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ADC-metal complexes as effective catalysts for hydrosilylation of alkynes

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ABSTRACT

Aminocarbene complexes *cis*-[$PtCl_2${C(N(H)N = CR^2R^3)=N(H)R^1}(CNR^1)] (**7**–**15**) prepared via the nucleophilic addition of hydrazones H_2N–N=CR^2R^3 [R^2, R^3 = Ph **4**; R^2/R^3 = 9*H*-fluorenyl **5**; R^2 = H, R^3 = 2-(OH)C_6H_4 **6**] to *cis*-[$PtCl_2(CNR^1)_2$] [R^1 = cyclohexyl (Cy) **1**, 2,6-$Me_2C_6H_3$ (Xyl) **2**, 2-Cl-6-MeC_6H_3 **3**] were evaluated as catalysts for the hydrosilylation of terminal alkynes with trisubstituted silanes giving vinyl silanes. The optimized catalytic system runs at 80–100 °C in dry toluene for 3–6 h with a typical catalyst loading of 0.1 mol%. A range of substrates with different steric hindrance and activity (Et_3SiH, Pr_3SiH, $^iPr_3SiH$, and $PhMe_2SiH$ as silanes; PhC≡CH, ^{t}BuC≡CH, and 4-(^{t}Bu)C_6H_4C≡CH as alkynes) were successfully transformed into the target silylated products in 83–99% yields attesting the versatility of our catalytic system. Decreasing the catalysts loading to 10^{-3} mol% guaranteed the maximum TONs of 4.0×10^4 and TOFs of 1.7×10^3 (h^{-1}) that were accomplished within 24 h of the reaction.

1. Introduction

Acyclic diaminocarbene ligands (ADCs, Scheme 1A) have recently gained prominence in catalysis of organic transformations as potential alternatives to the widely used *N*-heterocyclic species (NHCs) [1–8]. ADCs are structurally related to the NHCs and possess similar electronic stabilization and comparable donor properties [9–15]. The combination of the greater steric control (due to the wider N–C–N bond angles in the ADCs with respect to the NHCs) [16–18] with their rotational freedom (NHCs are rigid due to their cyclic structures) [19–23], on the one hand, leads potentially to an easier catalyst adaptation to inconsistent steric requirements of various stages of the catalytic process, while, on the other hand, it guarantees the high stability of the ADC-based catalysts.

Metal complexes with the ADC ligands can be easily accessed via several synthetic strategies (for the surveys in the field, see Refs. [1,24–26]). Among them, one that is based on a metal-mediated nucleophilic addition to isocyanides (Scheme 1B) permits a straightforward assembly of a wide range of well-defined metal-ADC species [24–26]. In addition, this approach is modular and facilitates an optimization of steric and electronic properties and, consequently, the catalytic efficiency of the target [M]-ADCs.

Up-to-date metal-ADC species have been successfully employed as catalysts for several organic transformations, *i.e.*, Suzuki–Miyaura, Sonogashira, Heck, Kumada, and Buchwald–Hartwig cross-coupling, as well as for various cyclizations/additions to substrates having the C≡C and C = C bonds [1,2,8]. Surprisingly, metal-ADCs have never been employed in hydrosilylation and, in particular, in the hydrosilylation of alkynes—one of the fundamental approaches for the laboratory and industrial synthesis of organosilicon and silicon-related compounds [27,28]—and even the use of metal-NHCs species for this purpose [29–34] is limited to scarce examples.

Recently, we [35–44] and others [45] reported the preparation of several new types of aminocarbene ligands via the integration of palladium- and platinum-bound isocyanides with sp^2-N (imines [35,36,40,41]) or mixed sp^2-N/sp^3-N (amidines [39,46] or hydrazones [37]) type nucleophiles. Among the thus-generated species, palladium complexes demonstrated elevated efficiency as catalysts

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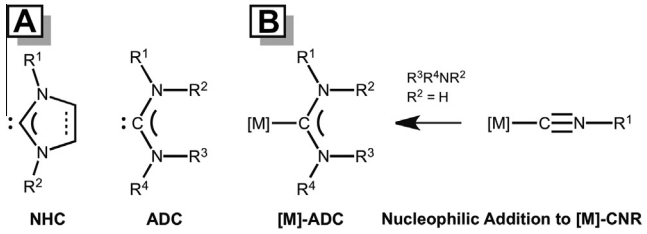


Scheme 1. Acyclic diaminocarbenes (ADCs) versus *N*-heterocyclic carbenes (NHCs) and generation of the [M]-ADC from the corresponding [M]-CNR species.

in Suzuki–Miyaura [37,40–42] and Sonogashira [39] couplings, while the corresponding platinum species were not active. Additionally, inspection of literature data led to the conclusion that the reported ADC-based catalytic systems contain palladium (in case of cross-coupling) [1,2] or gold (in case of cyclization reactions) [1,2] in the core of the catalyst, and only rare examples of other metals, e.g. nickel [47], copper [48], ruthenium [22], or rhodium [15], are known. To the best of our knowledge, no use of platinum-ADCs in catalysis has been demonstrated beforehand.

In order to verify whether metal-ADC species and, in particular, platinum-ADCs can be employed as catalysts for the hydrosilylation of terminal alkynes, we prepared several new aminocarbene derivatives (via the addition of hydrazones to platinum-bound isocyanides) and evaluated their catalytic properties. Consequently, we report herein on the first metal–ADCs catalysts for the hydrosilylation of alkynes and, also, on the first application of platinum-ADCs in catalysis. The results of our study are disclosed in the sections that follow.

2. Results and discussions

2.1. Synthesis and characterization of the platinum-aminocarbene complexes

The reaction between the platinum(II)-isocyanide *cis*-[$PtCl_2$(-$CNR^1)_2$] [R^1 = cyclohexyl (Cy) **1**, 2,6-$Me_2C_6H_3$ (Xyl) **2**] complexes and H_2N–N=CPh_2 (**4**) furnishing aminocarbene species **7** and **10**, correspondingly, was previously reported by some of us [37]. In the current study, we extended the scope of this coupling to the new platinum-isocyanide compound *cis*-[$PtCl_2(CNR^1)_2$] (R^1 = 2-Cl-6-MeC_6H_3 **3**) and also to the hydrazones H_2N–N=CR^2R^3 [R^2/R^3 = 9*H*-fluorenyl **5**; R^2 = H, R^3 = 2-(OH)C_6H_4 **6**] that were not previously explored in this reaction.

