Platinum(II) complexes with polydentate N-heterocyclic carbenes: synthesis, structural characterization and hydrosilylation catalysis†

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Received 23rd November 2009, Accepted 3rd March 2010
First published as an Advance Article on the web 24th March 2010
DOI: 10.1039/b924587a

The platinum(II) complexes of multidentate N-heterocyclic carbenes, $[Pt(L1)_2Cl](PF_6)$ (**1**, L1 = *N*-methyl-*N*-(2-pyrimidinyl)imidazolylidene), $[Pt(L2)Cl](PF_6)$ (**2**, L2 = *N*-butyl-*N*-(1,10-phenanthrolin-2-yl)imidazolylidene), $[PtL3](PF_6)_2$ (**3**, L3 = bis(*N*-picolylimidazolylidenyl)-methane), $[PtL4](PF_6)_2$ (**4**, L4 = (bis(*N*-2-pyrimidylimidazolylidenyl)methane) (**4**) and $[Pt(L5)_2](PF_6)_2$ [**5**, L5 = bis(*N*-pyridylimidazoliumyl)methane] have been synthesized and structurally characterized. All these complexes exhibit slightly distorted square-planar configuration. These complexes are efficient catalyst precursors for hydrosilylation of alkynes. Complexes **2** and **4** are much more active than complexes **1**, **3** and **5**. In the hydrosilylation of arylacetylenes, relatively long induction periods were observed for **1**, **3** and **5**.

Introduction

Hydrosilylation of alkynes is an important reaction for the preparation of unsaturated organosilicon compounds which are intermediates of silicon materials and versatile building blocks in organic transformations.[1] Traditionally, the Speier system (H_2PtCl_6/i-PrOH)[2] and the Karstedt complex ((Pt_2(dvtms)$_3$, dvtms = divinyltetramethyldisiloxane)[3] are most commonly employed. One of the disadvantages of these catalysts is the ease of generation of colloidal platinum species, which is responsible for a number of undesired reactions.[4] The side products and the coloration originated from the colloidal platinum species might influence their industrial applications. Therefore, many efforts have been made to improve the stability of platinum catalysts by using various ligands and the selectivity of hydrosilylation reaction.[5-7] N-Heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and catalysis.[8] N-Heterocyclic carbenes can form stable M–C bonds with various transition metals because of their strong σ-donating ability that provides the possibility to develop platinum NHC complexes as robust hydrosilylation catalysts. Recently, a class of novel [Pt(dvtms)(NHC)] (dvtms = divinyltetramethyldisiloxane) complexes have been synthesized by Markó *et al.*[9] and have shown efficiency and good selectivity in the hydrosilylation of a broad range of alkenes and alkynes. Structurally related $[Pt(alkene)_2(NHC)]$ complexes have been reported by Elsevier *et al.* and used as hydrosilylation catalysts.[5,6,7,10] Although such $[Pt(alkene)_2(NHC)]$ complexes are air- and moisture-stable, their preparation requires strict conditions such as air- and moisture-free atmosphere and a strong base has to be used. Pt(II) complexes of N-heterocyclic carbenes are better catalyst precursors since they can be easily synthesized from simple platinum(II) and imidazolium salts by using common bases such as Ag_2O or K_2CO_3. The platinum complex $[PtCl_2$(bzoxcarb)], which was prepared from 2-benzoxazolyl imidazolium and $Pt(cod)Cl_2$ *via* carbene transfer route, was found to be an active catalyst for the hydrosilylation of alkenes and alkynes.[11] A very recent report described the synthesis and structural characterization of a few mono- and biscarbene platinum(II) complexes, which are suitable catalyst precursors for hydrosilylation of phenylacetylene and trimethylsilylacetylene.[12]

We have been interested in the transition-metal chemistry of pyridine-, pyrazole- and naphthyridine-functionalized NHC ligands, and the palladium[13] and nickel complexes[14] containing such hemilabile ligands showed good catalytic activities for C–C coupling reactions of various aryl chlorides and bromides. Here in this paper, we report the synthesis and structural characterization of platinum(II) complexes supported by multidentate NHC ligands, and their catalytic applications in hydrosilylation of arylacetylenes.

Results and discussion

Reaction of *N*-methyl-*N*-pyrimidinylimidazolium with an excess of Ag_2O in acetonitrile yielded a silver imidazolylidene complex, which was not isolated. Further treatment of the resulting solution of the silver complex with an equivalent of $Pt(cod)Cl_2$ gave $[Pt(N\text{-methyl-}N\text{-pyrimidinylimidazolylidene})_2Cl](PF_6)$ (**1**) as a pale yellow solid. With this procedure we did not obtain the expected $[Pt(N\text{-methyl-}N\text{-pyrimidinylimidazolylidene})Cl_2]$. When a half equivalent of $Pt(cod)Cl_2$ was employed, the yield could be improved (Scheme 1). The compound gave analytical data consistent with the calculated C, H and N percentages. However, the ^1H and ^{13}C NMR spectra of **1** is complicated although we repeatedly measured spectra in different deuterated solvents including acetonitrile and dimethyl sulfoxide even using the single-crystal sample. This phenomenon might result from the fast dissociation–association process of two pyrimidine groups *via* distorted square-pyramid or trigonal-bipyramid intermediates.

