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N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations ($XH^+$, X = S, Se, Te)

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COMMUNICATION

# Triaza-adamantyl *N*-heterocyclic carbenes (NHC-TA): water-soluble ligands and silver complexes

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**We report high-yielding preparations of two water-soluble NHC pre-ligands bearing triazaadamantyl (TA) neutral hydrophilic groups. The NHC-TA derivatives have been utilized in the synthesis of [AgCl(NHC-TA)] complexes, which characterization has included $^{109}$Ag resonance determinations. The hydrolytic stability of the silver complexes has been found to depend on the NHC-TA ligand.**

The remarkable progress brought by N-heterocyclic carbene (NHC) ligands has established them among the most versatile ligands in organometallic chemistry, comparable to phosphines or cyclopentadienyls.[1] Their stability and strong metal–NHC bonds have enabled the design of robust complexes that are useful in catalysis for key reactions such as C–H activation, cross-coupling, and olefin metathesis.[2]

The binding features of NHC ligands[3] have also promoted research in organometallic chemistry using water as a solvent.[4] Once thought unsuitable, water is now recognized as a green medium offering advantages like enhanced reactivity, selectivity, and milder conditions,[5,6] thanks to pioneering studies by Breslow,[7] Joó,[8] and Kuntz.[9]

A large number of hydrophilic ligands have been developed for the preparation of water-soluble metal complexes.[4,10] One of the most popular water-soluble phosphines is **PTA** (1,3,5-triaza-7-phosphaadamantane, Figure 1a,), which was first synthesized and used as a ligand in metal chemistry by Daigle et al.,[11] and much later applied in metal catalysis in water,[12] then triggering the attention and research efforts on hydrophilic complexes with this cage adamantane-like phosphine.[5,13]

Phosphines have secularly been used as references to compare the behavior of NHC ligands.[1] The first stable crystalline carbene isolated by Arduengo in 1991 was 1,3-bis(adamantyl)-imidazol-2-ylidene (**IAd**, Figure 1b), another cage adamantane-like derivative.[14] Given the aforementioned extensive development of the field of NHCs that followed this finding, and that of the **PTA** chemistry also initiated in the early 90's, it is striking that no precedent has yet been described for an NHC ligand, or derived metal complex, containing triazaadamantyl substituents in its structure. Here we introduce silver complexes containing *N*-heterocyclic carbene ligands *N*-substituted with 1,3,5-triaza-7-adamantyl groups (**NHC-TA**, Figure 1c).

Our assumptions at the outset of this work were the usefulness of NHCs as ligands for use in aqueous media due to the robustness of the M-NHC bond against oxidation and hydrolysis, together with their well-known easy tunability of properties through tailored and versatile functionalization, combined with the fact that the hydrophilicity of azaadamantanes, such as **PTA** and its derivatives, arises from good hydrogen acceptor capabilities of the tertiary nitrogen groups of the cage framework.[15] Thus, after having identified a convenient synthetic procedure to access to 1,3,5-triazaadamantan-7-amine **TA-NH$_2$** (see Supplementary Information), we set out the synthesis of NHC precursors *N*-substituted with triaazaadamantyl groups, starting with **ITA**·HCl (Scheme 1a), analogous to the precursor of Arduengo's carbene (Figure 1b).

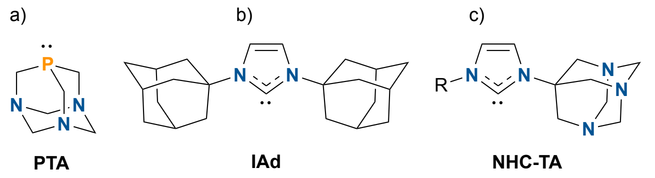

**Fig. 1** a) Water-soluble phosphine; b) First isolated NHC; c) NHCs target of this work.

Various approaches have been described for the synthesis of sterically encumbered N,N-disubstituted imidazolium salts.[16] We have tested one-pot routes involving the sequential addition of paraformaldehyde, amine **TA-NH$_2$**, and glyoxal in the presence of hydrochloric acid,[17] and cyclization pathways of the preformed 1,4-diazadiene (*i.e.*, di-(1,3,5-triazaadamantan-7-