We observed that the coupling between the equimolar amounts of **1**–**3** and **4**–**6** (in all possible combinations) proceeded smoothly under reflux in chloroform (Scheme 2). The reaction rate varied with the type of the starting materials used (in the previously reported coupling of **1** and **2** with **4** [37], all additions proceeded with a similar rate), i.e., bulky hydrazones and sterically hindered isocyanides, required longer reaction time. Therefore, the optimization of the time for each of isocyanide ligand/hydrazone pair, upon monitoring of the reaction mixture by IR spectroscopy, was undertaken (Table 1). When the reactions were completed, the subsequent workup afforded the carbene species *cis*-[$PtCl_2${-C(N(H)N=CR^2R^3)=N(H)R^1}(CNR^1)] (**7**–**15**) in good (75–85%) isolated yields. The reaction between *cis*-[$PtCl_2(CN^tBu)_2$] (**16**) and any of **4**–**6** in $CHCl_3$ even under prolonged reflux furnished no isolable carbene species. Only a mixture of the starting materials along with small amounts of yet unidentified decomposition products was identified after reflux for 2d.

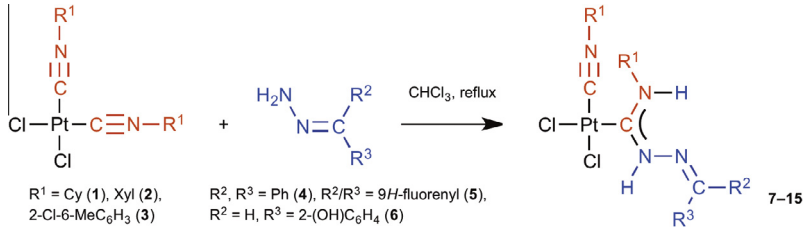
The prepared aminocarbene complexes **7**–**15** were characterized by elemental analyses (C, H, N), ESI^+–MS, IR, 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of three species (**11**, **13**, and **14**) were elucidated by single-crystal X-ray diffraction. For detailed characterization of aminocarbene species **7**–**15**, see Supplementary information.

The crystallographic data and processing parameters for **11**, **13**, and **14** are summarized in Table 1S (see Supplementary Information), while the corresponding molecular structure plots can be found in Figs. 1 and 1S, and bond lengths and angles are given in Table 2. As far as the most significant structural features are concerned, it is worth mentioning that in all three structures, the metal centers adopt square-planar geometries (τ_4 in the 0.061–0.077 range), and the carbene ligands {C(N(H)N=CR^2R^3)=N(H)R^1} are in the *cis* position with respect to the unreacted isocyanide. Furthermore, the carbene moiety is roughly planar and the angles including the C-carbene atoms (i.e., N–N–$C_{carbene}$, N–$C_{carbene}$–N and $C_{carbene}$–N–C) range from 111.5(19) to 132.1(16), therefore sustaining their sp^2 hybridization. The two C–N bonds of the carbene fragments are equal (in **13**) or differ insignificantly (*ca.* 0.04–0.06 Å in **11** and **14**).

2.2. Application of platinum-aminocarbene complexes as catalysts for hydrosilylation of terminal alkynes

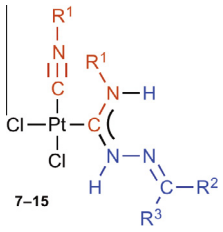
In the last decade, metal complexes featuring ADC ligands have been successfully employed as catalysts for several cross-coupling (e.g. Suzuki–Miayura, Heck, and Sonogashira reactions) and some cyclization reactions. Recent comprehensive reviews written by two of us [1] and by Slaughter [2] survey the accumulated experimental data indicating that M-ADCs species have never been previously employed as catalysts for hydrosilylation and, in particular, in the hydrosilylation of terminal alkynes with organosilanes. In pursuit of our on-going research on novel efficient catalytic systems [37,39–41], we decided to evaluate the catalytic properties of the aminocarbene complexes from this study in the hydrosilylation of terminal alkynes.

As a model system, we have chosen the reaction of phenylacetylene with triethylsilane furnishing a mixture of vinyl silanes (Scheme 3) employed previously for catalytic studies on hydrosilylation of terminal alkynes [33]. As it was previously reported [33] for the hydrosilylation reaction catalyzed by platinum compounds, no formation of (*Z*)-triethyl(styryl)silane (*β*-(*Z*) product) was observed [33]. Accordingly, in all our trials, the hydrosilylation reaction furnished a mixture of triethyl(1-phenylvinyl)silane (α



Scheme 2. Coupling between *cis*-[$PtCl_2(CNR^1)_2$] (**1**–**3**) and H_2N–N = CR^2R^3 (**4**–**6**) affording aminocarbene complexes **7**–**15**.

Table 1
Reaction times and numbering of the prepared aminocarbene species.

	R^1 in *cis*-[$PtCl_2(CNR^1)_2$]	R^2 and R^3 in $H_2N–N=CR^2R^3$	Reaction time, h	Product
	Cy **1**	R^2, R^3 = Ph **4**	8	**7** [37]
		R^2/R^3 = 9*H*-fluorenyl **5**	15	**8**
		R^2 = H, R^3 = 2-(OH)C_6H_4 **6**	17	**9**
	Xyl **2**	R^2, R^3 = Ph **4**	8	**10** [37]
		R^2/R^3 = 9*H*-fluorenyl **5**	26	**11**
		R^2 = H, R^3 = 2-(OH)C_6H_4 **6**	26	**12**
	2-Cl-6-MeC_6H_3 **3**	R^2, R^3 = Ph **4**	18	**13**
		R^2/R^3 = 9*H*-fluorenyl **5**	9	**14**
		R^2 = H, R^3 = 2-(OH)C_6H_4 **6**	18	**15**

product) and (*E*)-triethyl(styryl)silane (*β*-(*E*) product), and no (*Z*)-triethyl(styryl)silane (*β*-(*Z*) product) was isolated.

In the preliminary optimization of the conditions, we found toluene be the most appropriate solvent for the hydrosilylation of alkynes. In *dry* toluene, the reaction afforded high yields of the products at 80–100 °C for 3–6 h with catalyst loading of 0.1 mol%. When *non-dried* toluene was taken as a solvent, no significant difference in yields and composition of the reaction mixture was observed at temperatures below 90 °C suggesting that the water traces present in solvents do not affect our system. However, at 100 °C, a significant drop (more than 20%) in product yields was observed justifying the use of dry solvent for further studies.