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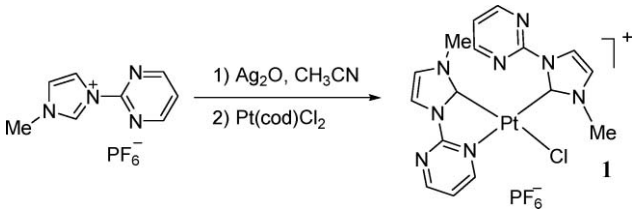
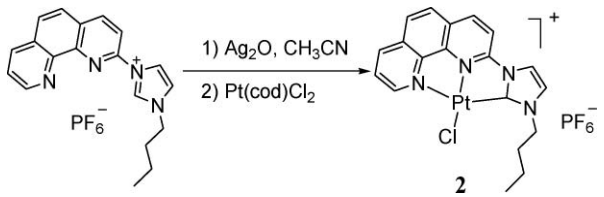
† CCDC reference numbers 755668–755672. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b924587a



Scheme 1 Synthesis of $[Pt(L1)_2Cl](PF_6)$ (**1**).



Scheme 2 Synthesis of $[Pt(L2)Cl](PF_6)$ (**2**).

Such intermediates have been known for nickel(II) complexes with similar imidazolylidene ligands.[14e]

Crystals of **1** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into its acetonitrile solution. The molecular structure of **1** is depicted in Fig. 1. The central platinum ion is coordinated by two *N*-methyl-*N*-(2-pyrimidinyl)imidazolylidene ligands one of which is bonded in a monodentate fashion. The two heterocyclic rings of the chelating ligand are almost perfectly coplanar with the coordination plane. The imidazole and pyrimidine ring of the mono-coordinated ligand bisect each other with a dihedral angle of 23.08°, whereas the dihedral angle between the coordination plane and imidazolylidene is 77.92°. The two imidazoylidenes are *cis*-positioned with Pt–C bond distances being 1.96 Å. The Pt–C and Pt–Cl bond distances are within the expected range of platinum complexes containing NHC ligands.[15]

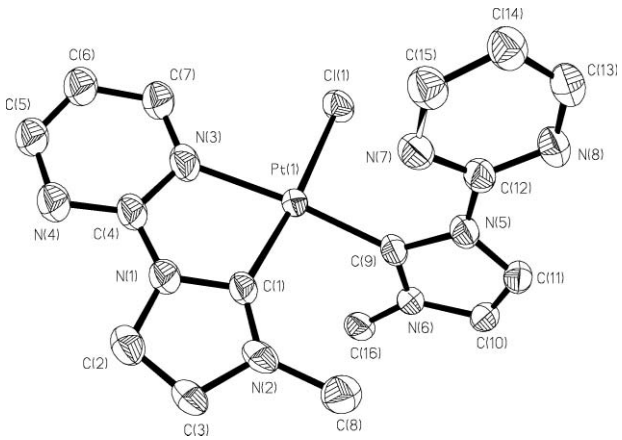


Fig. 1 Structural view of **1** showing 30% thermal ellipsoids. All H atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(9) 1.96(2), Pt(1)–C(1) 1.97(2), Pt(1)–N(3) 2.06(2), Pt(1)–Cl(1) 2.333(5); C(9)–Pt(1)–C(1) 96.7(9), C(9)–Pt(1)–N(3) 174.0(8), C(1)–Pt(1)–N(3) 79.6(9), C(9)–Pt(1)–Cl(1) 88.9(6), C(1)–Pt(1)–Cl(1) 173.8(6), N(3)–Pt(1)–Cl (1) 94.6(7).

