

Visible light accelerated hydrosilylation of alkynes using platinum-[acyclic diaminocarbene] photocatalysts

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Platinum-[diaminocarbene] complexes work as transition-metal photocatalysts for the hydrosilylation of alkynes. Catalytic system operates under visible light irradiation (blue LED) enabling the conversion of a range of terminal and internal alkynes to respective vinyl silanes in excellent yields.

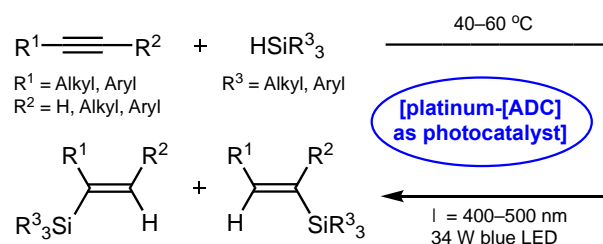
Starting from the pioneering reports on application of metal complexes with acyclic diaminocarbenes (ADCs) in cross-coupling by Fürstner¹ and Slaughter,² over the last decade these species have been widely used in a broad range of catalytic reactions.³ Arguably, major gains have been achieved in the field of cross-coupling, where catalysts on basis of palladium-[ADC]s allowed for high turnover numbers (TONs) to be achieved, frequently under mild and environmentally benign conditions.⁴ Whereas the catalytic properties of Pd- and Au-[ADC]s are well documented, the applications of the complexes derived from other metals, e.g. platinum-[ADC]s is limited to but a few examples.^{3b, 3c} Only recently we reported on the application of Pt-[ADC]s for the catalytic hydrosilylation of terminal^{4c, 5} and internal⁵ alkynes. Hydrosilylation of alkynes is the direct, powerful and atom-economic approach towards the preparation of vinyl silanes, important industrial synthons.⁶ Pt-[ADC]-based systems give reasonable product yields and ensure moderate TONs but operate at high temperature 80–100 °C making these conditions incompatible with thermally unstable substrates. Further improvements through the rational catalyst design are expected to address the issues raised.

In the recent years, visible light-induced reactions have emerged as a powerful tool in organic synthesis.⁷ Three main categories of photocatalytic reactions include (i) conventional photocatalysis based on photosensitisation by a photocatalyst that enables the transformation to proceed via redox-, atom transfer-, or energy transfer pathway,⁷ (ii) cooperative

photocatalysis, which combines photosensitisation by a photocatalyst with subsequent transition metal catalysis,⁸ and less developed (iii) transition-metal photocatalysis, in which a metal catalyst itself serves as both photo-absorbing species and enables catalysis.⁹ While advantages of the latter type catalytic system can be easily recognised, seemingly, the fine tuning of such systems is more difficult compared to that of the cooperative systems, partially due to limited scope of known ancillary ligands and complexes that exhibit light-absorbing properties, and lack of knowledge for the mechanism of their catalytic action. Herein, only a few types of ligands and complexes were attempted for this type of catalysis, including phosphine, amine, or oxime species.^{9a} Noteworthy, only a few metal-catalysed¹⁰ and metal-free¹¹ radical hydrosilylation of alkynes under photocatalytic conditions has been recently reported, and pure organometallic photocatalytic routes without a radical involvement remain scarce.

While being widely used in catalysis, metal-[ADC] species, to the best of our knowledge, have never been studied as transition-metal photocatalysts.^{3a-c} These powerful ligands combine a wide spectrum of donor properties with steric flexibility, important in the fine-tuning of the catalytic properties, and can easily be prepared via several well-established methods, i.e. starting from metal-isocyanides.^{3a}

In the course of our studies, we uncovered that platinum-[ADC] species derived upon the nucleophilic addition of 2-aminopyridine to platinum-bound isocyanides work as catalysts for the hydrosilylation of alkynes under visible light irradiation using blue LED (400–500 nm) source (Scheme 1).



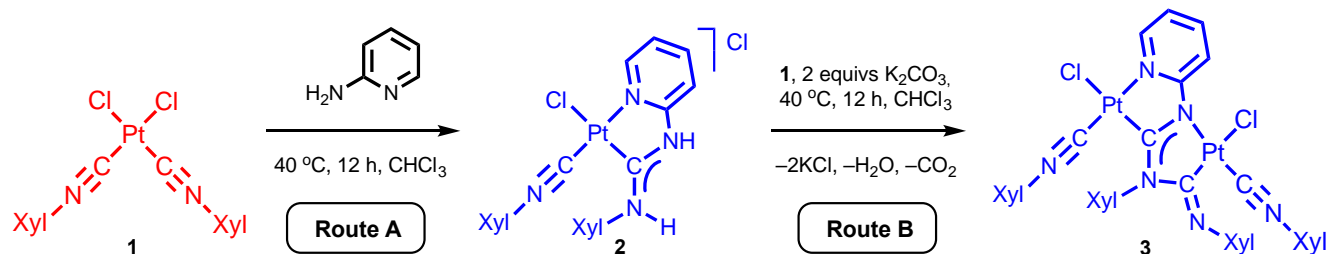
Scheme 1. Visible light accelerated Pt-[ADC]-catalysed hydrosilylation of alkynes.