Comparison of the catalytic activity of **7**–**15** in the model system was performed at two temperatures (80, 100 °C) and the duration of each trial was 3 or 6 h. The obtained results are summarized in Table 3. Among all the studied catalysts, complexes **14** and **15** were the most active under all examined conditions. Moreover, compounds **11** and **12** exhibited slightly lower efficiencies, and **7**–**10** and **13** were less active. With respect to the structure of the complexes, we noted that **11**, **12**, **14**, and **15** that are derived from the addition of sterically hindered hydrazones $H_2N–N=CR^2R^3$ **5** (R^2/R^3 = 9*H*-fluorenyl) and **6** (R^2 = H, R^3 = 2-(OH)C_6H_4) to aryl isocyanide in *cis*-[$PtCl_2(CNR^1)_2$] [R^1 = Xyl **2**, 2-Cl-6-MeC_6H_3 **3**] were generally more active than those derived from the addition of benzophenone hydrazone **4** (R^2, R^3 = Ph) to any of the *cis*-[$PtCl_2(CNR^1)_2$] (**1**–**3**) complexes.

For further screening of the functional group tolerance and scope of our system (Table 4), the most promising catalysts **14** and **15** were used. A range of substrates of different steric hindrance was successfully transformed employing our catalytic system, thus showing its versatility. The best results for each pair of the reactants are given in bold in Table 4. It is noteworthy that, except for the reactions of $^{i}Pr_3SiH$ and $^{t}BuC{\equiv}CH$ (entry 18, 87%), and Pr_3SiH with 4-(^{t}Bu)$C_6H_4C{\equiv}CH$ (entry 32, 83%), all the yields were higher than 90%.

Finally, we also examined the effect of catalyst loading in the model hydrosilylation system (Table 5). We found that performing the process with lower catalyst loadings (10^{-2}–10^{-3} mol%) requires longer times guaranteeing higher TONs and TOFs. Thus, the maximum TONs of 4.0×10^4 and TOFs 1.7×10^3 (h^{-1}) for catalyst **14**, and TONs of 3.3×10^4 and TOFs 1.4×10^3 (h^{-1}) for catalyst **15**, were accomplished within 24 h of the reaction although with low product yields (40% and 33%, correspondingly).

3. Final remarks

In pursuit of our studies, we have revealed that complexes with acyclic diaminocarbenes can be suitable catalysts for alkyne

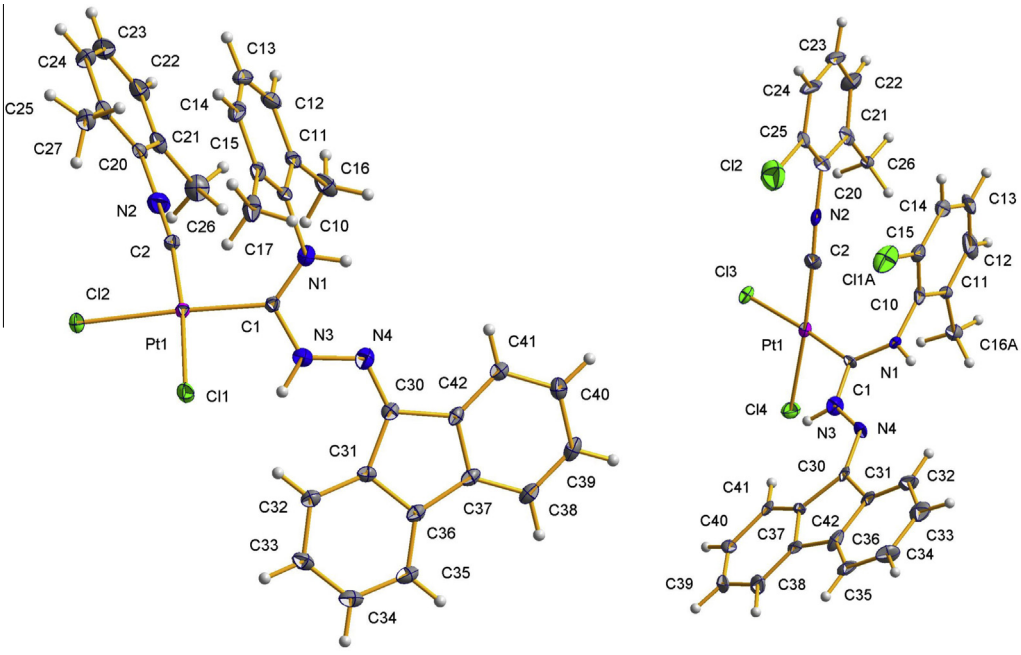


Fig. 1. View of **11** (left) and **14** (right) with the atomic numbering schemes. Thermal ellipsoids are drawn with the 30% probability. Hydrogen labels and chloroform molecules are omitted for simplicity. In **14**, only one component of the substitutional disorder (C16A and Cl1A) is shown.

Table 2
Selected bond lengths [Å] and angles [°] for **11**, **13**, and **14**.

	11	13[a]	14
Bond lengths			
Pt–C1	1.995(3)	1.96(2)	2.000(15)
Pt–C2	1.902(4)	–	1.862(14)
Pt–C11	–	1.88(2)	–
Pt–Cl1	2.3125(10)	2.312(5)	–
Pt–Cl2	2.3591(8)	2.361(6)	–
Pt–Cl3	–	–	2.358(4)
Pt–Cl4	–	–	2.302(4)
C1–N1	1.312(5)	1.35(3)	1.358(17)
C1–N3	1.350(4)	–	1.300(15)
C1–N12	–	1.35(3)	–
C2–N2	1.143(5)	–	1.181(16)
C11–N11	–	1.15(2)	–
N3–N4	1.374(4)	–	1.364(15)
N12–N13	–	1.36(2)	–
Bond angles			
Cl1–Pt1–Cl2	88.81(3)	89.5(2)	–
Cl3–Pt1–Cl4	–	–	88.43(13)
C1–Pt1–C2	95.45(15)	–	95.7(6)
C1–Pt1–C11	–	96.8(9)	–
Pt1–C1–N1	128.8(3)	129.3(16)	127.6(9)
Pt1–C1–N3	115.6(3)	–	116.7(11)
Pt1–C1–N12	–	119.4(15)	–
N1–C1–N3	115.6(3)	–	115.6(13)
N1–C1–N12	–	111.3(19)	–
C1–N3–N4	120.8(3)	–	122.3(13)
C1–N12–N13	–	121.8(17)	–

[a] Only the Pt1 containing molecule is presented.

