(CNR1)2] (R1 = Cy **1**, *t*-Bu **2**, Xyl **3**, 2-Cl-6-MeC6H3 **4**) with 3-iminoisoindolin-1-ones HN=C*a*(C6R2R3R4R5CON*b*H) (R2−R5 = H **5**; R3 = Me, R2, R4, R5 = H **6**; R3, R4 = Cl, R2, R5 = H **7**). New complexes **17**–**19** were characterized by elemental analyses (C, H, N), ESI+-MS, FT-IR, 1D (1H, 13C{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, 1H,13C-HMBC) NMR spectroscopy, while authenticity of known species **8**–**16** was confirmed by FT-IR and 1H and 13C{1H} NMR. Complexes **8**–**19** were assessed as catalysts for the hydrosilylation of terminal alkynes with hydrosilanes to give vinyl silanes, and complex [PtCl{C(N=C*a*(C6H3(5-Me)CON*b*))=N(H)(2-Cl-6-MeC6H3)}{CN(2-Cl-6-MeC6H3)}]*a*–*b* (**18**) showed the highest catalytic activity. Catalytic system proposed operates at 80–100 ºC for 4–6 h in toluene and with catalyst loading of 0.1 mol% enabling the reaction of a number of *terminal* alkynes (PhC≡CH, *t-*BuC≡CH, and 4-(*t*-Bu)C6H4C≡CH) with hydrosilanes (Et3SiH, Pr3SiH, *i*-Pr3SiH, and PhMe2SiH). Target vinyl silanes were prepared in 48–95% yields (as a mixture of / isomers) and with maximum TON of 8.4×103. Hydrosilylation of *internal* alkynes (PhC≡CPh, Me(CH2)2C≡C(CH2)2Me, and PhC≡CMe) with hydrosilanes (Et3SiH, PhMe2SiH) led to the corresponding trisubstituted silylated alkenes in 86–94% yields. Initial observations on the mechanism of the catalytic action of platinum-ADC catalysts **8**­–**19** suggested a molecular catalytic cycle.

INTRODUCTION

Metal complexes with acyclic diaminocarbenes ([M]ADCs) have proven to be a valuable alternative to metal-*N*-heterocyclic carbene ([M]NHCs) catalysts in contemporary transition metal catalysis.1 Both ADCs and NHCs possess a powerful combination of strong donor abilities with a wide range of steric properties, and akin binding characteristics upon coordination.2 From the synthetic perspective, a general approach to [M]NHCs involves the direct coordination of the *in situ* generated free NHCs to a metal center, while the most versatile route to [M]ADCs involves metal-mediated nucleophilic addition to isocyanides (**Scheme 1**).1a,2a The latter template approach allows for an upfront installation of a variety of functionalities within the generated acyclic aminocarbene ligand subsequently an efficient variation of electronic and steric properties, denticity of the carbene ligand, and eventually the catalytic properties of the metal-ADCs.1b,c This methodology can also be used for the preparation of [M]NHCs, although in this case the application of the pre-functionalized isocyanides3 and the specific nucleophiles2c are required.

Insofar as generation of [M]ADCs is concerned, different types of nucleophiles have been successfully added to metal-bound isocyanides, including amines, hydrazines (*sp*3-N), alcohols (*sp*3-O), imines (*sp*2-N), imidines, amidines, hydrazides, and hydrazones (mixed *sp*3-N*/sp*2-N).1a,b,2c,4 Coupling with mixed *sp*3-N*/sp*2-N nucleophiles led to unconventional amino(*imino*)- or amino(*hydrazido*)carbenes.5 It is noteworthy that application of these easily accessible and modular ADC species in catalysis allowed the discovery of new application fields, where metal-ADC catalysts were never previously used. For instance, recently prepared palladium-amino(*hydrazido*)carbenes derived from the addition of hydrazides exhibit an excellent activity in Suzuki–Miyaura reaction conducted in aqueous medium5b and also in Sonogashira coupling performed at room temperature.5h At the same time, we reported on the first use of platinum-ADCs in catalysis, *viz*. for the catalytic hydrosilylation of terminal alkynes with hydrosilanes.5h

Whereas catalytic properties of different palladium- and gold-ADCs are well documented, by contrast the application of platinum-ADCs in catalysis is restricted to only a few reports on the catalytic alkyne hydrosilylation.1b,5h We have recently revealed that amino(*imino*)carbene-palladium complexes derived from the addition of 3-iminoisoindolin-1-ones to palladium-bound isocyanides demonstrate a high efficiency in the Suzuki–Miyaura coupling (yields up to 81–99%, TONs up to 7.6×104).5d

Scheme 1. Routes to [M]NHCs and [M]ADCs.



