# Solvent-Reversible Addition of Alkyne C−H Bonds to Water-Soluble NHC Platinum(0) Complexes

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**S** *Supporting Information*
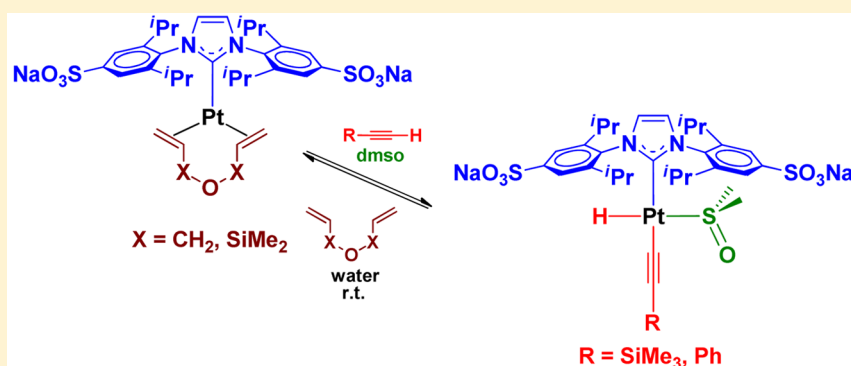
**ABSTRACT:** Oxidative addition of $CH_3I$ and alkynes to the platinum(0) complex [Pt(AE)NHC] (**1**), in which the NHC ligand is a sulfonated version of the IPr ligand (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and AE is diallyl ether, is reported. Reaction with the haloalkane affords the iodomethyl complex [PtI(Me)NHC] (**2**), whereas the addition of alkynes via C(sp)−H bond activation leads to the corresponding new water-soluble hydride (NHC)Pt$^{II}$ complexes **3** and **4**. Complexes **3** and **4** were found to be moderately stable in water, displaying an interesting behavior in this solvent. Thus, in the presence of the corresponding olefin, the reaction can be reversible under mild conditions, thus allowing the formation of diolefinic (NHC)Pt$^{0}$ complexes **1**, **5**, and **6**, with elimination of the alkyne.

The generation of reactive electron-rich (NHC)Pt$^{0}$ fragments (NHC = N-heterocyclic carbene) is of enormous interest for applications in C−H bond activation.[1] Indeed, C−H activation in alkynes has attracted a great deal of attention, mainly due to the implication of such processes in the alkyne/vinylidene tautomerization reaction, as well as in some catalytic processes involving platinum complexes.[2−4] In the present work, we report the activation of C−H bonds in alkynes by (NHC)Pt$^{0}$ fragments and, more importantly, we show that this activation can be reversible, which could be attractive for catalytic purposes. Pt(0) bisphosphine fragments are known for their potential to activate unreactive bonds by oxidative addition.[1b] Whitesides and co-workers, for instance, disclosed that transient (bisphosphine)Pt$^{0}$ species, prepared by thermolysis of a [L₂Pt(H)(alkyl)] complex, were able to activate C(sp)−, C(sp²)− and C(sp³)−H bonds.[5] For terminal alkynes, the coordination and the oxidative addition competed, giving a mixture of the ($\eta^2$-alkyne)Pt$^{0}$ and the hydrido(alkynyl)Pt$^{II}$ products that did not show interconversion upon continued heating. Reversible C−H activation of aromatic compounds has also been observed for these (bisphosphine)Pt$^{0}$ fragments.[5a,6] Although NHCs have proven to be an outstanding class of

ancillary ligands,[7] the application of (NHC)Pt$^{0}$ complexes in the cleavage of C−H bonds has remained relatively unexplored, as has been reverse reactions involving C−H reductive elimination from Pt(II). Nevertheless, Pt(0) complexes have been found to activate the C−H bonds of imidazolium rings to yield (NHC)Pt$^{II}$ hydride compounds.[8] A related example is the synthesis, by Markó and co-workers, of unique Y-shaped Pt(II) bis(silyl) species through oxidative addition of Me₂PhSiH to [Pt$^{0}$IPr($\eta^2,\eta^2$-diene)] (IPr = bis(2,6-diisopropylphenyl)-imidazo-2-ylidene).[9] During our studies on the aqueous-phase reactivity of water-soluble NHC complexes,[10] we observed the formation of metal nanoparticles stabilized by the coordination of NHC ligands to their surface when aqueous solutions of NHC dimethyl Pt(II) complexes were thermolyzed.[10d] These nanoparticles were formed via reductive C−C coupling, which likely resulted in the transient formation of (NHC)Pt$^{0}$ fragments. Here, we report the oxidative addition of terminal alkynes to complex **1**[10e] (Scheme 1), which leads to the formation of novel water-soluble hydride (NHC)Pt$^{II}$ complexes