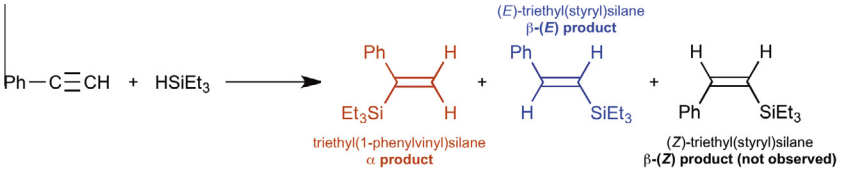
hydrosilylation; these species have never been employed for this purpose [1,2]. Thus, we have prepared several new platinum-(ADC) derivatives via the metal-mediated integration of isocyanides and hydrazones, fully characterized them, and evaluated their catalytic properties in the hydrosilylation of terminal alkynes with trisubstituted silanes giving vinyl silanes. Our optimized catalytic system runs at 80–100 °C in dry toluene for 3–6 h with a typical catalyst loading of 0.1 mol% and allows the successful transformation of a range of substrates with different steric hindrances (Et_3SiH, Pr_3SiH, $^iPr_3SiH$, and $PhMe_2SiH$ as silanes; PhC≡CH, ^{t}BuC≡CH, and 4-(^{t}Bu)C_6H_4C≡CH as alkynes). Under the described conditions, the target silylated products were obtained in 83–99% yields.

It is important to mention that despite the fact that platinum complexes with ADC ligands have never been previously employed in catalysis [1,2], the current study clearly validates their potential. In addition, the comparison of our results for the hydrosilylation of terminal alkynes with platinum-ADCs as catalysts with those reported for the structurally related platinum-NHCs [33,34,49] reveals a higher catalytic activity of the former species. In fact, the majority of platinum-NHC systems demand higher catalyst loading (0.5–1 mol%) [33,34,49], while with the lower (0.01–0.1 mol%) catalyst amount, the process required much longer time (up to 48 h) [33]. Among abovementioned systems that reported by de Jesús et al. [34] and based on platinum(0)-NHCs (0.1–0.5 mol%) worked in an aqueous medium at lower temperature of 30 °C and that should be recognized as one of its benefits. In our system running at 80–100 °C, reduced catalyst loading (0.001 mol%) assured the maximum TONs of up to 4.0×10^4 and TOFs of 1.7×10^3 (h^{-1}) that were achieved within 24 h, thus showing one of the best ever reported efficiencies for platinum-catalyzed hydrosilylation of terminal alkynes [33,34,49].

4. Experimental section

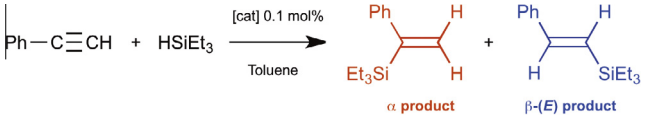
4.1. Materials and instrumentation

Solvents, $K_2[PtCl_4]$, all isocyanides, and hydrazones were obtained from commercial sources and used as received, apart from chloroform that was purified by conventional distillation over



Scheme 3. Model system for the hydrosilylation of alkynes.

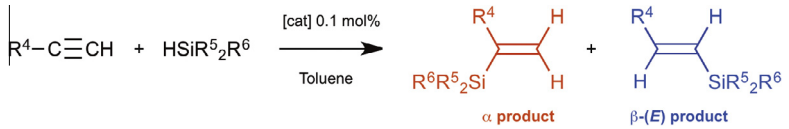
Table 3
Comparison of the catalytic activity of **7**–**15** [yields and (α/β ratio)].



Catalyst	Yields[a] and (α/β ratio) at T = 80 °C		Yields[a] and (α/β ratio) at T = 100 °C	
	Time = 3 h	Time = 6 h	Time = 3 h	Time = 6 h
7	63 (22/78)	85 (21/79)	73 (26/74)	89 (29/71)
8	34 (18/82)	66 (19/81)	76 (22/78)	92 (22/78)
9	20 (18/82)	56 (23/77)	80 (23/77)	97 (22/78)
10	51 (34/66)	63 (41/59)	70 (27/73)	91 (30/70)
11	55 (22/78)	92 (21/79)	71 (18/82)	98 (29/71)
12	64 (20/80)	95 (21/79)	84 (19/81)	93 (15/85)
13	55 (48/52)	72 (50/50)	79 (25/75)	56 (23/77)
14	93 (22/78)	99 (19/81)	99 (25/75)	99 (24/76)
15	78 (20/80)	92 (20/80)	84 (23/77)	98 (21/79)

PhC≡CH (5.0×10^{-4} mol, 1 equiv), Et_3SiH (5.0×10^{-4} mol, 1 equiv), any of catalysts **7**–**15** (5.0×10^{-7} mol); toluene (0.5 mL).
[a] Yields are based on ^{1}H NMR measurements.

Table 4
Scope of the hydrosilylation system employing catalysts **14** and **15** [yields and (α/β ratio)].[a,b]



Entry	Catalyst	Substrates	PhC≡CH	4-(^{t}Bu)C_6H_4C≡CH	^{t}BuC≡CH
1–3	**14**	Et_3SiH	93 (22/78)	80 (17/83)	**97 (6/94)**
4–6			**99 (25/75)**	86 (27/75)	90 (12/88)
7–9		Pr_3SiH	43 (17/83)	36 (17/83)	87 (5/95)
10–12			85 (31/69)	77 (34/66)	**99 (11/89)**
13–15		$^iPr_3SiH$	12 (83/17)	9 (87/13)	10 (41/59)
16–18			**99 (83/17)**	**94 (85/15)**	**87 (52/48)**
19–21		$PhMe_2SiH$	90 (28/72)	**97 (24/76)**	97 (3/97)
22–24			**99 (25/75)**	95 (26/74)	**99 (9/91)**
25–27	**15**	Et_3SiH	92 (20/80)	89 (17/83)	**97 (6/94)**
28–30			97 (21/79)	**97 (19/81)**	92 (9/91)
31–33		Pr_3SiH	59 (18/82)	**83 (16/84)**	72 (4/96)
34–36			**91 (20/80)**	73 (21/79)	75 (8/92)
37–39		$^iPr_3SiH$	18 (99/1)	26 (99/1)	55 (51/49)
40–42			90 (81/19)	**94 (85/15)**	84 (52/48)
43–45		$PhMe_2SiH$	71 (29/71)	91 (25/75)	97 (4/96)
48–48			91 (30/70)	95 (26/74)	85 (6/94)

Selected alkyne (5.0×10^{-4} mol, 1 equiv), selected sylane (5.0×10^{-4} mol, 1 equiv), selected catalyst (5.0×10^{-7} mol); toluene (0.5 mL).
[a] For each cell, data were obtained at 80 (first line) and 100 (second line) °C; yields are based on ^{1}H NMR measurements.
[b] Reaction time was 3 h for catalyst 14 and 6 h for 15.