Scheme 2. Preparation of platinum-ADC complexes via the coupling of 3-iminoisoindolin-1-ones (5–7) with   
*cis*-[PtCl2(CNR1)2] (1–4).



Inspired by these results we prepared corresponding platinum-aminocarbene derivatives and assessed their catalytic properties in a substantially more demanding reaction such as hydrosilylation of terminal alkynes.

Results and discussion

*Synthesis and structural characterization of the aminocarbene complexes.* Reaction of the platinum(II)-isocyanides *cis*-[PtCl2(CNR1)2] (R1 = cyclohexyl (Cy) **1**, *t*-Bu **2**, 2,6-Me2C6H3 (Xyl) **3,** 2-Cl-6-MeC6H3 **4**) with the 3-iminoisoindolin-1-ones HN=C*a*(C6R2R3R4R5CON*b*H) (R2−R5 = H **5**; R3 = Me, R2, R4, R5 = H **6**; R3, R4 = Cl, R2, R5 = H **7**) in CHCl3 under reflux conditions for 8 h gave platinum-aminocarbene complexes [PtCl{C(N=C*a*(C6R2R3R4R5CON*b*))=N(H)R1}(CNR1)]*a*–*b* (**8**–**19**),that were isolated in 65–75% yield (**Scheme 2**).

Complexes **17**–**19** were characterized using elemental analyses (C, H, N), ESI+-MS, FT-IR, 1H and 13C{1H} NMR spectroscopy, while the authenticity of known5a species **8**–**16** was established using FT-IR and 1H and 13C{1H} NMR. Satisfactory C, H, and N elemental analyses were obtained for **17**–**19**, and ESI+-MS for those showed peaks due to protonation of the molecular ion [M + H]+. In the FT-IR spectra of **17**–**19**, bands due to *ν*(Ccarbene–N) and *ν*(N–H) appeared within 1523–1521 cm–1 and 3248–3227 cm–1 ranges, respectively. A strong *ν*(C≡N) stretch due to the presence of the unreacted isocyanide ligand was found at ca. 2193 cm–1, while the corresponding bands due to overlapped ν(C=O) and ν(C=N) of the 3-iminoisoindolin-1-one moiety emerged between 1734 and 1611 cm–1. The 1H NMR spectra of the carbene complexes **17**–**19** displayed a broad peak in the range of *δ* 9.7–11.4 assigned to the Pt-{Ccarbene–N(*H*)R} proton, while the corresponding signal of the carbene carbon in the 13C{1H} spectra resonated at *ca*. 200–207 ppm. Gradient-enhanced 1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, and 1H,13C-HMBC spectra aided the 1H and 13C signal assignment in **17**–**19**. All spectroscopic and non-spectroscopic features of **17**–**19** match those for other platinum and palladium complexes, i.e. [MCl{C(N=C*a*(C6R2R3R4R5CON*b*))=N(H)R1}(CNR1)]*a*–*b* reported previously by some of us.5a,d

*Application of platinum-aminocarbene complexes as catalysts for the hydrosilylation of alkynes.* Hydrosilylation of *terminal* alkynes has become one of the most powerful ways for the preparation of organosilane species,6 that are useful intermediates in several synthetic transformations, including Hiyama, Hosomi–Sakurai-type allylation, and others.7 Despite being extensively studied, only a few types of catalysts are generally used for this process, in particular for industrial applications. Two commonly employed catalysts for the hydrosilylation reaction in the industry include the Speier’s catalyst (H2PtCl6 in *i*-PrOH) or the Karstedt’s catalyst Pt2(dvtms)2 (dvtms: divinyltetramethylsiloxane).8 Despite the popularity and the broad application scope, these catalysts suffer from a number of disadvantages and over the past years, alternative platinum catalysts for alkyne hydrosilylation were described. Those include platinum complexes with NHC ligands that work in toluene at 100 ºC with 1.0 mol% catalyst loading,9 or mixed platinum complexes with NHC and dvtms ligands that operate in *o-*xylene at 80 ºC.10 Recently we reported on the first application of [Pt]ADC species as catalysts for the alkyne hydrosilylation,5h and in the development of this project we assessed complexes **8**–**19** for this purpose.

Reaction of phenylacetylene with triethylsilane affording a mixture of vinyl silanes was chosen as a model hydrosilylation system (**Scheme 3**). Under the catalytic conditions specified below, only the formation of triethyl(1-phenylvinyl)silane ( product) and (*E*)-triethyl(styryl)silane (-(*E*) product) was observed; no (*Z*)-triethyl(styryl)silane (-(*Z*) product) was detected.

Scheme 3. Model system for the hydrosilylation of terminal alkynes with silanes.