We have already reported the synthesis and characterization of [M(*N*-butyl-*N*-(1,10-phenanthrolin-2-yl)imidazolylidene)Cl](PF_6) (M = Ni, Pd).[16] Similar reaction of *N*-butyl-*N*-(1,10-phenanthrolin-2-yl)imidazolium with Ag_2O and subsequently $Pt(cod)Cl_2$ afforded [Pt(*N*-butyl-*N*-(1,10-phenanthrolin-2-yl)imidazolylidene)Cl](PF_6) (**2**) as a yellow compound (Scheme 2). The ^1H NMR spectrum of **2** in DMSO-d_6 shows characteristic resonance signals due to phenanthroline and imidazoylidene moieties with a splitting pattern similar to its nickel and palladium analogues. The ^{13}C NMR spectrum of **2** in DMSO-d_6 exhibits a resonance signal at 150.6 ppm ascribed to the carbenic carbon atom, which is consistent with the reported values in the range of 132.5–198.2 ppm for Pt-NHC complexes.[17]

X-Ray crystallographic analysis showed that complex **2** has a square-planar geometry with platinum center surrounded by the pincer NNC ligand, *N*-butyl-*N*-(1,10-phenanthrolin-2-yl)imidazolylidene, and a chloride ion. The crystal structure contains two independent molecules per asymmetric unit which are basically the same, thus only one molecule is shown in Fig. 2. The compound is isostructural with its palladium and nickel analogues which have been previously reported by us.[16] All the atoms, excluding the butyl group are nearly perfectly coplanar. The Pt–C (1.942(8) Å) is quite normal as compared to those of many known platinum–NHC complexes.[15,17] The Pt–N(4) distance (2.089(6) Å) is much longer than that of Pt–N(3) (1.950(5) Å) due to steric requirement and large *trans* effect of imidazolylidene. Weak intermolecular Pt···Pt interaction is often observed for square-planar platinum(II) complexes.[18] The shortest Pt···Pt distance for **2** is 7.712 Å illustrating no intermolecular Pt···Pt interaction.

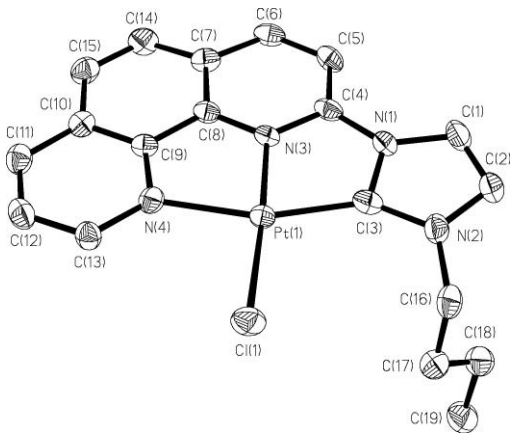
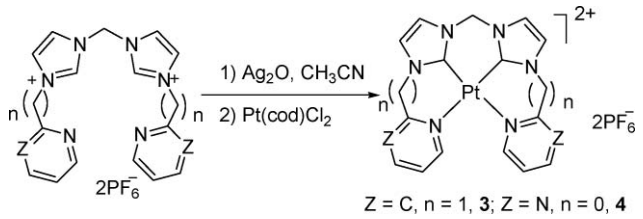


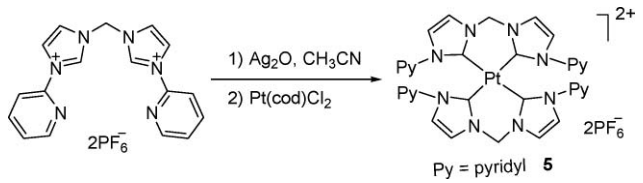
Fig. 2 Structural view of **2** showing 30% thermal ellipsoids. All H atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(3) 1.942(8), Pt(1)–N(3) 1.950(5), Pt(1)–N(4) 2.089(6), Pt(1)–Cl(1) 2.296(2); C(3)–Pt(1)–N(3) 78.9(3), C(3)–Pt(1)–N(4) 159.0(3), N(3)–Pt(1)–N(4) 80.1(2), C(3)–Pt(1)–Cl(1) 104.6(2), N(3)–Pt(1)–Cl(1) 176.52(18), N(4)–Pt(1)–Cl(1) 96.38(17).

Through carbene transfer reactions we were able to obtain [Pt(bis(*N*-picolylimidazolylidenyl)methane)]$(PF_6)_2$ (**3**) and [Pt(bis(*N*-pyrimidylimidazolylidenyl)methane)]$(PF_6)_2$ (**4**) from bis(*N*-picolylimidazoliumyl)methane and bis(*N*-pyrimidylimidazoliumyl)methane in moderate yields as shown in Scheme 3. Reaction of the *in situ* formed trisilver carbene complex, [Ag_3(bis-(*N*-pyridylimidazoliumyl)methane)$_2$$(CH_3CN)_2$]$(PF_6)_3$,[14a] with one



Scheme 3 Synthesis of $[Pt(L3)](PF_6)_2$ (**3**) and $[Pt(L4)](PF_6)_2$ (**4**).