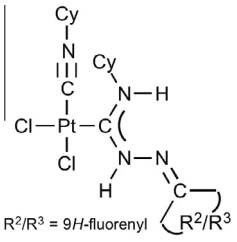
calcium chloride. The starting *cis*-[$PtCl_2(CNR)_2$] (R = Cy **1**, Xyl **2**, 2-Cl-6-MeC_6H_3 **3**, and *t*Bu **16**) [50–54], and known aminocarbene complexes **7** and **10** [37] were prepared as previously reported. C, H, and N elemental analyses were carried out by Microanalytical Service of Instituto Superior Técnico. ESI$^+$ mass-spectra were obtained on a VARIAN 500-MS LC ion trap mass-spectrometer in MeOH (ion spray voltage: +5 kV, capillary voltage: 30 V, RF loading: 100%). Infrared spectra (4000–400 cm^{-1}) were measured on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC) NMR spectra were recorded on Bruker Avance II + 400 MHz (UltraShield™ Magnet) and Bruker Avance II + 500 MHz (UltraShield™ Plus Magnet) spectrometers at ambient temperature using solvent resonances as a reference.

4.2. X-ray structure determinations

The X-ray quality single crystals of complexes **11**, **13**, and **14** were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 K (Table 1S). Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo Kα (λ 0.71073) radiation. Data were collected using ω scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [55] on all the observed reflections. Absorption corrections were applied using SADABS [56]. Structures were solved by direct methods by using the SHELXS-97 package and refined with SHELXL-97 [57]. Calculations were performed using the WinGX System–Version 1.80.03 [58]. All hydrogen atoms were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms (C8, C18, C48, C58 in **13** and C16A, C16B, Cl1B in **14** were exceptions) and isotropic for the remaining atoms were employed. There was a substitutional disorder in the structure of **14** in the phenyl ring of the aminocarbene ligand; the occupancies of its methyl carbon and the chlorine atoms were determined by using the "free variable" (FVAR) option in SHELXL software [59]. A value of 0.57 as an average for FVAR was obtained. Although *R*-values are relatively high for the resulting structure of **14** (Table 1S) as a result of the poor quality of crystals (disorder, weak diffraction), bond distances and angles were within a chemically reasonable range. CCDC 938950–938952 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

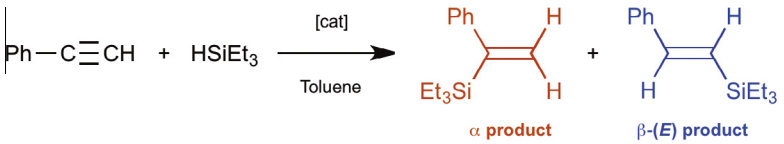
4.3. Synthetic work

Reactions of 1–3 and 4–6. A solution of H_2N–N=CR^2R^3 (0.50 mmol) in $CHCl_3$ (5 mL) was added to a solution of *cis*-[$PtCl_2$(-$CNR^1)_2$] (0.50 mmol) in $CHCl_3$ (10 mL), and the reaction mixture was refluxed for 8–26 h (see Table 1). During this period, the color of the mixture gradually turned from light orange to bright yellow. When the reaction was complete, the resulting mixture was evaporated to dryness at 20–25 °C under a stream of dinitrogen, and the product was extracted with two 5-mL portions of $CHCl_3$. The bright yellow solution was filtered to remove some insoluble material; the filtrate was evaporated to dryness at RT under a stream of N_2 and washed with five 5-mL portions of $^iPr_2O$, one 1-mL portion of cold (5 °C) Et_2O, and again with five 5-mL portions of $^iPr_2O$, whereupon dried *in vacuo* at RT. Yields of **7**–**15** were 75–85%, based on Pt. The authenticity of known species **7** and **10** was established upon comparison of their ^{1}H and ^{13}C{^{1}H} NMR and IR spectra with those reported previously [37].



(**8**, 75%). Anal. Calcd for $C_{27}H_{32}N_4Cl_2Pt$: C, 47.79; H, 4.75; N, 8.26. Found: C, 48.10; H, 4.93; N, 8.25%. ESI$^+$–MS, *m/z*: 642 [M–Cl]$^+$, 606 [M–2Cl–H]$^+$. IR (KBr, selected bands, cm^{-1}): 3354 mw,

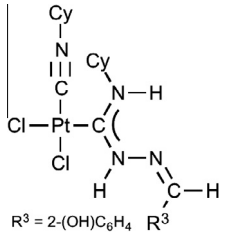
Table 5
Effect of catalyst loading and reaction time for **14** and **15**.



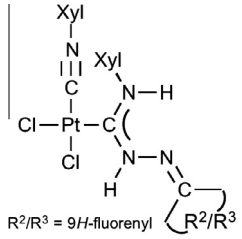
Catalyst	Catalyst loading, mol% and (time, h)	T = 80 °C				T = 100 °C			
		Yields (%)[a]	α/β ratio	TON	TOF (h^{-1})	Yields (%)[a]	α/β ratio	TON	TOF (h^{-1})
14	0.1 (3)	93	22/78	9.3×10^2	3.1×10^2	99	25/75	9.9×10^2	3.3×10^2
	0.1 (6)	99	19/81	9.9×10^2	1.7×10^2	99	24/76	9.9×10^2	1.7×10^2
	0.01 (12)	98	72/28	9.8×10^3	8.2×10^2	94	69/31	9.4×10^3	7.8×10^2
	0.001 (24)	28	83/17	2.8×10^4	1.2×10^3	40	78/22	4.0×10^4	1.7×10^3
15	0.1 (3)	78	20/80	7.8×10^2	2.6×10^2	84	23/77	8.4×10^2	2.8×10^2
	0.1 (6)	92	20/80	9.2×10^2	1.5×10^2	98	21/79	9.8×10^2	1.6×10^2
	0.01 (12)	72	63/37	7.2×10^3	6.0×10^2	99	71/29	9.9×10^3	8.3×10^2
	0.001 (24)	19	77/23	1.9×10^4	7.9×10^2	33	72/28	3.3×10^4	1.4×10^3

PhC≡CH (5.0×10^{-4} mol, 1 equiv), Et_3SiH (5.0×10^{-4} mol, 1 equiv); toluene (0.5 mL).
[a] Yields are based on ^1H NMR measurements.

