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NHC adducts of tantalum amidohalides: the first example of NHC abnormally coordinated to an early transition metal†‡

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The reaction of $\text{Ta}(\text{NMe}_2)_5$ with $\text{NHC}\cdot\text{HBF}_4$ ($\text{NHC} = \text{IMes}$ and SIMes) leads to new carbene adducts of the mixed Ta^{V} amidofluoride, $[(\text{NHC})\text{TaF}_3(\text{NMe}_2)_2]$. On the contrary, the reaction of $\text{Ta}(\text{NMe}_2)_5$ with $\text{IMes}\cdot\text{HCl}$ gives a complex mixture, where $[(\text{aIMes})\text{TaCl}_2(\text{NMe}_2)_3]$ is identified as one of the products. This is the first example of abnormal NHC coordination to an early transition metal.

N-Heterocyclic carbenes (NHC) and their complexes have been attracting much attention in the last few decades, mainly due to the ease of their functionalization and, consequently, the tunability of their properties.¹ The complexes of late transition metals (mainly noble metals) with NHC are widely used in homogeneous catalysis and, in addition, NHC themselves serve as organocatalysts. The chemistry of NHC complexes of main group elements is also intensively developing, in particular, because NHC coordination stabilizes homoelement molecules, formally regarded as unstable “allotropes” (for example, the phosphorus clusters P_2 to P_{12})² and otherwise transitory species, such as SiCl_2 ³ and BH ,⁴ in the neutral, ionic or radical form.⁵ In contrast, the coordination chemistry of NHC with the early transition metals (TM) remains much in the shadow, particularly where the group 5 metals are concerned. This scarcity of data is clearly due to high oxophilicity of the hard Lewis acids (V, Nb and Ta), which is expected to disfavor the coordination of relatively soft carbene ligands. In addition, both the commonly employed starting compounds (for instance, halides) of the early TM and their NHC adducts are often extremely moisture-sensitive, particularly in higher oxidation states; however, this ‘water hunger’ can be satisfied

with partial hydrolysis, which leads to more stable oxohalides that sometimes can be isolated as NHC adducts.⁶

The first examples of monodentate NHC adducts with Nb and Ta halides⁷ and oxohalides⁸ were very recently reported. In the reactions of $[\text{MX}_5]_2$ ($\text{X} = \text{F}$, Cl , or Br) with free carbene, either double salts $[\text{M}(\text{NHC})_2\text{Cl}_4][\text{MCl}_6]$ or molecular species $[\text{M}(\text{NHC})\text{X}_5]$ are formed. The main structural feature of these Nb and Ta adducts is abnormal elongation of the M–carbene bond and lack of π -contribution due to the absence of d electrons in these d^0 complexes. The electron deficiency of the coordinated carbene is believed to be satisfied with weak donation of electron density from a coordinated halide to the carbene carbon atom.^{6,7c} In addition to the ‘normal’ coordination mode of NHC (**A**, Fig. 1), the ‘abnormal’ coordination mode (*i.e.* *via* the C4 atom of the carbenazole cycle, **B**)⁹ is known, but, to our knowledge, no complexes of early TM with *a*NHC have been reported to date. The bimetallic complexes of anionic dicarbenes (**C**) containing an early d-metal are also rare.¹⁰

Given this scarcity of results we set out to explore new routes to NHC adducts of early TM, using metal amides in order to enable further functionalization *via* easy substitution of the NR_2 groups. The addition of free IMes to a solution of $\text{Ta}(\text{NMe}_2)_5$ in C_6D_6 does not lead to coordination, as is seen from the ^{13}C NMR shift of the carbene C atom (δ 219.6 ppm) (ESI, Fig. S2†). This is very likely due to both the high steric demands and strong π -donor nature of the NMe_2 groups, which decrease the acceptor strength of the Ta atom. Therefore, we tried the reaction of $\text{Ta}(\text{NMe}_2)_5$ with the protonated carbene precursor $\text{IMes}\cdot\text{HBF}_4$, which was supposed to

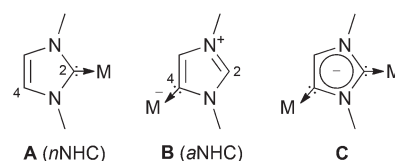


Fig. 1 Bonding modes of N-heterocyclic carbenes.