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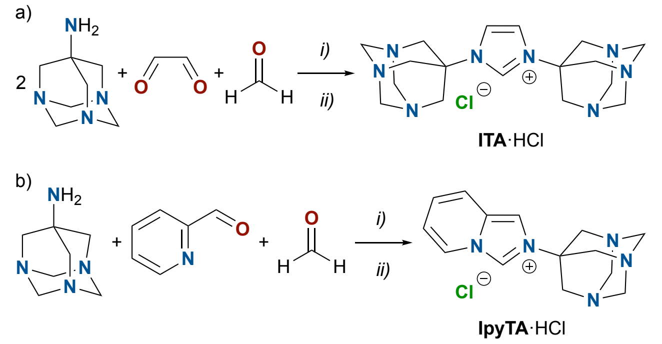
yl)ethane-1,2-diimine)[18] using different C1 building blocks for the ring closing and sources of the chloride counter anion, such as paraformaldehyde/HCl,[19] or chloromethyl alkyl ethers,[19c,20] or the paraformaldehyde/$Me_3SiCl$ couple as in the expedient syntheses developed by Hintermann.[21] All attempts afforded complex mixtures of addition compounds or no reaction at all. Instead, we have managed the synthesis of **ITA**·HCl by adapting the multicomponent and straightforward synthesis reported by Baslé and Mauduit (Scheme 1a).[22] The one-pot procedure is described to be efficient for chiral non-symmetrical N,N'-substitution pattern of NHCs tethering a carboxylic or cycloalkyl functions, which are otherwise inaccessible, and that we have also previously used diversifying the NHC precursors available of this type.[23] Gratifyingly, we found this strategy to be successful also for the symmetrically substituted **ITA**·HCl in preparations up to multigram scale (6.1 g) in virtually quantitative yields.

Another structure substituted with the triazaadamantyl motif of our interest is based on an imidazo[1,5-a]pyridine skeleton (Scheme 1b). Imidazo[1,5-a]pyridinylidenes were introduced in organometallic chemistry by the groups of Glorius and Lassaletta in 2005 as versatile and stable NHC ligands.[24] Thanks to their π-extended robust bicyclic framework, they rank among the strongest heteroatomic $\sigma$-donor,[25] and can also provide singular environments (*e.g.*, L-shaped or axially chiral NHC ligands) in the close proximity of the metal center by readily substitution at C5 position of the pyridinyl ring.[26]

As for **ITA**·HCl, various methods and conditions were attempted to synthesize **IpyTA**·HCl (*e.g.*, picolinaldehyde, **TA-NH₂**, formalin and HCl in EtOH;[27] pyridylimine py-2-CH=N-TA,[28] paraformaldehyde and $SiMe_3Cl$ in toluene or ethyl acetate;[21] or py-2-CH=N-TA and $K_2CO_3$ in chloromethyl methyl ether).[29] However, in our hands the only effective method for the synthesis of the pyridinium salt **IpyTA**·HCl is an adaptation of that described by Hutt et al. (Scheme 1b),[30] consisting in the nucleophilic attack of the amine on the formyl group, followed by the cyclization with formalin, in the presence of HCl, again in a one-pot procedure assessed up to grams scale (7.6 g) in quantitative yield.



**Scheme 1** a) *i)* AcOH, 60 ºC, 15 min, *ii)* HCl, r.t., 5 min; b) *i)* $H_2O$, HCl, r.t., o.n., *ii)* $CH_2Cl_2$/MeOH (20:1), $NaHCO_3$.