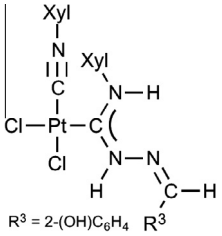
3276 mw ν(N–H); 2933 s, 2857 m ν(C–H from Cy); 2223 s ν(C≡N); 1608 m ν(N=C); 1579 s ν(N–$C_{carbene}$); 734 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 9.92 (s, 1H, $C_{carbene}$–NH), 8.81 (s, 1H, $C_{carbene}$–NHN), 8.42–7.12 (m, 8H, aryls), 4.51 (s) and 4.02 (s, 2H, CH-Cy), 2.42–1.28 (m, 20H, CH_2-Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 165.1 and 153.6 ($C_{carbene}$–NH and C=N), 142.3–127.3 (aryls), 59.1 and 52.2 (CH), 34.2–22.1 (CH_2).



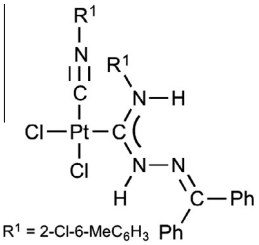
(**9**, 81%). Anal. Calcd for $C_{21}H_{30}N_4Cl_2OPt$: C, 40.65; H, 4.87; N, 9.03. Found: C, 40.62; H, 4.77; N, 9.07%. ESI^+–MS, *m/z*: 584 $[M–Cl]^+$, 548 $[M–2Cl–H]^+$. IR (KBr, selected bands, cm^{-1}): 3352 mw, 3232 mw ν(N–H); 2962 m, 2932 s ν(C–H from Cy); 2226 s ν(C≡N); 1621 s ν(N=C); 1578 s ν(N–$C_{carbene}$); 803 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 11.56 (s, 1H, OH), 9.98 (s, 1H, $C_{carbene}$–NH), 9.42 (s, 1H, $C_{carbene}$–NHN), 8.44 (s, 1H, CH=N), 7.18–6.74 (m, 4H, aryls), 4.58 (s) and 4.12 (s, 2H, CH-Cy), 2.40–1.32 (m, 20H, CH_2-Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 168.6 and 155.7 ($C_{carbene}$–NH and C=N), 152.8 (C–O), 131.6–128.1 (aryls), 58.7 and 53.2 (CH), 33.6–21.5 (CH_2).



(**11**, 76%). Anal. Calcd for $C_{31}H_{27}N_4Cl_2Pt$: C, 51.60; H, 3.77; N, 7.75. Found: C, 51.53; H, 3.91; N, 7.67%. ESI^+–MS, *m/z*: 723 $[M+H]^+$, 686 $[M–Cl]^+$. IR (KBr, selected bands, cm^{-1}): 3309 mw, 3220 mw ν(N–H); 2919–2851 m ν(C–H from Cy); 2196 s ν(C≡N); 1608 s ν(N=C); 1532 s ν(N–$C_{carbene}$); 730 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 10.94 (s, 1H, $C_{carbene}$–NH), 9.64 (s, 1H, $C_{carbene}$–NHN), 8.35–6.93 (m, 18H, aryls), 2.49 (s), 2.44 (s), 2.29 (s), and 2.16 (s, 12H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.0 and 151.6 ($C_{carbene}$–NH and C=N), 151.6–120.3 (aryls), 19.5, 19.4, 18.7, and 18.6 (Me).

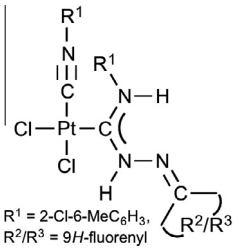


(**12**, 78%). Anal. Calcd for $C_{25}H_{26}N_4Cl_2OPt$: C, 45.19; H, 3.94; N, 8.43. Found: C, 45.42; H, 3.87; N, 8.27%. ESI^+–MS, *m/z*: 665 $[M+H]^+$, 629 $[M–Cl]^+$. ESI^-–MS, *m/z*: 663 $[M–H]^-$. IR (KBr, selected bands, cm^{-1}): 3254 mw, 3181 mw ν(N–H); 2196 s ν(C≡N); 1622 s ν(N=C); 1562 s ν(N–$C_{carbene}$); 764 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 11.72 (s, 1H, OH), 10.12 (s, 1H, $C_{carbene}$–NH), 9.72 (s, 1H, $C_{carbene}$–NHN), 8.44 (s, 1H, CH=N), 7.16–6.71 (m, 10H, aryls), 2.38 (s), 2.29 (s), 2.09 (s), and 2.03 (s, 12H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$:DMSO-d_6, 9:1 v/v, δ): 166.2 and 153.7 ($C_{carbene}$–NH and C=N), 151.9 (C–O), 131.6–128.1 (aryls), 19.2, 19.0, 18.8, and 18.3 (Me).

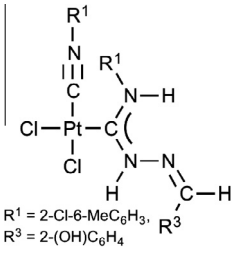


(**13**, 76%). Anal. Calcd for $C_{29}H_{24}N_4Cl_4Pt$: C, 45.51; H, 3.16; N, 7.32. Found: C, 45.42; H, 3.05; N, 7.27%. ESI^+–MS, *m/z*: 729 $[M–Cl]^+$. ESI^-–MS, *m/z*: 763 $[M–H]^-$. IR (KBr, selected bands, cm^{-1}): 3254 mw, 3187 mw ν(N–H); 2189 s ν(C≡N); 1618 m ν(N=C); 1536 s ν(N–$C_{carbene}$); 777 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 9.74 (s, 1H, $C_{carbene}$–NH), 9.52 (s, 1H, $C_{carbene}$–NHN), 7.65–6.92

(m, 16H, aryls), 2.70 (s) and 2.17 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.1 and 158.2 ($C_{carbene}$–NH and C=N), 138.9–125.5 (aryls), 20.6 and 19.2 (Me).