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lead to the elimination of one equivalent of HNMe_2 and simultaneous coordination of an NHC molecule. Much to our surprise, the reaction resulted in the formation of a mixed amido-fluoride complex $[(\text{IMes})\text{TaF}_3(\text{NMe}_2)_2]$ (**1a**), which was isolated after the appropriate workup in moderate yield as large colorless crystalline blocks (Scheme 1). **1a** indeed contains a coordinated IMes, and, in addition, three F atoms (obviously derived from the BF_4^- anion) are coordinated to the Ta atom, which illustrates the enormous affinity of tantalum(v) for fluoride. The isostructural complex $[(\text{SIMes})\text{TaF}_3(\text{NMe}_2)_2]$ (**1b**) with a saturated carbene was prepared in a similar way from $\text{Ta}(\text{NMe}_2)_5$ and SIMes-HBF_4 . Mixed amido-fluoride complexes are commonly synthesized by ligand metathesis between a metal amide and fluoride in the desired ratio, and the only known NHC adduct of a transition metal amido-fluoride, $[(\text{TiF}_2(\text{NEt}_2)(\text{NHC}))_2(\mu\text{-F})_2]$, was isolated following precisely this pathway.¹¹

Both **1a** and **1b** adopt the *mer*, *cis* ligand arrangement with all the fluoride ligands being in *cis* positions relative to NHC (Fig. 2). The Ta–C_{carbene} bond length in **1a** (2.389(5) Å) is comparable to that in $[\text{IPrTaCl}_5]$ (2.373(5) Å)^{7c} and $[\text{IPrTaBr}_5]$ (2.383(10) Å)^{7b} and is slightly longer than that found in the *trans*-dicarbene cation $[(\text{IMes})_2\text{TaCl}_4]^+$ (2.346(6) Å).^{7c} The Ta–N lengths *cis* and *trans* to NHC are almost equal, which suggests that the carbene is not involved in π -bonding with Ta. The fluorides are oriented toward the NHC ligand (the C_{carbene}–Ta–F angles fall within the range of 79.77(15)–82.65(15)°, but this is not the case with the *cis*-NMe₂ group where the C(1)–Ta–N(3) angle is 98.65(15)°. The C...F distances between the *cis* fluorides and the C_{carbene} atom (2.852(6), 2.879(6), and 2.781(6) Å, for F(1), F(2) and F(3), respectively) are less than the sum of the van der Waals radii for carbon and fluorine (3.17 Å),¹² which is a situation that is typical for reported NHC adducts of the early TM halides.^{7,13} The imidazoline cycle is slightly (by 13.5°) turned away from the C(1)F(2)N(3)N(4) plane. The NHC ligand is also slightly tilted away from the *cis*-NMe₂ ligand (the C(1)–Ta(1)–N(3) angle is 98.65(18)°, clearly to ease steric repulsion.

Complex **1b** retains the major structural features of its congener **1a**. The main difference is that the Ta–C_{carbene} length (2.432(2) Å) is *ca.* 0.04 Å longer than that in **1a**. The reason for this elongation is unclear; in imido alkylidene complexes $[(\text{NHC})\text{Mo}^{\text{VI}}(=\text{CHR})(=\text{NAr})]$, the difference in the Mo–C