Table 1. Effect of solvent on the reaction course [yields and isomeric content (/ ratio)].*a*

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Solvent | Yield and isomeric ratio at 80 ºC/6 h | Yield and isomeric ratio at 100 ºC/4 h |
| 1­–2 | Toluene (dried) | 90 (19/81) | 86 (48/52) |
| 3–4 | Toluene*b* (undried) | 82 (56/44) | 85 (48/52) |
| 5–6 | *p*-Xylene | 67 (22/78) | 88 (28/72) |
| 7–8 | Ethanol | <5 | <5 |
| 9–10 | Water | <5 | <5 |
| 11–12 | none | 65 (41/59) | 64 (48/52) |
| PhC≡CH (5.0×10–4 mol, 1 equiv), Et3SiH (5.0×10–4 mol, 1 equiv), catalyst **18** (5.0×10–7 mol); solvent (0.5 mL). *a*Yields of products were determined by 1H NMR spectroscopy using 1,2-dimethoxyethane as standard, while the isomeric content was determined on the basis of the alkene coupling constants; *b*Water content in this solvent was 0.1% (v/v) based upon Karl Fischer coulometry. | | | |

Table 2. Effect of temperature on the reaction [yields and isomeric content (/ ratio)].*a*

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Time, h | Temperature, ºC | Yield and  isomeric content |
| 1 |  | 60 | 29 (30/70) |
| 2 | 2 | 80 | 56 (21/79) |
| 3 |  | 100 | 78 (52/48) |
| 4 |  | 60 | 37 (29/71) |
| 5 | 4 | 80 | 82 (20/80) |
| 6 |  | 100 | 85 (47/53) |
| 7 |  | 60 | 35 (23/77) |
| 8 | 6 | 80 | 90 (19/81) |
| 9 |  | 100 | 77 (25/75) |
| 10 |  | 60 | 25 (41/59) |
| 11 | 12 | 80 | 80 (51/49) |
| 12 |  | 100 | 58 (39/61) |
| PhC≡CH (5.0×10–4 mol, 1 equiv), Et3SiH (5.0×10–4 mol, 1 equiv), catalyst **18** (5.0×10–7 mol); toluene (0.5 mL). *a*Yields of products were determined by 1H NMR spectroscopy using 1,2-dimethoxyethane as standard, while the isomeric content was determined on the basis of the alkene coupling constants. | | | |

Although the formation of three isomers is possible in a such reaction, the majority of previous reports indicate that platinum-catalyzed hydrosilylation of alkynes typically brings about the formation of two isomers, namely  and -(*E*) products. Three isomers are also expected for the process involving radical pathways.9a,11

From the industrial perspective, it is important to develop a catalytic system that can run in undried solvents in air. Therefore, we started this project by assessing the solvent effect, and the presence of moisture and air on the course of the hydrosilylation process. Conditions previously reported by some of us for other platinum-ADC catalysts were used (catalyst loading 0.1 mol%, 80 °C for 6 h and/or 100 °C for 4 h).9a Several dry and undried solvents were used in air or under dinitrogen atmosphere and the results for runs in air are presented in **Table 1**.

No marked difference was observed between dried and undried toluene as the reaction medium (entries 1–4), and overall yields of product of 82–90% were achieved at both 80 and 100 °C. Use of *p*-xylene (entries 5 and 6) resulted in the decrease of the product yield to 67% at 80 °C, while reaction course at 100 °C seemed to be unaffected. We believe the major reason for this is the insufficient solubility of catalyst and substrates at lower temperatures. Application of ethanol or water as the solvent (entries 7–10) was unsuccessful and only traces of the vinyl silanes were detected. In this case, a mixture of starting hydrosilanes alongside the products of their hydrolysis or alcoholysis (formed upon reaction with water or EtOH, correspondingly)12 was generated. Finally, fairly surprising results were obtained without any solvent (entries 11 and 12). Moderate products yield (ca. 64–65%) were subsequently achieved showing of a potential to development of this system into a solvent free one. When reaction in toluene was attempted under dinitrogen atmosphere under the conditions of **Table 1**, no change in the product yield was detected, showing that the system is not influenced by the presence of air. For further studies in this report, all catalytic runs were performed in air with undried toluene as solvent.

As the next step, we verified the effect of temperature (60–100 °C range) on the model reaction (**Table 2**). At RT, no catalytic reaction occurred and only the mixture of starting materials was recovered after 48 h. At 60 °C, maximum yield of 37% were achieved after 4 h and no further accumulation of the products was observed even after 12 h of heating (entries 1, 4, 7, 10). We observed that in this case, the reaction stops at conversion of *ca*. 40% and the unreacted starting material remains in the reaction mixture. At 80 °C, nearly quantitative conversion of the starting material was achieved to afford silylated products with yields of up to 90% after 6 h (entry 8). The same process at 100 °C led to the maximum yield of 85% achieved after 4 h. Increasing the reaction time (entries 9, 11, and 12) did not further improve the yield, but resulted in the partial decomposition of the silylated products; this process occurred faster at 100 °C when compared to 80 °C. Monitoring of this reaction by 1H NMR and GC-MS allowed the detection of styrene and triethyl(vinyl)silane. We believe that these species are formed in a similar fashion as reported by Marciniec13 and Seki,14 who showed that metal hydride complexes—that can be generated *in situ* from the hydrosilanes and metal source—can catalyze the conversion of vinyl silanes to styrene. Taking these results into account, all further catalytic tests were undertaken at two sets of temperature/reaction time, *i*.*e*. at 80 °C/6 h and 100 °C/4 h.