equivalent of $[Pt(cod)Cl_2]$ yielded [Pt(bis(*N*-pyridylimidazoliumyl)methane]]$(PF_6)_2$ (**5**) as a white solid (Scheme 4). The ^{1}H NMR spectrum of **3** showed four set of peaks at 8.53 (d), 7.81 (t), 7.37 (t) and 7.23 (d) ppm assignable to the pyridine group. Two doublets appeared at 7.73 and 7.41 ppm with small coupling constants (J = 2 Hz) which can be ascribed to imidazolylidene backbone protons. The methylene linking the two imidazolylidene groups was found at 6.40 and 6.36 ppm as doublets with ^2J = 13.6 Hz, whereas the methylenes linking imidazolylidene and pyridine also showed their peaks as two doublets at 5.08 and 4.65 ppm with ^2J = 14.4 Hz, illustrating that the two protons attached to each methylene are magnetically inequivalent. In the ^{1}H NMR spectrum of **4**, the methylene group only shows a singlet at 7.26 ppm. Complex **5** shows two doublets at 6.64 and 6.48 ppm due to CH_2 groups. These platinum bis(carbene) and tetrakis(carbene) complexes gave a carbenic carbon resonance at around 162 ppm without significance difference.



Scheme 4 Synthesis of $[Pt(L5)_2](PF_6)_2$ (**5**).

Crystals of **3** were obtained by slow diffusion of diethyl ether into an acetonitrile solution of **3**. The molecular structure of **3** is shown in Fig. 3. The coordination geometry is distorted square planar with platinum coordinated to two carbenes and two pyridine groups. The two *cis*-arranged imidazolylidene rings are approximately parallel to the coordination plane with small dihedral angles of 10.07 and 15.31°. The two pyridine groups extend out of the coordination plane. The Pt–C bond distances are typical for platinum–NHC complexes. The Pt–N distances are slightly longer than those of platinum(II) complexes containing pyridine ligands, which are normally in the range of 2.0–2.1 Å, because of large *trans* effect of NHC ligands.[19]

The structure of **4** as determined by X-ray diffraction analysis is shown in Fig. 4. The platinum center has slightly distorted square-planar conformation with the imidazolylidene and pyrimidine rings lying in the coordination plane. The co-planarity can be illustrated by the small dihedral angles ranging from 2.65 to 6.78° between the four heteroaryl rings and the coordination plane. The planar structure resembles those of other metal (M = Fe, Co, Ni) complexes containing bis(*N*-pyrimidylimidazolylidenyl)methane and bis(*N*-pyridylimidazolylidenyl)methane ligands.[14a,20] The Pt–C bonds are shorter compared to those of complexes **1–3**.

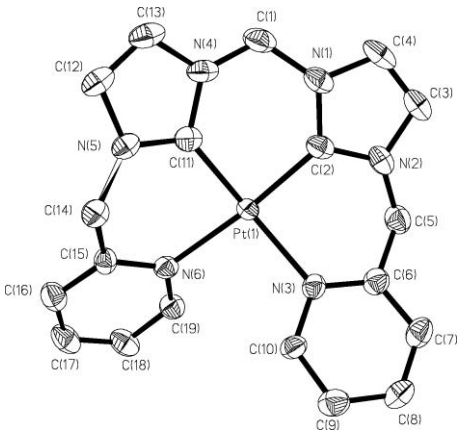


Fig. 3 Structural view of **3** showing 30% thermal ellipsoids. All H atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(11) 1.932(7), Pt(1)–C(2) 1.952(8), Pt(1)–N(3) 2.101(6), Pt(1)–N(6) 2.101(6); C(11)–Pt(1)–C(2) 89.3(3), C(11)–Pt(1)–N(3) 165.3(3), C(2)–Pt(1)–N(3) 90.7(3), C(11)–Pt(1)–N(6) 88.5(3), C(2)–Pt(1)–N(6) 169.5(2), N(3)–Pt(1)–N(6) 94.1(2).

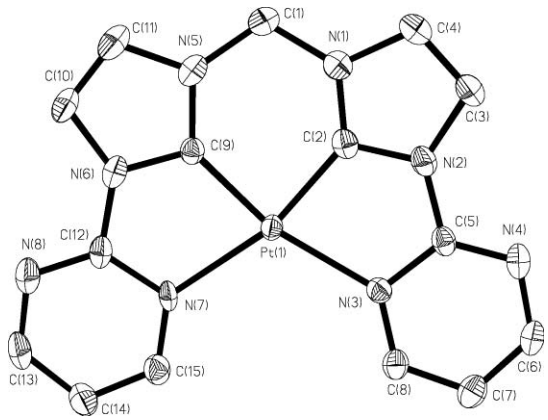


Fig. 4 Structural view of **4** showing 30% thermal ellipsoids. All H atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(9) 1.881(9), Pt(1)–C(2) 1.898(10), Pt(1)–N(3) 2.129(8), Pt(1)–N(7) 2.148(7); C(9)–Pt(1)–C(2) 86.5(4), C(9)–Pt(1)–N(3) 165.3(4), C(2)–Pt(1)–N(3) 79.2(4), C(9)–Pt(1)–N(7) 78.0(4), C(2)–Pt(1)–N(7) 164.5(4), N(3)–Pt(1)–N(7) 116.1(3).