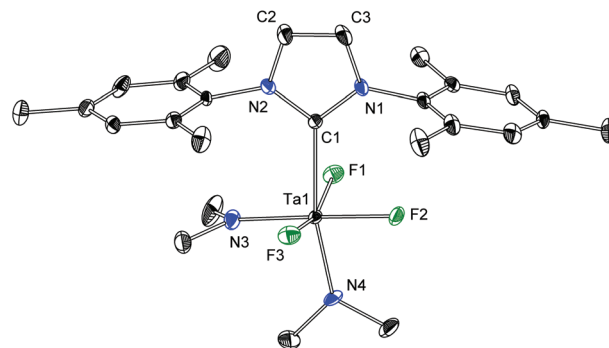
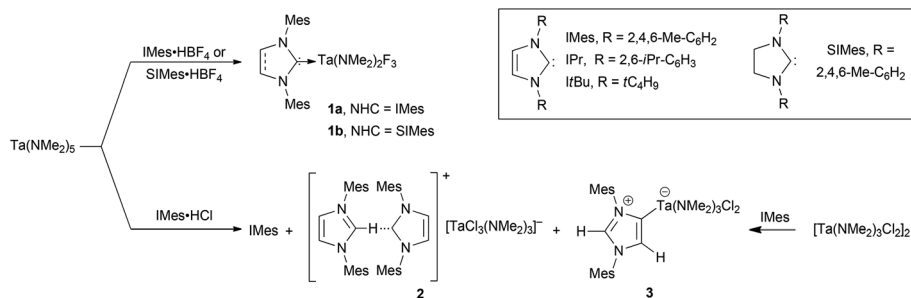


Fig. 2 Molecular structure of **1a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°) are given for **1a** and the isostructural complex **1b**. For **1a**: Ta1–C1 2.389(5), Ta1–F1 1.898(3), Ta1–F2 1.941(3), Ta1–F3 1.911(3), Ta1–N3 1.987(4), Ta1–N4 1.991(4), C1–Ta1–N3 98.65(18), and C1–Ta1–N4 167.03(17). For **1b**: Ta1–C1 2.432(2), Ta1–F1 1.9127(12), Ta1–F2 1.9398(12), Ta1–F3 1.9114(12), Ta1–N3 2.0017(18), Ta1–N4 1.9861(18), C1–Ta1–N3 99.70(7), and C1–Ta1–N4 167.22(7).

lengths for IMes and SIMes lies within the 0.01 Å range.¹⁴ The Ir–C bond lengths in the $[(\text{NHC})\text{Ir}(\text{CO})_2\text{Cl}]$ and $[(\text{NHC})\text{Ir}(\text{cod})\text{Cl}]$ systems (cod = 1,5-cyclooctadiene) also insignificantly depend on the saturation of the NHC backbone.¹⁵

The NMR spectra of **1a** and **1b** in C_6D_6 (ESI, Fig. S3–S8†) are consistent with the solid state structures. The ¹⁹F NMR spectra show two signals in a 1 : 2 ratio corresponding to a fluoride *trans* to the NMe₂ group and to a pair of mutually *trans* fluorides. The ¹³C{¹H} NMR spectra show well-resolved quartets at 194.9 (**1a**) and 217.0 (**1b**) ppm due to spin-spin coupling with the three nearly equivalent F atoms *cis* to carbene. The signals of the carbene C atom are shifted *ca.* 25 ppm downfield from the free IMes (219.7)¹⁶ and SIMes (243.8),¹⁷ as is common for the early TM complexes.

In an unexpected contrast to the rather smooth formation of **1a** and **b**, the reaction of $\text{Ta}(\text{NMe}_2)_5$ with IMes–HCl in a 1 : 1 molar ratio proceeds in a much more complicated manner. After heating in THF and evaporating all the volatiles, the reaction mixture was consecutively extracted with pentane and toluene. Slow evaporation of the pentane extract afforded a complex mixture of crystals, in which only free IMes and the



Scheme 1



novel complex $[\text{IMes-H}\cdots\text{IMes}][\text{fac-TaCl}_3(\text{NMe}_2)_3]$ (**2**) could be identified (ESI, Fig. S1†). The cation in **2** contains an IMes molecule bound with a hydrogen bond to the parent imidazolium cation IMesH^+ , which retains the common structural features of such adducts.¹⁸ The isolation of free IMes and **2** shows severe competition between the coordination of the softer NHC (primarily σ -donor) and harder chloride and amide anions (π -donors) to the hard d^0 Ta^V center, and thus one can deduce that even H-bond formation with a C–H moiety rivals the coordination of NHC to Ta^V.