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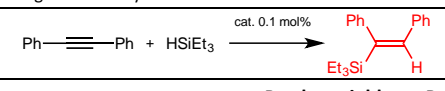


Scheme 2. Generation of platinum-[ADC] complex via the addition of 2-aminopyridine to an isocyanide in *cis*-[PtCl₂(CNXyl)₂] (Route A) and formation of dinuclear platinum-[ADC] complex containing two distinct types of the aminocarbene ligand (Route B).

Representative platinum-[ADC] complexes were prepared via the nucleophilic addition to platinum-isocyanides. Hence, the reaction of 1 equiv of 2-aminopyridine with *cis*-[PtCl₂(CNXyl)₂] (**1**) in CDCl₃ at 40 °C for 12 h gave the corresponding diaminocarbene species [PtCl{C(NHC₅H₄N)-N(H)Xyl}(CNXyl)]Cl (**2**), Scheme 2, route A) in 85% isolated yield. Further reaction of the thus prepared platinum-[ADC] species **2** with an equimolar amount of starting *cis*-[PtCl₂(CNXyl)₂] (**1**) in CDCl₃ at 40 °C for 12 h in the presence of 2 equivs of solid K₂CO₃ led to binuclear complexes containing two distinct types of ADC ligands (**3**), Scheme 2, route B). In this reaction, complex **2** plays a role of a metalla-nucleophile towards the CNR ligand of the second molecule of the starting **1**. Complex **3**, that was isolated in 75% yield, is the structural analogue of the corresponding palladium derivative reported previously by our group.¹² Prepared complexes were characterized using elemental analyses (C, H, N), HR-ESI-MS, FT-IR, ¹H and ¹³C{¹H} NMR spectroscopy, and by a single crystal X-ray diffraction (see Supplementary Information, SI, Figure S1).

To understand whether complexes **2** and **3** absorb light, UV-Vis measurements were undertaken (see SI, Figure S2). Both diaminocarbene species are noticeably yellow, and they absorb light below 450 nm; absorption extends to the UV region down to ca. 350 nm. Complexes **2** and **3** are not fluorescent and/or phosphorescent, and no emission bands were detected. Taking these results into account we looked for a suitable light source and focused our attention on blue LED H150B from Kessil (36 W) that produces an emission spectrum in the 400–500 nm range with two maxima at ca. 420 and 440 nm, that is within the absorption region for **2** and **3**. With complexes **2** and **3** in hand, we probed the hydrosilylation of alkynes under photocatalytic conditions using a model reaction of diphenylacetylene with triethylsilane affording (*E*)-(1,2-diphenylvinyl)triethylsilane (full results are given in Table S4, Table 1 contains an extract of the most important findings). Representative Pt, Pd and Ir complexes containing other types of ligands frequently used in catalysis were also evaluated for comparison (see Table S4).

Table 1. Screening of the catalytic conditions.^a



Entry	Catalyst	Product yield with light ON	Product yield with light OFF
Reactions at 40 °C for 24 h			
1–2	No catalyst added	<5	<5
3–4	<i>cis</i> -[PtCl ₂ (CNXyl) ₂] (1)	8	<5
5–6	Catalyst 2	24	<5
7–8	Catalyst 3	32	<5
9–10	Catalyst 2	14 ^b	<5
11–12	Catalyst 3	16 ^b	<5
Reactions at 60 °C for 12 h			
13–14	No catalyst added	<5	<5
15–16	<i>cis</i> -[PtCl ₂ (CNXyl) ₂] (1)	12	<5
17–18	Catalyst 2	78	8
19–20	Catalyst 3	87	12
21–22	Catalyst 2	14 ^b	8
23–24	Catalyst 3	16 ^b	12
25–26	Catalyst 3 ^c	89	14

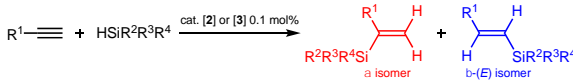
PhC≡CPh (5.0×10⁻⁴ mol), Et₃SiH (5.0×10⁻⁴ mol), selected catalyst (5.0×10⁻⁷ mol, 0.1 mol%); toluene (2.0 mL); 34 W Kessil H150B blue LED used for experiments under visible light irradiation. ^aYields of the product were determined with the help of ¹H NMR spectroscopy. ^bIrradiation with light for 1 h only, then the reaction proceeded in the darkness. ^cCatalyst loading 1 mol%, time 4 h.