Single crystals of **5** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its acetonitrile solution. The structure of complex **5** is depicted in Fig. 5. The structure consists of a platinum(II) complex in a square-planar coordination geometry with two coordinated bis(*N*-pyridylimidazolylidenyl)methane ligands. The pyridine groups are not coordinated. The Pt–C bond distances of 2.036(5) and 2.041(5) Å are relatively longer than those of complexes **1–4** due to large *trans* effect of the NHC ligand and the steric repulsion. The two *trans*-positioned imidazolylidene rings are basically coplanar, and the *cis*-arranged imidazolylidene rings show a dihedral angle of 55.01°. The imidazolylidene rings are all bisected with the coordination plane defined by C(10)C(2)C(10A)C(2A) (symmetry code: A $-x, -y, -z + 2$) with dihedral angles of 39.46 and 41.20°. So far, N-heterocyclic platinum(II) tetra(carbene) complexes are rare. The first platinum complex containing a multidentate tetracarbene

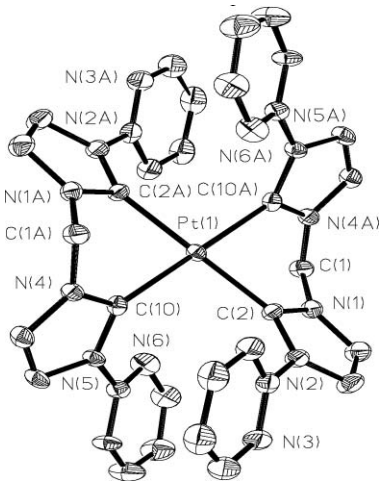


Fig. 5 Structural view of **5** showing 30% thermal ellipsoids. All H atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(10) 2.036(5), Pt(1)–C(2) 2.041(5); C(10)–Pt(1)–C(10A) 180.0, C(10)–Pt(1)–C(2) 95.71(19), C(10)–Pt(1)–C(2A) 84.29(19), C(2)–Pt(1)–C(2A) 180.0. Symmetry code: A $-x, -y, -z + 2$.

ligand with crown ether topology was reported by Hahn *et al.* in 2005 *via* a smart template-controlled reaction.[21a] Very recently, a few homoleptic tetra(carbene) complexes were prepared from bis(imidazolium) salts and $PtCl_2$ or $Pt(acac)_2$ in the presence of NaOAc at elevated temperature.[21b,c]

Catalytic hydrosilylation of acetylenes

Initially, we screened the catalytic activities of complexes **1–5** in a model reaction involving the hydrosilylation of phenylacetylene with triethylsilane at a catalyst loading of 1 mol% at 100 °C. The hydrosilylation of phenylacetylene with 1.2 equiv. of Et_3SiH gave full conversion within 24 h, generally yielding a mixture of (*E*)-triethyl(styryl)silane (A), triethyl(1-phenylvinyl)silane (B) and (*Z*)-triethyl(styryl)silane (C). Similar to other platinum catalysts, the reaction afforded *cis* addition products A and B as the major products, and trace amounts of *trans*-addition product C were also detected in less than 1% yield. The hydrogenated product, styrene was not observed by gas chromatography. The reaction profiles of phenylacetylene hydrosilylation catalyzed by **1–5** are shown in Fig. 6. Obviously, complexes **2** and **4** show much higher catalytic activities than **1**, **3** and **5**. The hydrosilylation could be completed within 1–2 h in the cases of **2** and **4**, whereas the reactions took 10–20 h under the same conditions when **1**, **3** and **5** were employed. For catalysts **2** and **4**, after an induction period of *ca.* 10 min, the catalytic transformation of alkyne to vinylsilane commenced giving full conversion within 1 h. The hydrosilylation with complexes **1**, **3** and **5** occurred with relatively long induction periods of 2–8 h followed by a rapid increase in catalytic activities. The reactions with **2** and **4** as catalysts conducted under the same conditions occurred without any kinetically significant induction period. These long induction periods suggest that the kinetic behavior should be related with propensity of the reduction of Pt(II) to Pt(0) species. It has been recognized that Pt(0) is the real catalytically active species in hydrosilylation.[1,5–7] Hydrosilane can act as a reducing agent. We have not been able to isolate and identify Pt(0) species or platinum–silyl species from the reactions