**Scheme 1. Synthesis of 2 by Oxidative Addition of MeI**



**Scheme 2. Reversible Addition of Alkynes to 1**
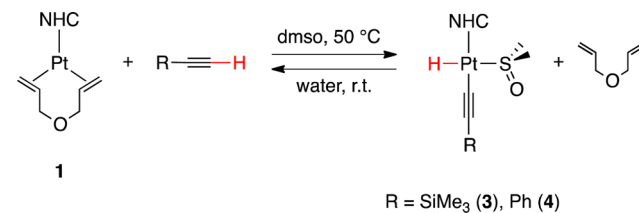


R = SiMe$_3$ (**3**), Ph (**4**)
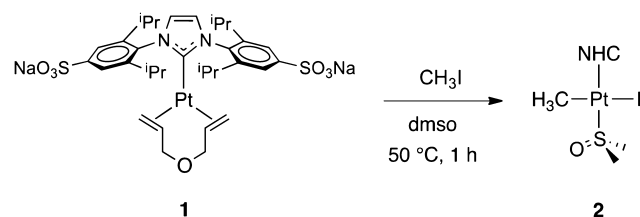
via the activation of C(sp)−H bonds. The reversibility of this reaction (i.e., reductive elimination) in water in the presence of different olefins, to afford either [Pt$^0$(NHC)($\eta^2$-olefin)$_2$] or [Pt$^0$(NHC)($\eta^2$:$\eta^2$-diolefin)] complexes, is also reported.

We initially tested the propensity of complex **1** to undergo oxidative addition of CH$_3$I. The reaction was complete after 1 h at 50 °C in dmso, according to the $^1$H NMR spectra (Scheme 1). The haloalkyl complex **2** was obtained in high yield (90%) as a yellow, analytically pure solid after a simple workup. Compound **2** is stable in water, and its characterization was indicative of a stereoselective oxidative addition in **1**, leading solely to the SP-4-4 diastereoisomer of **2**. Related monomethyl chlorido complexes with less sterically hindered NHC ligands were obtained by protonolysis of dimethyl mono-(NHC)Pt$^{II}$ complexes with HCl$_{aq}$, which afforded a mixture of two diastereoisomers.[10c]

Complex **2** was characterized by NMR spectroscopy, mass spectrometry (ESI-TOF), and elemental analysis. The last finding suggested the presence of water molecules in the samples, as also observed in the $^1$H NMR spectra obtained upon dissolving **2** in dry dmso-$d_6$. It should be noted that this class of compounds is hygroscopic in the solid state and quickly takes up water from the air.[10] The coordination of dmso to platinum was confirmed by the observation of a $^1$H resonance at 3.10 ppm in D$_2$O, while a singlet with platinum satellites was observed for the methyl group at 0.25 ppm ($^3J_{Pt-H}$ = 75 Hz). The platinum satellites of the $^{13}$C carbene resonance at 162.2 ppm were not detected, probably due to their broadening in solvents of relatively high viscosity.[11] The chemical shift for the carbene carbon and the $^3J_{Pt-H}$ value mentioned above for the methyl ligand are comparable to those found for other (SP-4-4)-[PtCl(L)Me(NHC)] complexes (162−163 ppm and 78−88 Hz, respectively).[10c] The stereochemistry in complex **2** was corroborated by a NOESY experiment, which revealed proximity between the N-aryl substituents of the carbene and the methyl ligand.

The addition of terminal alkynes was subsequently tested. Treatment of **1** with an excess of trimethylsilyl- or phenyl-acetylene in dmso-$d_6$ at 50 °C afforded the corresponding hydride alkynyl complexes **3** and **4** after, respectively, 6 and 3 h of reaction ($^1$H NMR monitoring on an NMR tube). The reaction was stereoselective, leading to the cis addition products in both cases. These complexes were obtained on a preparative scale and isolated in high yields (>90%) as spectroscopically pure yellow solids (Scheme 2). To the best of our knowledge, water-soluble hydride complexes of Pt(II) stabilized with NHC ligands have not been reported to date.

Hydrides **3** and **4** were stable in dmso-$d_6$, where no changes were perceived after 10 days at 50 °C. In D$_2$O solution, however, the hydride resonance at ca. −12 ppm disappeared completely after 10 days at room temperature. Among the complex mixture of products produced in this decomposition, the presence of free alkyne was detected by $^1$H NMR

spectroscopy after extraction with CDCl$_3$. The absence of deuteration, corroborated by $^2$H NMR spectroscopy, ruled out formation of the alkyne by solvolysis of the metal−alkynyl bond. Supposing that the hydride alkynyl complexes were undergoing reductive elimination of alkyne, freshly prepared aqueous solutions of **3** and **4** were treated with diallyl ether. Under these conditions, reductive elimination took place rapidly and complex **1** was quantitatively recovered after 3 h of reaction at room temperature.