Slow evaporation of the toluene extract afforded a brown oil with a few yellow needles, which, according to X-ray analysis, turns out to be $[(a\text{IMes})\text{TaCl}_2(\text{NMe}_2)_3]$ (**3**), the Ta complex featuring the abnormal coordination of the NHC ligand. To the best of our knowledge, including a search in the Cambridge Structural Database,¹⁹ this is the first example of this coordination mode of a neutral NHC to early transition metals.

The structure of **3** (Fig. 3) represents a distorted octahedral complex with the *mer*, *cis* ligand arrangement. The Ta–N length *trans* to NHC (2.0165(18) Å) is longer than the two Ta–N lengths *trans* to Cl (1.9760(18) and 1.9710(17) Å). The Ta–C_{carbene} length (2.339(2) Å) is appreciably shorter than that in both **1a** and $[\text{TaCl}_5(n\text{IPr})]$ (2.373(5) Å),^{7c} even taking into account the much greater steric hindrance caused by the NMe₂ groups. Both the elongated Ta–N and shortened Ta–C lengths might reflect the enhanced donor strength of *a*NHC compared to the ‘normal’ coordination mode.⁹ The pairs of complexes that differ exclusively in the coordination manner of NHC are still scarce; however, in complexes that simultaneously contain normally and abnormally coordinated carbene, the M–C_{*a*NHC} length can be shorter, equal or even slightly longer than the M–C_{*n*NHC} length.²⁰ Similarly to the *n*NHC complexes, the *cis*-chlorides in **3** form short contacts with the C_{carbene} atom

(C(2)–Cl(1) 3.042(4), C(2)–Cl(2) 3.242(2) Å, C(2)–Ta(1)–Cl(1) 77.66(5), and C(2)–Ta(1)–Cl(2) 82.84(5)°), falling well within the sum of the van der Waals radii for C and Cl (3.45 Å).

Elucidation of the structure of **3** enabled us to develop its rational synthesis *via* the cleavage of the dimer $[\text{TaCl}_2(\text{NMe}_2)_3]_2$ with free NHC. Reaction with IMes (1 : 2 molar ratio) in toluene afforded **3** in good yield as a yellow powder, which was identified by IR spectra and cell parameters. One can conclude that chloride ligands enhance the Lewis acidity of the metal center in $\text{TaCl}_2(\text{NMe}_2)_3$ compared to $\text{Ta}(\text{NMe}_2)_5$; therefore, it forms a dimer that can be cleaved by NHC.

Recently Dagorne *et al.* reported a pathway to *a*NHC adducts of the sterically demanding *ItBu* carbene and group 13 metals, namely, isomerization of $[(n\text{ItBu})\text{MX}_3]$ (M = Al, Ga, and In; X = Hal, and alkyl), induced by heating or the addition of a polar solvent (THF).²¹ In contrast, complexes of the less bulky carbenes IPr or IMes did not isomerize. However, with the more crowded precursor, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, IPr shows fast *n*NHC to *a*NHC conversion, whereas *ItBu* forms only the *a*NHC complex but not the *n*NHC complex.²² Heating of $[(n\text{IPr})\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2]$ also leads to isomerization to the *a*IPr complex, whereas $[(n\text{ItBu})\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2]$ decomposes upon heating to give $[(t\text{BuIm})_2\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2]$ (*tBuIm* – *N-tert*-butylimidazole), $\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2$ and isobutene.²³ In our case, complex **3** is formed under mild conditions (toluene, rt), implying that the steric hindrance around the Ta center is the main driving force for the *a*NHC coordination. A solution of the less sterically hindered **1a** in C₆D₆ remained intact upon heating at 70 °C for 5 days, showing no changes in its NMR spectra.