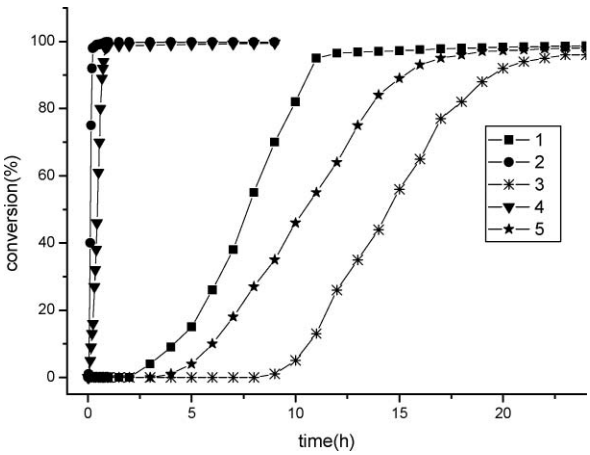


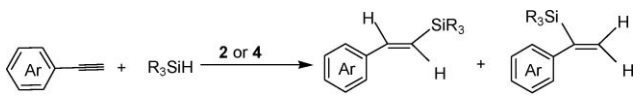
Fig. 6 Conversion *vs.* reaction time of hydrosilylation of phenylacetylene in toluene. Reaction conditions: triethylsilane/alkyne = 1.2, $T = 100$ °C.

of complexes **1–5** with different hydrosilanes. Further work is needed to clarify the mechanism.

In the hydrosilylation of phenylacetylene with triethylsilane catalyzed by **1–4**, (*E*)-triethyl(styryl)silane was found to be the major product with A/B ratios of 1.1–4.5. However, when **5** was employed, triethyl(1-phenylvinyl)silane (B) became the major product with A/B ratio of 0.6.

Complexes **2** and **4** are superior to complexes **1**, **3** and **5** in terms of rate of the hydrosilylation of phenylacetylene, and thus the reaction can be performed at quite low catalyst loading with satisfactory conversions. They were thus selected for further studies of other silanes and alkynes. At a catalyst loading of 0.1 mol%, the hydrosilylation of phenylacetylene and *p*-tolylacetylene with different hydrosilanes were studied, and the results are summarized in Table 1. Both phenylacetylene and *p*-tolylacetylene could be converted to unsaturated silanes in nearly quantitative yields. We found that the activities of the catalysts decreased slightly when the more hindered silane was employed; the reaction time was longer but the selectivity did not change. When phenylacetylene

Table 1 Hydrosilylation of alkynes with different silanes in toluene catalyzed by **2** and **4**[a]



Entry	Alkyne	Silane	Cat.	*t*/h	Conv. (%)	A	B
1	Phenylacetylene	Ph_2MeSiH	**2**	1	98	82	18
2	Phenylacetylene	Ph_3SiH	**2**	8	95	87	13
3	Phenylacetylene	Ph_2MeSiH	**4**	2	95	80	20
4	Phenylacetylene	Ph_3SiH	**4**	24	85	85	15
5	*p*-Tolylacetylene	Et_3SiH	**2**	0.5	98	85	15
6	*p*-Tolylacetylene	Ph_2MeSiH	**2**	0.4	99	88	12
7	*p*-Tolylacetylene	Ph_3SiH	**2**	6	99	79	21
8	*p*-Tolylacetylene	Et_3SiH	**4**	1	98	64	36
9	*p*-Tolylacetylene	Ph_2MeSiH	**4**	1	95	76	24
10	*p*-Tolylacetylene	Ph_3SiH	**4**	24	90	90	10

[a] Reaction conditions: silane/alkyne ratio = 1.2, $T = 100$ °C; yield and selectivity of products were measured by ^{1}H NMR and GC-MS.

was replaced with *p*-tolylacetylene to test the activity of the catalysts **2** and **4**, we found that *p*-tolylacetylene was hydrosilylated more quickly. In the cases of Et_3SiH and Ph_2MeSiH, over 95% conversions to silylated products were obtained after 1 h. When alkynes are hydrosilylated in the presence of either **2** or **4**, only α- and β-(*E*) regioisomers are produced with the latter being predominant.

In summary, we have successfully synthesized several platinum(II) complexes supported by multidentate N-heterocyclic carbenes *via* simple carbene transfer reaction between *in situ* formed silver carbene complexes and $Pt(cod)Cl_2$. These square-planar complexes have been crystallographically characterized. The platinum(II) complexes are air- and moisture-stable, and they are efficient catalyst precursors for hydrosilylation of alkynes at low catalyst loading and mild conditions. The catalyst activity varies depending upon the ancillary ligands and thus one can further improve the catalytic efficiency by tuning N-heterocyclic carbenes.