(**14**, 85%). Anal. Calcd for $C_{29}H_{22}N_4Cl_4Pt$: C, 45.63; H, 2.90; N, 7.34. Found: C, 45.42; H, 3.04; N, 7.27%. ESI^+–MS, *m/z*: 764 $[M+H]^+$, 726 $[M–Cl]^+$. IR (KBr, selected bands, cm^{-1}): 3220 w, 3187 mw ν(N–H); 2194 s ν(C≡N); 1607 s ν(N=C); 1534 s ν(N–$C_{carbene}$); 781 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 10.93 (s, 1H, $C_{carbene}$–NH), 9.72 (s, 1H, $C_{carbene}$–NHN), 8.33–6.93 (m, 14H, aryls), 2.74 (s) and 2.21 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.9 and 152.5 ($C_{carbene}$–NH and C=N), 133.1–120.2 (aryls), 20.7 and 19.2 (Me).



(**15**, 75%). Anal. Calcd for $C_{23}H_{20}N_4Cl_4OPt$: C, 39.17; H, 2.86; N, 7.94. Found: C, 38.98; H, 2.72; N, 7.78%. ESI^+–MS, *m/z*: 669 $[M–Cl]^+$. ESI^-–MS, *m/z*: 704 $[M–H]^-$. IR (KBr, selected bands, cm^{-1}): 3220 mw, 3156 mw ν(N–H); 2194 s ν(C≡N); 1622 s ν(N=C); 1561 s ν(N–$C_{carbene}$); 757 m δ(C–H from Ar). ^1H NMR ($CDCl_3$, δ): 12.08 (s, 1H, OH), 10.46 (s, 1H, $C_{carbene}$–NH), 9.82 (s, 1H, $C_{carbene}$–NHN), 8.92 (s, 1H, CH=N), 7.26–6.76 (m, 10H, aryls), 2.34 (s) and 2.12 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 169.2 and 157.1 ($C_{carbene}$–NH and C=N), 154.6 (C–O), 138.9–125.1 (aryls), 20.4 and 19.6 (Me).

4.4. General procedure for the catalytic hydrosilylation of terminal alkenes (specific conditions are provided in Tables 3–5)

A solution of a particular complex **7**–**14** (1.0×10^{-7} mol) in dry chloroform (0.5 mL) and a Teflon-coated magnetic bar were placed in a 5-mL vial. It was closed with a septum and an aluminum crimp seal, and the solution was evaporated to dryness under stream of dinitrogen at RT. Toluene (0.5 mL), the alkyne (0.50 mmol), and the silane (0.50 mmol) were added in quick succession via syringes. The vial was ventilated several times with dinitrogen and then kept under vigorous stirring in the thermostated oil bath at 80–100 °C for 3–6 h (see Tables 3–5 for details). After cooling to RT, the reaction mixture was evaporated to dryness under a stream of N_2, and 1,2-dimethoxyethane (1 equiv, used as an NMR internal standard) was added. The content of the vial was extracted with three 0.20-mL portions of $CDCl_3$, and all fractions were joined and analyzed by ^1H NMR spectroscopy. The product peak assignments were based on authentic samples or on published data [29–34], while the isomeric content was determined on the basis of the olefinic coupling constants in the ^1H NMR spectra (e.g., for model reaction of phenylacetylene and triethylsilane leading to a mixture of triethyl(1-phenylvinyl)silane (α product, $J^2_{HH} = ca.\,3$ Hz) and (*E*)-triethyl(styryl)silane (β-(*E*) isomer, $J^3_{HH} = ca.\,19$ Hz) [33,34]. Quantifications were performed upon integration of the selected peaks of the product with those of the standard. In some cases, the products were isolated by extraction of the residue after evaporation of the reaction mixture with CH_2Cl_2, followed by column chromatography on silica gel (Fluka 40/60; hexane/ethyl acetate).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.09.003.

References

[1] V.P. Boyarskiy, K.V. Luzyanin, V.Yu. Kukushkin, Coord. Chem. Rev. 256 (2012) 2029–2056.
[2] L.M. Slaughter, ACS Catal. 2 (2012) 1802–1816.
[3] C. Bartolomé, Z. Ramiro, D. García-Cuadrado, P. Pérez-Galán, M. Raducan, C. Bour, A.M. Echavarren, P. Espinet, Organometallics 29 (2010) 951–956.
[4] A.S.K. Hashmi, T. Hengst, C. Lothschütz, F. Rominger, Adv. Synth. Catal. 352 (2010) 1315–1337.
[5] A.S.K. Hashmi, C. Lothschutz, C. Böhling, F. Rominger, Organometallics 30 (2011) 2411–2417.
[6] A.S.K. Hashmi, T. Haffner, M. Rudolph, F. Rominger, Eur. J. Org. Chem. (2011) 667–671.
[7] M.C.B. Jaimes, C.R.N. Böhling, J.M. Serrano-Becerra, A.S.K. Hashmi, Angew. Chem., Int. Ed. Engl. 52 (2013) 7963–7966.
[8] V.P. Boyarskiy, K.V. Luzyanin, V.Yu. Kukushkin, Palladium-(acyclic diaminocarbene) species as alternative to palladium-(nitrogen heterocyclic carbenes) in cross-coupling catalysis, in: A.J.L. Pombeiro (Ed.), Advances in Organometallic Chemistry: The Silver/Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book, John Wiley & Sons, Inc., 2014 (in press).
[9] K. Denk, P. Sirsch, W.A. Herrmann, J. Organomet. Chem. 649 (2002) 219–224.
[10] W.A. Herrmann, K. Öfele, D.V. Preysing, E. Herdtweck, J. Organomet. Chem. 684 (2003) 235–248.
[11] M.-T. Lee, C.-H. Hu, Organometallics 23 (2004) 976–983.
[12] G.D. Frey, W.A. Herrmann, J. Organomet. Chem. 690 (2005) 5876–5880.
[13] G.D. Frey, E. Herdtweck, W.A. Herrmann, J. Organomet. Chem. 691 (2006) 2465–2478.
[14] L.M. Slaughter, Comm. Inorg. Chem. 29 (2008) 46–72.
[15] D.R. Snead, I. Chiviriga, K.A. Abboud, S. Hong, Org. Lett. 11 (2009) 3274–3277.
[16] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361–363.
[17] A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, J. Am. Chem. Soc. 117 (1995) 11027–11028.
[18] R.W. Alder, P.R. Allen, M. Murray, A.G. Orpen, Angew. Chem., Int. Ed. Engl. 35 (1996) 1121–1123.
[19] B.V. Johnson, J.E. Shade, J. Organomet. Chem. 179 (1979) 357–366.
[20] R.W. Alder, M.E. Blake, J.M. Oliva, J. Phys. Chem. A 103 (1999) 11200–11211.
[21] E.L. Rosen, M.D. Sanderson, S. Saravanakumar, C.W. Bielawski, Organometallics 26 (2007) 5774–5777.
[22] E.L. Rosen, D.H. Sung, Z. Chen, V. Lynch, C.W. Bielawski, Organometallics 29 (2010) 250–256.
[23] M.S. Collins, E.L. Rosen, V. Lynch, C.W. Bielawski, Organometallics 29 (2010) 3047–3053.
[24] R.A. Michelin, A.J.L. Pombeiro, M.F.C. Guedes da Silva, Coord. Chem. Rev. 218 (2001) 75–112.
[25] J. Vignolle, X. Catton, D. Bourissou, Chem. Rev. 109 (2009) 3333–3384.