Unlike **1a** and **b**, the crystals of **3** are almost insoluble in hydrocarbons. The NMR spectrum of a freshly prepared solution in THF-*d*₈ shows two sets of non-equivalent Mes resonances and two doublets of the imidazoline ring protons at 7.88 and 8.40 ppm, which are characteristic of *a*NHC complexes.† Two more pairs of such doublets of lower intensity appear immediately after sample preparation, very likely due to the protonation of an NMe₂ group with traces of water. ¹³C{¹H} NMR shows the C_{carbene} resonance at 186.9 ppm. After several days, however, extensive protonation of the NHC moiety becomes apparent, and complex **3** decomposes almost completely in 2 weeks. This process is accompanied by a gradual increase in the signal at 3.60 ppm, which corresponds to the protons entering the 2,5-positions of THF-*d*₈ and indicates participation of the solvent in the decomposition. The activation of THF-*d*₈ with an *a*NHC complex was reported recently by Goicoechea *et al.*²⁴ In addition, the HC=CH backbone of imidazoline-base NHC is known to be liable for the H/D exchange.²⁵

In CD₂Cl₂ **3** behaves similarly. Immediately after preparation, its ¹H NMR spectrum features characteristic C²H and C⁵H doublets at 7.90 and 7.74 ppm, respectively, along with minor signals belonging to another *a*NHC complex yet to be identified, and at least one additional Mes-containing species. The C_{carbene} atom of **3** resonates at 187.2 ppm. However, both **3** and the other *a*NHC species gradually evolve into a complex mixture of yet unidentified species, demonstrating the above-

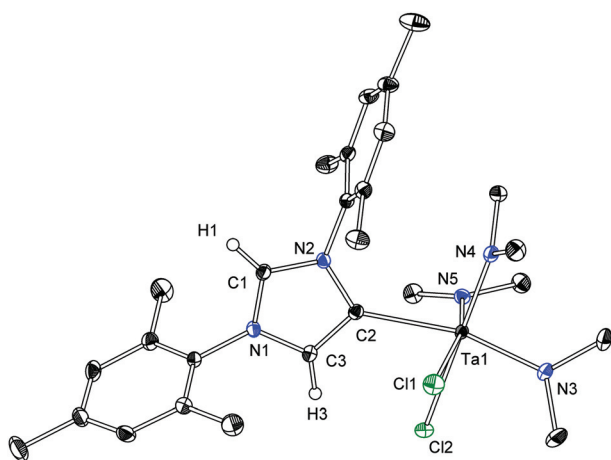


Fig. 3 Molecular structure of **3**, omitting hydrogen atoms except for those at C1 and C3. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Ta1–C2 2.339(2), Ta1–Cl1 2.5081(6), Ta1–Cl2 2.5546(5), Ta1–N3 2.0165(18), Ta1–N4 1.9760(18), Ta1–N5 1.9710(17), C2–Ta1–N3 162.50(7), C2–Ta1–N4 97.46(7), and C2–Ta1–N5 90.05(7).



mentioned sensitivity of early TM NHC complexes towards solvolysis. Complicated solution dynamics is characteristic of early transition metal amidohalide complexes: the solution of the parent $[\text{Ta}(\text{NMe}_2)_3\text{Cl}_2]_2$ in toluene is unstable towards ligand redistribution and converts into a mixture of $[\text{Ta}(\text{NMe}_2)_n\text{Cl}_{5-n}]$ and other unidentified products.²⁶

To conclude, $\text{Ta}(\text{NMe}_2)_5$ and $[\text{TaCl}_2(\text{NMe}_2)_3]_2$ prove to be excellent precursors for the preparation of Ta^{V} complexes with NHC. The first complex of an early transition metal with *a*NHC has been prepared taking advantage of the steric constraints caused by coordinated dialkylamido groups. Novel, simple pathway towards Ta mixed amidofluorides through BF_4^- salts was found, and the first NHC adducts of Ta^{V} amido-fluoride were isolated. Further studies are underway to investigate the reactivity of this compound.

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