Without catalyst added, no reaction was observed in the 20–80 °C range with or without visible light irradiation (Table 1, entries 1, 2, 13, and 14) indicating that irradiation itself is not sufficient to initiate this process. Furthermore, at 20 °C no catalytic effect of any metal complexes studied was observed even after 48 h with or without light. At 40 °C, both **2** and **3** showed some moderate activity (24 and 32% product yields, correspondingly, entries 5 and 7) upon visible light irradiation. All other complexes studied showed very low activity (for *cis*-[PtCl₂(CNXyl)₂] and [Ir(ppy)₂(μ-Cl)]₂), or no activity (complexes *cis/trans*-[PtCl₂(NCEt)₂], *cis*-[PdCl₂(NCMe)₂], *cis*-[PdCl₂(CNXyl)₂] and [IrHCl₂(PPh₃)₃]) (see Table S4 in SI). Raising the temperature

to 60 °C, increased the product yield upon visible light irradiation to 87% with catalyst [3] (entry 19) closely followed by the catalyst [2] (78%, entry 17). Overall, nearly an order of magnitude rate acceleration is observed for the process under visible light irradiation versus similar one without light (e.g. entries 18 and 20). At 60 °C, application of 1 mol% of catalyst shortens reaction time to 4 h (entry 25), suggesting that system with higher catalyst loading can be used if shorter reaction time is preferred over greater TON. Further increase of temperature to 80 °C attenuates the effect of light on the course of reaction resulting in similar yields of silylated products with and without light (88/74% for catalyst [3] and 79/68% for catalyst [2]).

Interesting results were obtained when catalytic systems with [2] or [3] were irradiated with light for 1 h only and then the reaction was allowed to proceed in the dark (entries 21 and 23 for [2] and [3], correspondingly). In this case, lower yields of products were achieved, consistent with the results for the same reaction to run for 1 h only. This is indicative that the irradiation with light is crucial throughout the entire reaction course and excludes the possibility for the light to be solely responsible for the initial generation of the catalytically active species as known for the UV-light-induced hydrosilylations.^{6a, 13}

Table 2. Hydrosilylation of the terminal alkynes [yields and isomeric content (α/β ratio)].^a



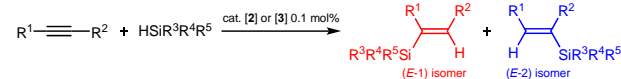
Entry	Substrates	PhC≡CH	4-(<i>t</i> -Bu)-C ₆ H ₄ C≡CH	<i>t</i> -Bu-C≡CH
1–3	Et ₃ SiH	86 (19/81) cat. [3]	85 (19/81) cat. [2]	61 (7/93) cat. [2]
4–6	Pr ₃ SiH	87 (65/35) cat. [3]	82 (63/37) cat. [3]	63 (7/93) cat. [3]
7–9	<i>i</i> -Pr ₃ SiH	73 (75/25) cat. [3]	83 (81/19) cat. [3]	58 (7/93) cat. [3]
10–12	PhMe ₂ SiH	94 (29/71) cat. [3]	92 (25/75) cat. [3]	59 (7/93) cat. [3]

Alkyne (5.0×10⁻⁴ mol), silane (5.0×10⁻⁴ mol), selected catalyst (5.0×10⁻⁷ mol); toluene (2.0 mL), reaction temperature: 60 °C, 12 h. ^aProduct yields and isomeric ratio were determined by ¹H NMR (see SI).

To further assess the effect of light on the course of the hydrosilylation using catalysts [2] and [3], all subsequent experiments were performed at 40–60 °C, where visible light irradiation showed a pronounced effect. A scope of the catalytic system included both terminal and internal alkynes (Tables 2 and 3) that reacted with a range of hydrosilanes. Hence, 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 became subject to hydrosilylation, giving corresponding vinyl silane products as a mixture of α/β -*E*-products with yields up to 94%. Moderate product yields were achieved for *t*-BuC≡CH presumably due to lower reactivity of this aliphatic terminal alkyne. Generally, yields with binuclear catalyst [3] were marginally better when compared to the yields achieved with mononuclear ADC species [2]. Similar satisfactory results were observed for the hydrosilylation of internal alkynes. Herein,

symmetric disubstituted acetylenes (Table 3, entries 1–4) reacted with silanes with a high degree of stereoselectivity to afford target *E*-silylated alkenes in 86–92% yields after 4 h at 60 °C. For asymmetrically disubstituted alkyne (entries 5 and 6) an expected mixture of *E*-silylated alkenes was obtained. In all examples reported herein, the amount of corresponding *Z*-silylated products formed were below 1%. All the product yields in Tables 2 and 3 correspond to the full conversion of the starting materials.