Comparison of the catalytic activity for all prepared aminocarbene complexes **8**–**19** in the model hydrosilylation system is given in **Table 3**. All catalysts studied are scarcely selective for Markovnikov vs. anti-Markovnikov addition to alkyne. Complex **18** was the most active (entries 21 and 22; 85–90% products yield), closely followed by complexes **15** and **16** (entries 15–18; 81–83%), **14** (entries 13–14; 49–82%), **17** (entries 19–20; 42–80%), and **19** (entries 23–24; 41–75%). For **14**–**19**, a nearly quantitative conversion of starting material was achieved at 100 ºC; the same was also observed with catalysts **15**, **16**, and **18** at 80 ºC. For all other catalysts and conditions, an incomplete conversion of the starting materials occurs and the reaction stops presumably due to the deactivation of the catalyst.

Table 3. Comparison of the catalytic activity of 8–19 in the model hydrosilylation system [yields and isomeric content (/ ratio)].*a*

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Catalyst | Yield and isomeric ratio at 80 ºC/6 h | Yield and isomeric ratio at 100 ºC/4 h |
| 1–2 | **8** | 83 (67/33) | 25 (60/40) |
| 3–4 | **9** | 64 (35/65) | 60 (28/72) |
| 5–6 | **10** | 66 (38/62) | 60 (27/73) |
| 7–8 | **11** | <5 | 14 (57/43) |
| 9–10 | **12** | 7 (49/51) | 44 (66/34) |
| 11–12 | **13** | 5 (44/56) | 83 (67/33) |
| 13–14 | **14** | 49 (52/48) | 82 (35/65) |
| 15–16 | **15** | 81 (62/38) | 82 (60/40) |
| 17–18 | **16** | 81 (60/40) | 83 (55/45) |
| 19–20 | **17** | 42 (41/59) | 80 (42/58) |
| 21–22 | **18** | 90 (20/80) | 85 (48/52) |
| 23–24 | **19** | 41 (54/46) | 75 (43/57) |
| PhC≡CH (5.0×10–4 mol, 1 equiv), Et3SiH (5.0×10–4 mol, 1 equiv), catalyst **8–19** (5.0×10–7 mol); toluene (0.5 mL). *a*Yields of products were determined by 1H NMR spectroscopy using  1,2-dimethoxyethane as standard, while the isomeric content was determined on the basis of the alkene coupling constants. | | | |

All the most efficient catalysts **14**–**19** arederived from the coupling of the aryl isocyanides in *cis*-[PtCl2(CNR1)2] [R1 = Xyl **3**, 2-Cl-6-MeC6H3 **4**] with 3-iminoisoindolin-1-ones, while less active catalysts **8**–**13** are derived from the addition to the aliphatic isocyanides. These results are also in agreement with those previously observed for the corresponding palladium complexes with amino(*imino*)carbenes derived from the addition of 3-iminoisoindolin-1-ones to palladium-bound isocyanides that were studied as catalysts for Suzuki–Miyaura reaction.5d We believe that in this case both steric and electronic factors might be responsible for this effect. From the steric perspective, planar aromatic groups in both XylCN and 2-Cl-6-MeC6H3NC exhibit lower hindrance upon oxidative addition of silane substrates, particularly at lower temperature. From the electronic viewpoint, moderate electron donation from the aminocarbenes derived from the aromatic isocyanides to metal center makes it more susceptible to reductive elimination of the silylated product. It is also known that many carbene ligands with aromatic substituents exhibit superior stability when compared to the aliphatic counterpart that might also account for a plausible reason for their superior catalytic efficiency. More examples of catalyst structure/catalytic activity relationship for metal-ADCs are required before more definitive conclusions can be drawn.

We assessed the scope of our system(**Table 4**) using representative catalyst **18**. A selection of terminal alkynes (PhC≡CH, 4-(*t*-Bu)C6H4C≡CH, and *t*-BuC≡CH) and silanes (Et3SiH, Pr3SiH, PhMe2SiH, and *i*-Pr3SiH) with different steric hindrances and electronic properties was used, thus, attesting the versatility of our system for preparation of corresponding vinyl silane products.