The above results suggested an interesting influence of the solvent on the forward or reverse direction of the addition reaction. Thus, whereas **1** undergoes oxidative addition of terminal alkynes in dmso, water seems to favor the reverse reaction. The synthesis of other olefinic Pt(0) NHC complexes in water was also possible using this procedure (Scheme 3). For

**Scheme 3. Synthesis of NHC Pt(0) Complexes by Reductive Elimination of Alkyne in Water**
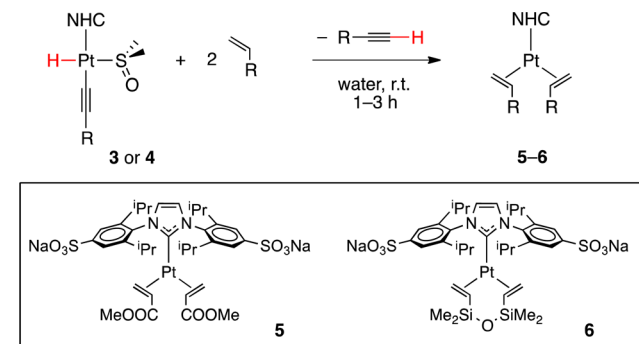


example, treatment of complex **3** (or **4**) with methyl acrylate or divinyltetramethyldisiloxane (dvtms) in water afforded complexes **5** and **6** in high yields (≥95%) after 1 and 3 h of reaction, respectively. The longer reaction time required for **6** is likely a consequence of the lower solubility of dvtms in water.

The new complexes **3**−**5** were characterized by NMR and IR spectroscopy and mass spectrometry. Complex **6** was identified on the basis of previously reported NMR data.[10a] In the case of **3** and **4**, the infrared absorptions for the C≡C and Pt−H groups were found at normal wavenumbers for terminal−alkynyl and hydrido ligands in platinum complexes (2037 and 2135 cm$^{-1}$ for **3** and 2105 and 2145 cm$^{-1}$ for **4**, respectively; reported values in the ranges $\nu_{C≡C}$ 2000−2100, and $\nu_{Pt-H}$ 2040−2240 cm$^{-1}$).[2a,12] The carbenic carbon was observed at around 175 ppm, whereas the hydride ligand appeared at −12 ppm ($^1J_{Pt-H}$ ≈ 1400 Hz). The cis positioning of the hydride and the NHC ligands was supported by the observation of transfer NOE between the hydride ligand and the isopropyl (methyl and methine) protons in NOESY experiments carried out in dmso-$d_6$. Ion peaks corresponding to H$^+$ addition to, or Na$^+$ subtraction from, the neutral formula were observed in the ESI-TOF mass spectra of all the complexes, accompanied by

loss of dmso for **4**. The $^1$H and $^{13}$C NMR spectra for **5** revealed the presence of *rac* and *meso* diastereoisomers ($^{13}$C carbene resonances at 173 and 172 ppm, respectively), as a consequence of the coordination of methyl acrylate to the metal via the *re* or *si* enantioface (Chart 1).[13] As expected, the

**Chart 1. *rac* and *meso* Isomers of Complex 5**



*rac*-**5** (*si/si* enantiomer), $C_2$
major (70%)

*meso*-**5**, $C_s$
minor (30%)
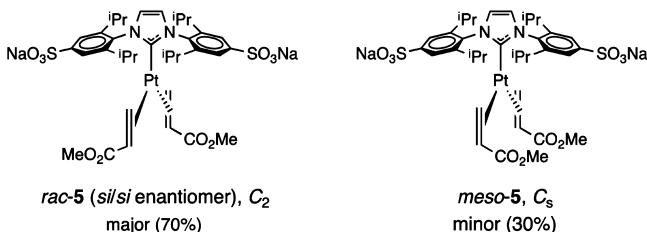
major compound was the less sterically hindered *rac* isomer (70%). Due to the hindered rotation around the NHC–aryl bond, the two moieties of each aryl group are nonequivalent in the *rac* isomer, while the fast rotation of the NHC ligand around the Pt–C bond makes both moieties equivalent in the *meso* isomer (Figure S8 in the Supporting Information).

In conclusion, studies of the reactivity of the NHC Pt(0) complex **1** illustrate two important reactions in organometallic chemistry, namely oxidative addition and reductive elimination, which can be carried out under mild conditions. The transformations reported here disclose a sharp solvent effect, with the oxidative addition of alkynes to **1** to yield hydrido(alkynyl)platinum(II) complexes seemingly favored in dmso, whereas the reverse reaction (i.e., reductive elimination) takes place in water, yielding (diolefin)platinum(0) with liberation of the alkyne. We consider this finding relevant not only for synthetic purposes aimed at the preparation of (NHC)Pt$^0$ complexes in water but also, and for example, for the grafting of (NHC)Pt complexes to metallic surfaces modified with olefin groups by simple addition of hydrido-(alkynyl)platinum(II) NHC complexes in water, such as in related approaches reported for gold.[14] Moreover, the results here obtained could shed some light on the hydrosilylation reactions of alkynes described by the group of Markó[3] or on the selective dimerization of terminal alkynes recently reported by Pietraszuk[4] in which transient hydrido(alkynyl)platinum(II) species might be involved. Further efforts to study the chemical behavior and possible applications of these water-soluble hydride(N-heterocyclic carbene)platinum(II) complexes are currently underway in our laboratories.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00207.

General and synthetic procedures, characterization data, and NMR spectra of complexes **2**−**6** (PDF)

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**Notes**

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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