Cyclization to form both heterocycles is verified by their NMR spectra (see Supplementary Information). Thus, the protons of the imidazolic moieties are observed downfield (8-10 ppm) as a triplet and a doublet (1:2) for **ITA**·HCl, and as two doublets (1:1) for **IpyTA**·HCl, due to $^4J_{H-H}$ coupling (1.8-1.6 Hz) within the synthesized five-membered rings. In addition, the carbon in the carbenic position resonates at 133 or 125 ppm, respectively, which are similar to the chemical shifts observed for the corresponding non-azo adamantly-substituted analogues.[17b,30] Two $^{15}N$ resonance frequencies for **ITA·**HCl (197 (Imz) and 47 (TA) ppm) and three for **IpyTA**·HCl (205 (Imz), 193 (py) and 48 (TA) ppm), are found by $^1H,^{15}N$-HMBC correlations.

The molecular structure of **ITA**·HCl was determined using X-ray diffraction methods carried out with single crystals obtained from aqueous solutions. As shown in Figure 2, the desired structure is confirmed. The presence of crystallization water molecules interacting with an adamantyl nitrogen atom and the chloride ion via hydrogen bonds is also observed. The cation is $C_{2v}$ symmetric, with an N1-C2-N1a angle (108.4(2)°) within the range found for other imidazolium rings (108–110°), and with C2-N bond lengths (1.383(2) Å) also normal considering the multiplicity of these bonds.[14] All triazaadamantyl group atoms adopt the expected tetrahedral arrangement.

Both azolium salts are highly soluble in water, with solubilities of 150 and 144 g/100mL (4.0 and 4.9 mol/L) at r.t. for **ITA**·HCl and **IpyTA**·HCl, respectively, which exceed that of **PTA** (24 g/100mL or 1.5 mol/L),[12] or that of **IAd**·HCl (1.25 g/100mL or 0.03 mol/L). The five-membered ring in **IpyTA**·HCl undergoes H/D-exchange in $D_2O$ (completed in a couple of days, but immediate for the proton on the carbenic position), in a process that is fully reversible by simply replacing $D_2O$ for $H_2O$. Interestingly, although both salts are sparingly soluble in $CH_2Cl_2$ or in MeOH, a cooperative effect has been noticed with these solvents, observing that suspensions of any of these salts in $CH_2Cl_2$ rapidly turn to solutions by the addition of just a few dops of MeOH (20:≤$1_{v/v}$). This mixture of solvents has precisely enabled the synthesis of the silver NHC complexes.

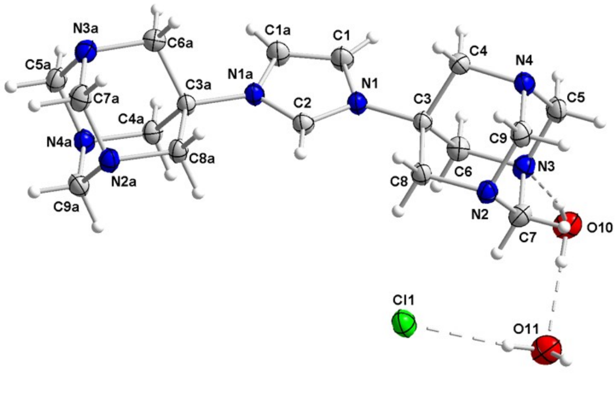


**Fig. 2** Molecular structure of **ITA**·HCl showing two of the crystallization water molecules. Thermal ellipsoids depicted at 50% probability. Selected bond lengths (Å) and angles (º): N1-C1 1.383(2), N1-C2 1.334(2), N1-C3 1.474(2), C1–C1a 1.346(3), C3 – C4 1.539(2), C3–C8 1.531(2), N2–C7 1.474(2), N3–C6 1.478(2), N1-C2-N1a 108.4(2), C1a–C1–N1 107.2(1), C2–N1–C1 108.6(1), C1–N1–C3 125.0(1), C2–N1–C3 126.4(1), N1–C3–C4 110.0(1), C8–C3–C4 108.9(1), N2–C8–C3 109.3(1), C5– N3–C6 108.7(1), C7–N2–C9 108.1(1).