Table 4. Hydrosilylation of the terminal alkynes employing catalyst 18 [yields and isomeric content (/ ratio)].*a*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | | | | |
| Entry | Substrates | PhC≡CH | 4-(*t*-Bu)-C6H4C≡CH | *t*-Bu-C≡CH |
| 1–3 | Et3SiH | 90 (19/81) (6 h) | 86 (19/81) (3 h)*b* | 61/52  (7/93) (6 h) |
| 4–6 | Pr3SiH | 88 (65/35) (3 h)*b* | 80 (63/37) (3 h)*b* | 77/70  (7/93) (1 h)*b* |
| 7–9 | *i*-Pr3SiH | 70 (75/25) (6 h)*b* | 89 (81/19) (3 h)*b* | 48/40*c* (51/48) (1 h)*b* |
| 10–12 | PhMe2-SiH | 96 (29/71) (4 h)*b* | 95 (25/75) (6 h) | 83/78  (5/95) (6 h) |
| Alkyne (5.0×10–4 mol, 1 equiv), silane (5.0×10–4 mol, 1 equiv), catalyst **18** (5.0×10–7 mol); toluene (0.5 mL), reaction temperature: 80 ºC. *a*Yields of products were determined by 1H NMR spectroscopy using 1,2-dimethoxyethane as standard, while the isomeric content was determined on the basis of the alkene coupling constants; *b*Reaction temperature: 100 ºC. | | | | |

Yields of vinyl silanes were up to 96%. For aliphatic terminal alkyne *t*-BuC≡CH moderate product yields were achieved presumably due to its lower reactivity when compared to the aromatic alkynes. For some of the alkyne/silane pairs the variation of the reaction time and temperature gave higher products yield when compared to the standard conditions of 80 ºC/6 h and 100 ºC/4 h.

To extend the application scope for our system, we also assessed the hydrosilylation of *internal* alkynes (**Table 5**).15 To our satisfaction, we observed that symmetric disubstituted acetylenes (entries 1–4) reacts with silanes with a high degree of stereoselectivity to afford target *E*-silylated alkenes in 86–92% yields after 4h at 100 ºC. For asymmetrically disubstituted alkyne (entries 5 and 6) an expected mixture of /-*E*-silylated alkenes is generated. For all these examples, the amount of corresponding *Z*-silylated products formed were below 1%.



**Figure 1. Plausible intermediates of the catalytic cycle detected.**

The effect of catalyst loading has been assessed in the model hydrosilylation reaction with terminal alkynes (**Table 6**). The maximum catalyst turnover number (TON) of 8.4×103 was achieved with 0.01 mol% loading of 18 within 6 h of reaction at 80 ºC (entry 5). With higher catalysts loadings (entries 1–4, 0.1–1.0 mol%), no considerable improvement in the yield was achieved, while with lower catalyst loadings (entries 7–10, 0.001–0.0001 mol%) only traces of products were detected.

Table 5. Hydrosilylation of the internal alkynes employing catalyst 18 [yields and isomeric content (/ ratio)].*a*

|  |  |  |  |
| --- | --- | --- | --- |
|  | | | |
| Entry | Alkyne | Silane | Yield and  isomeric ratio at 100 ºC/4 h |
| 1 | PhC≡CPh  (R6, R10 = Ph) | Et3SiH | 92 |
| 2 | PhMe2SiH | 88 |
| 3 | Me(CH2)2C≡C(CH2)2Me (R6, R10 = Me(CH2)2) | Et3SiH | 86 |
| 4 | PhMe2SiH | 91 |
| 5 | PhC≡CMe  (R6 = Ph, R10 = Me) | Et3SiH | 87 (81/19) |
| 6 | PhMe2SiH | 94 (45/55) |
| Alkyne (5.0×10–4 mol, 1 equiv), silane (5.0×10–4 mol, 1 equiv), catalyst **18** (5.0×10–7 mol); toluene (0.5 mL). *a*Yields of products were determined by 1H NMR spectroscopy using 1,2-dimethoxyethane as standard, while isomeric content was determined based upon matching of chemical shifts against the authentic compounds. | | | |

Finally, we undertook additional tests in order to shed some light on the mechanism of catalytic action of **8**–**19**. A catalytic run in the presence of metallic mercury (mercury drop test16) showed similar results to those in the absence of mercury, and no change in the reaction rate or product yields was observed. Furthermore, the accumulation of the products in the initial period followed a nearly linear time-dependence and no induction period in the system was evident. These observations clearly indicated that no formation of platinum nanoparticles occurs during the reaction; catalytic system operates under typically homogeneous conditions and the mechanistic cycle should involve molecular compounds. Several platinum and gold systems were reported to operate through formation of catalytically competent ligand-free metal clusters.17