[26] K.V. Luzyanin, A.J.L. Pombeiro, Carbene complexes derived from metal-bound isocyanides, in: V. Nenajdenko (Ed.), Isocyanide Chemistry, Wiley-VCH, 2012, pp. 531–550.
[27] E. Langkopf, D. Schinzer, Chem. Rev. 95 (1995) 1375–1408.
[28] L.N. Lewis, K.G. Sy, G.L. Bryant, P.E. Donahue, Organometallics 10 (1991) 3750–3759.
[29] J. Berding, J.A. van Paridon, V.H.S. van Rixel, E. Bouwman, Eur. J. Inorg. Chem. (2011) 2450–2458.
[30] M.V. Jiménez, J.J. Pérez-Torrente, M.I. Bartolomé, V. Gierz, F.J. Lahoz, L.A. Oro, Organometallics 27 (2008) 224–234.
[31] M.R. Chaulagain, G.M. Mahandru, J. Montgomery, Tetrahedron 62 (2006) 7560–7566.
[32] G. de Bo, G. Berthon-Gelloz, B. Tinant, I.E. Markó, Organometallics 25 (2006) 1881–1890.
[33] M. Poyatos, A. Maisse-Francüois, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 25 (2006) 2634–2641.
[34] G.F. Silbestri, J.C. Flores, E. de Jesús, Organometallics 31 (2012) 3355–3360.
[35] K.V. Luzyanin, A.J.L. Pombeiro, M. Haukka, V.Yu. Kukushkin, Organometallics 27 (2008) 5379–5389.
[36] K.V. Luzyanin, M.F.C. Guedes da Silva, V.Yu. Kukushkin, A.J.L. Pombeiro, Inorg. Chim. Acta 362 (2009) 833–838.
[37] K.V. Luzyanin, A.G. Tskhovrebov, M.C. Carias, M.F.C. Guedes da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, Organometallics 28 (2009) 6559–6566.
[38] A.G. Tskhovrebov, K.V. Luzyanin, F.M. Dolgushin, M.F.C. Guedes da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, Organometallics 30 (2011) 3362–3370.
[39] A.G. Tskhovrebov, K.V. Luzyanin, M.L. Kuznetsov, V.N. Sorokoumov, I.A. Balova, M. Haukka, V.Yu. Kukushkin, Organometallics 30 (2011) 863–874.
[40] R.S. Chay, K.V. Luzyanin, Inorg. Chim. Acta 380 (2012) 322–327.
[41] R.S. Chay, K.V. Luzyanin, V.Yu. Kukushkin, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Organometallics 31 (2012) 2379–2387.
[42] M.A. Kinzhalov, K.V. Luzyanin, V.P. Boyarskiy, M. Haukka, V.Yu. Kukushkin, Organometallics 32 (2013) 5212–5223.
[43] M.A. Kinzhalov, V.P. Boyarskiy, K.V. Luzyanin, F.M. Dolgushin, V.Yu. Kukushkin, Dalton Trans. (2013) 10394–10397.
[44] M.A. Kinzhalov, K.V. Luzyanin, V.P. Boyarskiy, M. Haukka, V.Yu. Kukushkin, Izv. Akad. Nauk: Ser. Khim. (Russ. Chem. Bull.) 3 (2013) 757–765.
[45] A.S.K. Hashmi, C. Lothschütz, C. Böhling, T. Hengst, C. Hubbert, F. Rominger, Adv. Synth. Catal. 352 (2010) 3001–3012.
[46] N.A. Bokach, T.V. Kuznetsova, S.A. Simanova, M. Haukka, A.J.L. Pombeiro, V.Yu. Kukushkin, Inorg. Chem. 44 (2005) 5152–5160.
[47] D. Kremzow, G. Seidel, C.W. Lehmann, A. Furstner, Chem. Eur. J. 11 (2005) 1833–1853.
[48] D. Hirsch-Weil, D.R. Snead, S. Inagaki, H. Seo, K.A. Abboud, S. Hong, Chem. Commun. (2009) 2475–2477.
[49] J.J. Hu, F. Li, T.S.A. Hor, Organometallics 28 (2009) 1212–1220.
[50] K.V. Luzyanin, A.G. Tskhovrebov, M. Haukka, V.Yu. Kukushkin, J. Chem. Crystallogr. 42 (2012) 1170–1175.
[51] R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino, R.J. Angelici, Inorg. Chem. 27 (1988) 85–92.
[52] F. Bonati, G. Minghetti, J. Organometal. Chem. 24 (1970) 251–256.
[53] R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino, R.J. Angelici, Inorg. Chem. 27 (1988) 93–99.
[54] A.G. Tskhovrebov, K.V. Luzyanin, M. Haukka, V.Yu. Kukushkin, J. Chem. Crystallogr. 42 (2012) 1170–1175.
[55] Bruker APEX2 & SAINT, in: Bruker, AXS Inc., Madison, Wisconsin, USA, 2004.
[56] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467–473.
[57] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.
[58] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.
[59] G.M. Sheldrick, G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.