Silver(I)-NHC complexes are appealing due to their structural plasticity, the key role they play as carbene transfer agents to other metals, and important applications in

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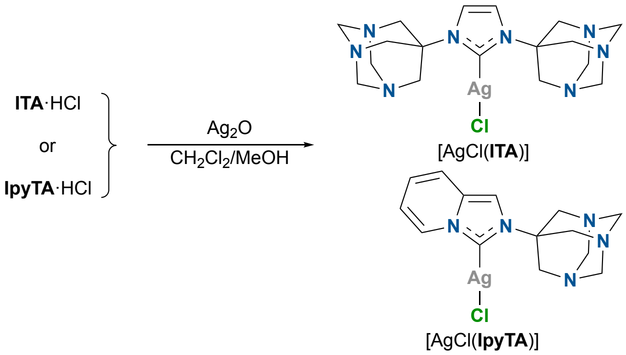
biomedicine and in catalysis.[31] The direct deprotonation of imidazolium salts using silver bases, such as Ag(OAc), $Ag_2O$, or $Ag_2CO_3$, has been reported by Bertrand, Lin, and Danopoulos groups, respectively, as straightforward synthetic protocols that circumvent the often difficult generation and handling of free carbenes.[32] A wide range of solvents have been used in the silver oxide pathway,[31a,b] including alcohols. Therefore, we utilized the $Ag_2O$ route with the triazaadamantyl azolium salts in $CH_2Cl_2$/MeOH mixtures (Scheme 2).



**Scheme 2** Synthesis of [AgCl(**NHC-TA**)] complexes.

The procedure allows the isolation of the two silver complexes in a moderate yield (≥65%, see Supplementary Information). The synthesis of [AgCl(**ITA**)] requires the presence of molecular sieves (4 Å) to ensure the complete consumption of the initial **ITA**·HCl. The same occurs when using Ag(OAc) as the silver source. In this case, an excess of a strong base ($K_2CO_3$, 3 equiv) is also needed to obtain comparable results. On the contrary, no drying material is required when preparing [AgCl(**IpyTA**)] with $Ag_2O$.

The deprotonation of the preligands leading to the silver complexes results in the absence of proton resonances assignable to carbene positions (9-10 ppm) and $^4J_{H\text{-}H}$ coupling in the remaining protons of the imidazolic rings in their NMR spectra. The coordination of the ligands to the silver centers is supported by the $^{13}C$-chemical shifts found for the carbene carbons (singlets at 175 and 168 ppm, for [AgCl(**ITA**)] and [AgCl(**IpyTA**)], respectively). These values are in good agreement with those reported for [AgCl(**IAd**)] (174 ppm)[33] and related [AgCl(imidazo-pyridinylidene)] complexes (168-172 ppm).[26] The $^{15}N$ chemical shifts for [AgCl(**IpyTA**)] (217 (Imz), 209 (py) and 48 (TA) ppm), could also be determined by $^1H,^{15}N$-HMBC.

The existence of dynamic processes involving heteroleptic and homoleptic silver species in equilibrium (*i.e.*, [AgCl(NHC)] ⇋ $[Ag(NHC)_2]^+AgCl_2^-$) has been evidenced for a number of complexes of this type.[31-34] The observation of the carbene carbon peaks as singlets indicates a fast exchange of ligands between metal centers on the NMR time scale, thereby precluding the $^1J_{C\text{-}Ag}$ couplings with $^{107}Ag$ (52% abundance) and $^{109}Ag$ (48%), both spin ½ nuclei. However, the $^{109}Ag$ resonance for [AgCl(**ITA**)] could be determined by $^1H,^{109}Ag$-HMBC experiments by slowing down that exchange. In studies with [AgCl(**IMes**)], John *et al.* have shown that this indirect detection relies on the coupling with the imidazolic protons ($^4J_{H\text{-}Ag} \simeq 2$ Hz), only observable at temperatures low enough to slow down the dynamic process.[35] We have observed the $^4J_{H\text{-}Ag}$ coupling at –40 ºC for [AgCl(**ITA**)] in $CDCl_3$ (averaging 2.2 Hz with both silver isotopes), and the correlating $^{109}Ag$-chemical shift at 679 ppm (Figure 3). We have repeated the experiment with [AgCl(**IAd**)], whose heteroleptic structure in the solid state is known,[33] finding the $^{109}Ag$ resonance at 669.4 ppm in $CDCl_3$ and at –40°C, a value that is close to that found for [AgCl(**ITA**)].