Table 6. Effect of the catalyst loading on the reaction efficiency [yields, isomeric content (/ ratio) and TONs].*a*

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Catalyst loading, mol% | Yields, isomeric ratio, and  TON under selected conditions | |
| 80 ºC/6 h | 100 ºC/4 h |
| 1–2 | 1 | 83 (17/83) 83 | 82 (17/83) 82 |
| 3–4 | 0.1 | 90 (19/81) 900 | 85 (48/52) 850 |
| 5–6 | 0.01 | 85 (68/32)  8500 | 77 (68/32)  7700 |
| 7–8 | 0.001 | 9 (64/36)  9000 | 7 (62/38)  7000 |
| 9–10 | 0.0001 | <5 | <5 |
| PhC≡CH (5.0×10–4 mol, 1 equiv), Et3SiH (5.0×10–4 mol, 1 equiv), catalyst **18**; toluene (0.5 mL).  *a*Yields of products were determined by 1H NMR spectroscopy using  1,2-dimethoxyethane as standard, while the isomeric content was determined on the basis of the alkene coupling constants. | | | |

In our case, some of the plausible intermediates of the catalytic cycle were detected using ESI-MS with catalyst **17** and phenylacetylene/propyl silane as substrates (Figures 1 and 1S). Intermediates A and B (*m/z*: 673.14 and 685.14) represent a product of an oxidative addition of the H–Si bond of the hydrosilane to the catalyst core. The composition of these intermediates suggests that the bidentate carbene ligand remains attached to the metal, while the isocyanide and chloride are lost presumably upon the catalyst activation step. Intermediate C (*m/z*: 751.22) represents a product of the 1,2-alkyne insertion into the Pt–H bond of the catalyst core already containing silyl fragment immediately before the reductive elimination step to afford the target vinyl silane product.

Although the exact mechanism of the catalytic action for platinum-ADCs remains unclear and requires further elucidation, our initial observations are consistent with other catalytic applications of metal-ADC species reported previously.1b,5h,18

Final Remarks

Results of this study can be considered from both synthetic and catalytic perspectives. From the *synthetic* point of view, we prepared a series of twelve platinum-aminocarbene complexes [PtCl{C(N=C*a*(C6R2R3R4R5CON*b*))=N(H)R1}(CNR1)]*a*–*b* via the reaction of *cis*-[PtCl2(CNR1)2] with 3-iminoisoindolin-1-ones. All new complexes were characterized by elemental analyses (C, H, N), ESI+-MS, FT-IR, and 1H, and 13C{1H}) NMR spectroscopy. From the *catalytic* perspective, we evaluated the properties of platinum-aminocarbene prepared as catalysts for the hydrosilylation of terminal alkynes with hydrosilanes. Highest catalytic efficiency was achieved with the complex [PtCl{C(N=C*a*(C6H3(5-Me)CON*b*))=N(H)(2-Cl-6-MeC6H3)}{CN(2-Cl-6-MeC6H3)}]*a*–*b* (**18**) that is derived from platinum-mediated coupling of the aromatic isocyanide CN(2-Cl-6-MeC6H3) with HN=C*a*(C6R2R3R4R5CON*b*H) (R3 = Me, R2, R4, R5 = H **6**). The designed catalytic system operates at 80–100 ºC for 4–6 h in toluene with a typical catalyst loading of 0.1 mol% and allows the transformation of a variety of hydrosilanes (Et3SiH, Pr3SiH, *i*-Pr3SiH, and PhMe2SiH) and terminal alkynes (PhC≡CH, *t-*BuC≡CH, and 4-(*t*-Bu)C6H4C≡CH) into the respective vinyl silanes in yields of up to 96%. Lowering the catalyst loading to 0.01 mol% increased the TON to 8.4×103. Hydrosilylation of the *internal* alkynes PhC≡CPh, Me(CH2)2C≡C(CH2)2Me, and PhC≡CMe with the hydrosilanes Et3SiH and PhMe2SiH gave corresponding trisubstituted silylated alkenes in 86–94% yields. The results of the mercury drop test, absence of an induction period, and the linear initial kinetics are supportive of a molecular catalytic cycle that operates under homogeneous conditions. It is notable that that while amino(*imino*)carbene catalysts from this study are just slightly less active than amino(*hydrazido*)carbene reported previously,5h one of the major advantages of the former species is their substantial thermal stability. It enables the catalytic applications at temperatures up to 150 °C, and nearly indefinite storage at RT. It was recently shown that platinum- and iridium- complexes with parent isocyanides exhibit outstanding and unexpected catalytic properties in the cross-linking of silicone rubbers at high temperature.19 While use of platinum-ADCs for this tremendously important industrial process is not yet revealed, our current catalysts might serve as logical candidates for this application. Future studies aiming to expand the field of catalytically relevant metal-ADCs and to understand the mechanism of their catalytic action are currently underway in our group.