Experimental

All the chemicals were obtained from commercial suppliers and used without further purification. The imidazolium salts[13d,14e,16] and $Pt(cod)Cl_2$[22] were prepared according to the known procedure. Elemental analyses were performed on a Flash EA1112 instrument. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm and coupling constants (J) are expressed in Hz.

Synthesis of [Pt(L1)$_2$Cl](PF$_6$) (1)

A solution of HL1(PF_6) (61.2 mg, 0.20 mmol) in 5 mL of acetonitrile was treated with Ag_2O (23.2 mg, 0.10 mmol) at 50 °C. After 10 h, Ag_2O completely disappeared and $Pt(cod)Cl_2$ (74.8 mg, 0.20 mmol) was added to the filtrate. After it was stirred for 12 h at room temperature, the solution was filtered. The filtrate was then concentrated to *ca.* 2 mL. Addition of Et_2O (20 mL) to the filtrate afforded a yellow precipitate. The precipitate was collected and washed with Et_2O to obtain the pale yellow solid. Yield: 25 mg, 17%. Anal. Calc. for $C_{16}H_{18}ClF_6N_8OPPt$ **1**: C, 26.92; H, 2.54; N, 15.70. Found: C, 26.98; H, 2.52; N, 15.36%.

Synthesis of [Pt(L2)Cl](PF$_6$) (2)

The compound was obtained as a yellow solid using the same procedure as for **1** by using HL2(PF_6) (44.2 mg, 0.1 mmol), Ag_2O (11.6 mg, 0.05 mmol) and $Pt(cod)Cl_2$ (37.4 mg, 0.10 mmol). Yield: 60 mg, 75%. Anal. Calc. for $C_{19}H_{18}ClF_6N_4PPt$ **2**: C, 33.66; H, 2.68; N, 8.27. Found: C, 33.72; H, 2.65; N, 7.84%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.99 (d, J = 8.8 Hz, 1H), 8.90 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 4.4 Hz, 1H), 8.46, 7.85 (both d, J = 2.0 Hz, $C_3H_2N_2$, each 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.10 (m, 1H), 4.27 (t, J = 6.8 Hz, –CH_2CH$_2$CH$_2$CH$_3$, 2H), 1.77 (m, –CH$_2$$CH_2CH_2CH_3$, 2H), 1.32 (m, –CH$_2CH_2$$CH_2CH_3$, 2H), 0.91 (t, J = 7.2 Hz, –CH$_2$CH$_2$CH$_2$$CH_3$, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.6 (Pt–C), 149.2, 147.9, 144.1, 142.8, 142.7, 140.8, 131.8, 127.9, 127.8, 127.5, 126.9, 124.1, 120.0, 112.9, 49.8, 32.5, 19.6, 13.8.

Synthesis of [Pt(L3)](PF$_6$)$_2$ (3)

The compound was obtained as a yellow solid using the same procedure as for **1** by using $H_2L3(PF_6)_2$ (186.6 mg, 0.30 mmol), Ag_2O (69.6 mg, 0.30 mmol) and $Pt(cod)Cl_2$ (112.2 mg, 0.30 mmol). Yield: 91 mg, 38%. Anal. Calc. for $C_{21}H_{25}F_{12}N_7OP_2Pt$ (**3**·CH_3CN): C, 28.78; H, 2.87; N, 11.19. Found: C, 28.78; H, 2.87; N, 10.89%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.53 (d, J = 4.4 Hz, C_5H_4N, 2H), 7.82 (t, J = 7.6 Hz, C_5H_4N, 2H), 7.73, 7.41 (both d, J = 1.2 Hz, $C_3H_2N_2$, 2H), 7.37 (t, J = 5.2 Hz, C_5H_4N, 2H), 7.23 (d, J = 7.2 Hz, 2H), 6.40, 6.36 (both d, J = 13.6 Hz, CH_2, each 1H), 5.08, 4.65 (both d, J = 14.4 Hz, CH_2, each 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8 (Pt–C), 154.5, 150.9, 138.6, 124.2, 123.9, 123.8, 123.2, 63.5 (CH_2), 55.1 (CH_2).

Synthesis of [Pt(L4)](PF$_6$)$_2$ (4)

The compound was obtained as a pale yellow solid using the same procedure as for **1** by using $H_2L4(PF_6)_2$ (23.3 mg, 0.05 mmol), Ag_2O (11.6 mg, 0.05 mmol) and $Pt(cod)Cl_2$ (18.7 mg, 0.05 mmol). Yield: 26.4 mg, 68%. Anal. Calc. for $C_{15}H_{14}F_{12}N_8OP_2Pt$ **4**: C, 22.32; H, 1.75; N, 13.88. Found: C, 22.73; H, 1.63; N, 13.57%. ^1H NMR (400 MHz, DMSO-d_6): δ 9.54 (d, J = 5.2 Hz, 4- and 6-$C_4H_3N_2$, 4H), 8.54 (d, J = 2.0 Hz, $C_3H_2N_2$, 2H), 8.26 (d, J = 2.0 Hz, $C_3H_2N_2$, 2H), 8.08 (t, J = 4.8 Hz, 5-$C_4H_3N_2$, 2H), 7.26 (s, CH_2, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.8 (Pt–C), 157.2, 144.7, 124.5, 121.3, 119.2, 66.6 (CH_2).