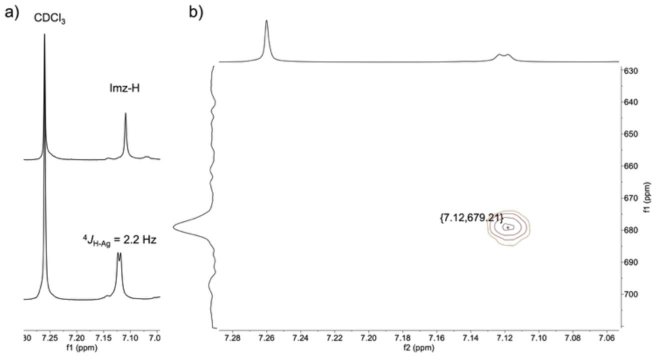
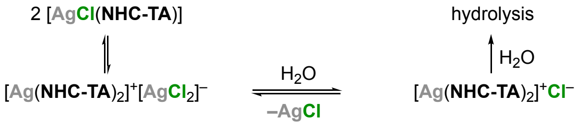


**Fig. 3** a) NMR resonance for the imidazolic protons of [AgCl(**ITA**)] in $CDCl_3$ at 25 ºC (up), –40 ºC (down). b) $^{109}Ag$-$^1H$(Imz) correlation detected for [AgCl(**ITA**)] at –40 ºC in $CDCl_3$.

The two [AgCl(**NHC-TA**)] complexes dissolve readily in water, undergoing immediate hydrolysis of the Ag-$C_{carbene}$ bond. In wet DMSO, however, [AgCl(**ITA**)] rapidly releases the imidazolium cation ($t_{1/2}$ = 24 h), whereas [AgCl(**IpyTA**)] remains unchanged at least two weeks in an open NMR tube in DMSO-*d*$_6$. In water, the shift towards charged homoleptic species (*i.e.*, $[Ag(NHC)_2]^+X^-$) is favored by the poor stability of $AgCl_2^-$ in $H_2O$ (Scheme 3).[36] The steric hindrance in the bis-NHC structures appear to be fatal for the Ag-$C_{carbene}$ bond in water–inherently labile in an NHC transfer agent. However, the species with the **IpyTA** ligand are better protected against hydrolysis in DMSO, most likely due to the less hydrophilic environment and lower steric hampering caused by this ligand, together with better solvation and shift of the equilibria to [AgCl(**IpyTA**)] in this solvent.



**Scheme 3** Equilibria involving mono and bis-**NHC-TA** silver(I) species proposed to participate in their hydrolysis.

In summary, the present study introduces water-soluble chimeric ligands that combine features of **PTA** and NHC structures. Efficient high-yielding procedures for the synthesis of two NHC-TA preligands up to multigram scales have been developed. The utility of these novel precursors has been assessed through the synthesis of [AgCl(NHC-TA)] complexes, which exhibit variations in their hydrolytic stability. Further work is underway to explore the scope of the chemistry of this type of ligands and complexes, and their applications in water.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Supplementary Information. See DOI: 10.1039/x0xx00000x.

CCDC 2505167 contains the supplementary crystallographic data for this paper.

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## Data availability

The data supporting this article have been included as part of the Supplementary Information. See DOI: 10.1039/x0xx00000x.

CCDC 2505167 contains the supplementary crystallographic data for this paper.