EXPERIMENTAL SECTION

**Materials and instrumentation**. Solvents, K2[PtCl4], and all isocyanides were obtained from commercial sources and used as received, apart from chloroform that was purified by conventional distillation over calcium chloride. The starting *cis*-[PtCl2(CNR1)2] (R1 = Cy **1**,*t-*Bu **2**, Xyl **3**, 2-Cl-6-MeC6H3 **4**) complexes,20 substituted and unsubstituted 3-iminoisoindolin-1-ones21 and aminocarbene complexes **8**–**16**5a were prepared as previously reported. C, H, and N elemental analyses were carried out by Microanalytical Service of the Instituto Superior Técnico. ESI+ mass-spectra were obtained on Thermo Scientific LCQ Fleet and QqTOF Impact II mass-spectrometers in MeOH. Infrared spectra (4000–400 cm–1) were measured on a Bruker Vertex-70 instrument in KBr pellets. 1D (1H, 13C{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC and 1H,13C-HMBC) NMR spectra were recorded on Bruker Avance II+ 300, 400 and 500 MHz (UltraShieldTM Plus Magnet) spectrometers at ambient temperature using the solvent resonances as a reference.

**Synthetic Work. Coupling of *cis*-[PtCl2(C**≡**NR1)2] (R1** = **Cy, *t-*Bu, Xyl, 2-Cl-6-MeC6H3) with 3-iminoisoindolin-1-one.** The corresponding solid 3-iminoisoindolin-1-one (**5­**–**7**) (0.20 mmol) was added to a solution of *cis*-[PtCl2(C≡NR1)2] (0.20 mmol) in 10 mL of CHCl3. The reaction mixture was subsequently refluxed for ca. 8 h; during the reaction course the color of the mixture changed from yellow to bright yellow-orange. After cooling down, the reaction mixture was evaporated to dryness at RT under a stream of dinitrogen and the solid residue was extracted with two 5-mL portions of CHCl3. The bright yellow solution formed was filtered off to remove some insoluble material. The filtrate was evaporated to dryness under a stream of dinitrogen at RT to give a yellow precipitate, which was washed with five 5-mL portions of *i-*Pr2O, one 1-mL portion of cold (5 ºC) Et2O, and again with five 5-mL portions of *i-*Pr2O, and dried in *vacuo* at RT. Yields of **8**–**19** were 65–75%. The authenticity of known species **8**–**16** was established upon comparison of their FT-IR, and 1H, and 13C{1H} NMR spectra with those previously reported 5a.

** [PtCl{C(N**=**C(C6H4CON))**=**N(H)(2-Cl-6-MeC6H3)}{C**≡**N(2-Cl-6-MeC6H3)}] (17)**. Anal. Calcd for C24H17N4Cl3OPt: C, 42.46; H, 2.52; N, 8.25. Found: C, 41.90; H, 2.41; N, 8.55. ESI+-MS, *m*/*z*: 678 [M + H]+. IR (KBr, selected bands, cm-1): 3248 w *ν*(N–H), 2968 mw, 2922 w, 2863 w *ν*(C–H), 2192 s *ν*(C≡N), 1734 m, 1676 mw, 1617 w *ν*(C=N) + *ν*(C=O), 1522 s *ν*(Ccarbene–N), 776 s *δ*(C–H from Ar). 1H NMR (DMSO-*d*6, *δ*): 9.89 (s, br, 1H, NH), 7.83–7.76 (m, 4H) (aryls from isoindolin-1-one moiety), 7.34–7.13 (m, 6H, aryls), 2.59 and 2.52 (s, 6H). 13C{1H} NMR (DMSO-*d*6, *δ*): 206.8 (Ccarbene–N), 187.4 (C=O), 184.4 (C=N), 134.8 and 133.1 (C–Cl), 132.5, 131.4, 130.0, 129.8, 129.2, 129.1, 128.2, 127.6, 127.0, 126.5, 123.4 (aryls), 19.4 and 18.4 (Me).