Table 3. Hydrosilylation of the internal alkynes.^a



Entry	Alkyne	Silane	Yield, % and isomeric ratio
1	PhC≡CPh	Et ₃ SiH	87 cat. [3]
2	PhC≡CPh	PhMe ₂ SiH	84 cat. [2]
3	Me(CH ₂) ₂ C≡C(CH ₂) ₂ Me	Et ₃ SiH	82 cat. [3]
4	Me(CH ₂) ₂ C≡C(CH ₂) ₂ Me	PhMe ₂ SiH	85 cat. [3]
5	PhC≡CMe	Et ₃ SiH	96 (84/16) cat. [2]
6	PhC≡CMe	PhMe ₂ SiH	80 (71/29) cat. [2]

Alkyne (5.0×10⁻⁴ mol), silane (5.0×10⁻⁴ mol), selected catalyst (5.0×10⁻⁷ mol); toluene (2.0 mL), reaction temperature: 60 °C, 12 h. ^aProduct yields were determined by ¹H NMR (see SI).

At the next step, we attempted to shed some light on the mechanism of the photocatalytic action of [2] and [3] (see SI for more details). Firstly, irradiation experiments over shorter period of time (1 h, entries 21 and 23) suggest that the effect of visible light is critical throughout the entire reaction course. Mercury drop test¹⁴ and a linear initial kinetics without induction period suggest that a molecular catalytic cycle under homogeneous conditions should be expected.¹⁵ Secondly, throughout the catalytic run, we detected the presence of free xylil isocyanide in the catalytic mixture using mass-spectrometry and IR spectroscopy. It is consistent with the dissociation of the isocyanide ligand from [2] or [3] generating an additional vacancy at metal centre. Only traces of isocyanide were detected in the reaction without light. Noteworthy, UV-light-induced dissociation of the isocyanides from the metal centre were previously observed by Jones and co-workers.¹⁶

Using mass-spectrometry approach, plausible products of the oxidative addition of silane to the activated metal core containing one bidentate carbene ligand, and one after the migratory insertion of alkyne, were detected. In both intermediates, platinum centre has an oxidation state +2, that is consistent with the initial loss of the isocyanide and chloride ligands from the starting pre-catalysts and the reduction of the metal centre to platinum(0) by a sacrificial amount of silane substrate. At this point, we believe that light accelerates the dissociation of the isocyanide species from [2] and [3] making it more prone to the subsequent reduction. Estimated quantum yield for our photocatalytic process ($\Phi_{\text{apparent}} \approx 0.2$, see SI for more details) disfavors the possibility of an ATRA-type¹⁷ (Atom Transfer Radical Addition) process.

Taking these experiments into account, we hypothesised the photocatalytic cycle with catalyst [2] (see Figure S4) on basis

of Chalk-Harrod mechanism that includes the oxidative addition of silane, π -coordination of alkyne, its 1,2-migratory insertion and the reductive elimination of the silylated product.¹⁸ In our hypothesis, irradiation with the visible light is essential at two steps of this cycle. First, it facilitates the removal of the isocyanide ligand followed by the reduction of metal core by a sacrificial amount of silane. Oxidative addition of silane leads to the coordinatively saturated species, whose subsequent transformation requires one additional vacancy at metal core to become available for the alkyne binding. Herein, we believe that a reversible visible-light-mediated dissociation of the pyridyl moiety of the bidentate aminocarbene ligand generate a vacancy at the metal core in a similar way as reported previously by Turro and co-workers¹⁹ for ruthenium-pyridine complexes. Since the visible-light-mediated dissociation of the pyridyl-ligand can be reversed, continuous irradiation with light is essential to govern this process. Similar pathways can be drawn for [3], however, further mechanistic studies are required before more definitive conclusions could be withdrawn for mechanism of photocatalytic action of [2] and, in particular for [3], where additional influence of the secondary metal centre should be carefully considered.

As a summary, we have demonstrated for the first time that complexes with acyclic diaminocarbene ligands work as photocatalysts for the hydrosilylation of terminal and internal alkynes. Good to excellent yields of products were obtained for a number of terminal and internal alkynes under visible light irradiation. Although the exact mechanism of the photocatalytic action for platinum-ADCs is not fully understood at this point, our findings clearly attest to the potential of the ADC ligands in photocatalysis. Future studies aimed at understanding the mechanism of the photocatalytic action of the metal-[ADC]s and widening the scope of their catalytic applications are currently being expanded within our group.

Acknowledgements

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