Synthesis of [Pt(L5)$_2$](PF$_6$)$_2$ (5)

The compound was obtained as a colorless solid using the same procedure as for **1** by using $H_2L5(PF_6)_2$ (118.8 mg, 0.2 mmol), Ag_2O (46.4 mg, 0.2 mmol) and $Pt(cod)Cl_2$ (37.4 mg, 0.1 mmol). Yield: 18.4 mg, 23.0%. Anal. Calc. for $C_{34}H_{34}F_{12}N_{12}O_3P_2Pt$ (**5**·CH_3CN): C, 35.70; H, 3.00; N, 14.70. Found: C, 35.55; H, 2.64; N, 14.36%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.56 (d, J = 3.6 Hz, C_5H_4N, 4H), 8.03 (t, J = 7.2 Hz, C_5H_4N, 4H), 7.85 (d, J = 8.0 Hz, C_5H_4N, 4H), 7.69, 7.60 (both s, $C_3H_2N_2$, each 4H), 7.45 (t, J = 6.0 Hz, 4H), 6.64, 6.48 (both d, J = 13.6 Hz, CH_2, each 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4 (Pt–C), 149.0, 148.9, 138.7, 124.6, 122.8, 121.4, 63.3 (CH_2).

General procedure for the hydrosilylation of terminal alkynes

In a Schlenk tube a solution of **1** (0.01 mmol) in toluene (2.0 mL) was prepared under N_2 atmosphere. Alkyne (1.0 mmol) together with silane (1.2 mmol) was added in quick succession *via* a syringe. The yellow solution was stirred at 100 °C. Samples were taken periodically in intervals for GC analysis. After the reaction was completed, the reaction was stopped and the solvent was removed under vacuum. The obtained residue was purified by flash chromatography to give the desired product and the ratio of products was determined by ^1H NMR spectroscopy.

X-Ray diffraction analysis

Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart-CCD area-detector diffractometer with a Mo-Kα radiation (λ = 0.71073 Å) by using a ω–2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. The data were corrected for Lorentz and polarization effects with SMART

Table 2 Crystallographic data for complexes **1–5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{36}H_{39}Cl_2F_{12}N_{18}P_2Pt_2$	$C_{19}H_{18}ClF_6N_4PPt$	$C_{19}H_{18}F_{12}N_6P_2Pt$	$C_{15}H_{12}F_{12}N_8P_2Pt$	$C_{38}H_{34}F_{12}N_{14}P_2Pt$
M_r	1474.87	677.88	815.42	789.36	1171.82
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	6.9251(8)	13.274(1)	10.543(1)	8.566(1)	8.436(1)
b/Å	21.38(2)	13.558(1)	10.909(1)	9.606(1)	11.517(1)
c/Å	33.695(3)	14.973(1)	12.935(2)	14.532(2)	12. 600(1)
α/°	90	114.853(2)	82.480(2)	78.945(1)	107.890(2)
β/°	90	105.017(1)	72.266(1)	81.359(2)	102.804(1)
γ/°	90	103.731(1)	64.247(1)	74.986(1)	100.030(1)
V/Å^3	4988(5)	2169.5(4)	1276.3(2)	1127.1(2)	1096.5(2)
Z	4	4	2	2	1
D_c/Mg m^{-3}	1.964	2.075	2.122	2.326	1.775
Reflections collected	26228	11278	6662	5859	5772
Reflections independent	8807	7517	4427	3915	3814
R_{int}	0.0689	0.0294	0.0238	0.0437	0.0274
Goodness-of-fit on F^2	1.109	1.012	1.021	1.019	1.048
R ($I > 2\sigma I$)	0.0731, 0.1625	0.0354, 0.0871	0.0374, 0.0940	0.0474, 0.1128	0.0353, 0.0901

suite programs[23] and for absorption effects with SADABS.[24] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTXL package.[25] Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and $U_{iso}(H) = 1.2$ or $1.5 \times U_{eq}(C)$. Further details of the structural analyses are summarized in Table 2.

Acknowledgements

We are grateful to the NSF of China (20872129 and J0830413), the PhD Programs Foundation of Ministry of Education of China (200803350011) and the Chinese Universities Scientific Fund (2009QNA3004) for financial support.

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