** [PtCl{C(N**=**C(C6H3(5-Me)CON))**=**N(H)(2-Cl-6-MeC6H3)}{C**≡**N(2-Cl-6-MeC6H3)}] (18)**. Anal. Calcd for C25H19N4Cl3OPt: C, 43.34; H, 2.76; N, 8.09. Found: C, 42.95; H, 2.65; N, 7.95. ESI+-MS, *m*/*z*: 692 [M + H]+. IR (KBr, selected bands, cm-1): 3246 w *ν*(N–H), 2968 mw, 2923 w, 2862 w *ν*(C–H), 2194 s *ν*(C≡N), 1735 mm, 1677 mw, 1617 w *ν*(C=N) + *ν*(C=O), 1523 s *ν*(Ccarbene–N), 776 s *δ*(C–H from Ar). 1H NMR (CDCl3, *δ*): 9.67 (s, br, 1H, NH), 7.78–7.58 (m, 3H) (aryls from isoindolin-1-one moiety), 7.40–7.12 (m, 6H, aryls), 2.55, 2.53 (s, 6H, Me), 2.44 (s, 3H, Me from isoindolin-1-one moiety). 13C{1H} NMR (CDCl3, *δ*): 199.9 (Ccarbene–N), 180.0 (C=O), 173.6 (C=N), 138.1 and 134.9 (C–Cl), 133.9, 131.4, 131.2, 130.0, 129.3, 128.1, 127.7, 126.4, 123.7, 123.5, 123.2, 122.9 (aryls), 22.8 (Me from from isoindolin-1-one moiety), 19.1 and 18.7 (Me).

** [PtCl{C(N**=**C(C6H2(Cl2)CON))**=**N(H)C6H3(2-Cl-6-Me)}{C**≡**NC6H3(2-Cl-6-Me)}] (19)**. Anal. Calcd for C24H15N4Cl5OPt: C, 38.55; H, 2.02; N, 7.49. Found: C, 38.20; H, 2.15; N, 7.30. ESI+-MS, *m*/*z*: 748 [M + H]+. IR (KBr, selected bands, cm-1): 3227 w *ν*(N–H), 2967 mw, 2922 w, 2865 w *ν*(C–H), 2193 s *ν*(C≡N), 1736 m, 1675 mw, 1611 w *ν*(C=N) + *ν*(C=O), 1521 s *ν*(Ccarbene–N), 775 s *δ*(C–H from Ar). 1H NMR (DMSO-*d*6, *δ*): 11.41 (s, br, 1H, NH), 8.10–7.98 (m, 2H) (aryls from isoindolin-1-one moiety), 7.53–7.29 (m, 6H, aryls), 2.39 and 2.34 (s, 6H, Me). 13C{1H} NMR (DMSO-*d*6, *δ*): 201.4 (Ccarbene–N), 185.0 (C=O), 167.7 (C=N), 138.0, 137.6, 137.0, and 133.1 (C–Cl), 130.0, 129.7, 129.5, 129.1, 128.1, 127.6, 127.4, 127.0, 126.0 (aryls), 19.8 and 18.2 (Me).

**General procedure for the catalytic hydrosilylation of alkenes with hydrosilanes (specific conditions are provided in Tables 1**–**5)**. Alkyne (5.0×10–4 mol), silane(5.0×10–4 mol), selected catalyst **8**–**19** (5.0×10–7 mol), toluene (1 mL), and a PTFE-coated magnetic bar were placed in a 5-mL vial. The vial was closed with a septum, sealed with an aluminum crimp seal with an open top, and vented using a needle through several cycles of vacuum/dinitrogen flow. The vial was kept at 60–100 °C for 2–12 h (see **Tables 1**–**5** for details), cooled down to RT, and the reaction mixture was evaporated to dryness under a stream of dinitrogen. The contents of the vial were extracted with three 0.20 mL portions of CDCl3; all fractions were joined followed by the addition of 1,2-dimethoxyethane (1 equiv, used as an NMR internal standard), and then analyzed by 1H NMR spectroscopy. The isomeric content was determined on the basis of the alkene coupling constants in the 1H NMR spectra (e.g. for the model reaction of phenylacetylene and triethylsilane leading to a mixture of triethyl(1-phenylvinyl)silane (** product, *J*2HH = *ca*. 3 Hz) and (*E*)-triethyl(styryl)silane (**-(*E*) isomer, *J*3HH = *ca*. 19 Hz),9a,15a,22 or the analysis and matching of chemical shifts for products against authentic samples. Quantifications were performed upon integration of the selected peaks of the product against peaks of 1,2-dimethoxyethane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Spectroscopic data for prepared hydrosilylation products, and proposed structures of the catalytic intermediates detected using mass-spectrometry (PDF)

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AUTHOR INFORMATION

**Corresponding Authors**

\* Armando J. L. Pombeiro, e-mail: pombeiro@ist.utl.pt

\* Konstantin V. Luzyanin, e-mail:

[konstantin.luzyanin@liverpool.ac.uk](mailto:konstantin.luzyanin@liverpool.ac.uk)

**Authors**

Rogério S. Chay, e-mail: rogerio.chay@tecnico.ulisboa.pt

Bruno G. M. Rocha, e-mail: bruno.g.m.rocha@tecnico.ulisboa.pt

Vadim Yu. Kukushkin, e-mail: v.kukushkin@spbu.ru

The authors declare no competing financial interests.

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**Table of Contents artwork**

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