

Preliminary communication

# Isolation and characterization of a monomeric metallapyridine complex: models for pyridine hydrodenitrogenation intermediates<sup>1</sup>

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## Abstract

We report the preparation of a stable metallapyridine complex of tantalum prepared in the course of model studies of hydrodenitrogenation reactions. Monomeric  $\text{Ta}(\text{=NC}^t\text{Bu}=\text{CHC}^t\text{Bu}=\text{CH})(\text{OAr})_2(\text{THF})(\mathbf{5} \cdot \text{THF})$  is isolated upon thermolyzing the  $\eta^2(N,C)$ -pyridine complex  $[\eta^2(N,C)\text{-}2,4,6\text{-NC}_5^t\text{Bu}_3\text{H}_2]\text{Ta}(\text{OAr})_2\text{Me}$  (**2**) in THF, while the metallapyridine dimer  $[\text{Ta}(\mu\text{-NC}^t\text{Bu}=\text{CH}-\text{C}^t\text{Bu}=\text{CH})(\text{OAr})_2]_2$  (**6**) is isolated when this reaction is carried out in benzene. Complete NMR characterization of  $\mathbf{5} \cdot \text{THF}$  is described, along with its conversion into **6**.

*Keywords:* Imide; Pyridine; Metallacycle; Tantalum; Hydrotreating; Hydrodenitrogenation

## 1. Introduction

One major goal of petroleum hydrotreating is the catalytic removal of sulfur-, nitrogen-, oxygen- and metal-containing impurities from assorted feedstocks [1,2]. Hydrotreating is typically carried out over sulfided CoMo- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or NiMo- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and is normally optimized for hydrodesulfurization (HDS), since sulfur is present in higher concentrations than nitrogen or oxygen [3,4]. However, as crude oil quality declines as a result of increasing organonitrogen contaminants, improving hydrodenitrogenation (HDN) catalysis takes on a new urgency [5]. We recently reported HDN model studies in which a pyridine C–N bond scission was achieved and led to a cascade of subsequent heterocycle rearrangement and degradation reactions [6–8]. In this report, we describe the isolation of an elusive intermediate in this pyridine degradation sequence, viz. a monomeric metallapyridine complex, and demonstrate its conversion to the thermodynamic degradation product (Wolczanski and coworkers have delineated a very different type of C–N bond scission process, see Ref. [9]).

## 2. Results and discussion

The  $\eta^2(N,C)$ -pyridine complex  $[\eta^2(N,C)\text{-}2,4,6\text{-NC}_5^t\text{Bu}_3\text{H}_2]\text{Ta}(\text{OAr})_2\text{Cl}$  (**1**, Ar = 2,6-C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>) reacts with MeMgCl to ultimately afford a stable metallapyridine dimer  $[\text{Ta}(\mu\text{-NC}^t\text{Bu}=\text{CHC}^t\text{Bu}=\text{CH})(\text{OAr})_2]_2$  (**6**), Scheme 1 [7]. The kinetic product in this sequence,  $[\eta^2(N,C)\text{-}2,4,6\text{-NC}_5^t\text{Bu}_3\text{H}_2]\text{Ta}(\text{OAr})_2\text{Me}$  (**2**), has been shown to undergo an intramolecular metal-to-ligand alkyl migration [8] to induce ring opening and formation of the metallacyclic imido complex  $\text{Ta}(\text{=NC}^t\text{Bu}=\text{CHC}^t\text{Bu}=\text{CHC}^t\text{BuMe})(\text{OAr})_2$  (**3**). Further studies of **3** revealed that this seven-membered metallacycle itself is unstable and rearranges to afford  $\text{Ta}(\text{=NC}^t\text{Bu}=\text{CHC}^t\text{Bu}=\text{CHC}^t\text{BuHCH}_2)(\text{OAr})_2$  (**4**) that further decomposes to give the metallapyridine dimer  $[\text{Ta}(\mu\text{-NC}^t\text{Bu}=\text{CHC}^t\text{Bu}=\text{CH})(\text{OAr})_2]_2$  (**6**) and <sup>t</sup>BuCH=CH<sub>2</sub>, Scheme 1.

With the exception of **5**, all of the complexes in Scheme 1 have been observed via <sup>1</sup>H NMR, and **1**, **2**, **3**, and **6** have been isolated as the complexes shown, with **4** being isolated as its MeC≡N adduct [7]. We believe that the metallapyridine dimer **6** is formed from the dimerization of a monomer **5**, which is sufficiently short-lived in solution that it is not observed. We now report the isolation of an adduct of **5**.

Thermolyzing toluene–THF solutions of  $[\eta^2(N,C)\text{-}2,4,6\text{-NC}_5^t\text{Bu}_3\text{H}_2]\text{Ta}(\text{OAr})_2\text{Me}$  (**2**) affords a new,

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<sup>1</sup> Dedicated to our mentor, advisor, and friend, Professor Malcolm L.H. Green, FRS, on the occasion of his 60th birthday.



Table 2

Summary of observed NMR connectivities for  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  (**5**·**THF**) by NOESY, HETCOR, and HMBC methods<sup>a</sup>

<sup>1</sup> H NMR signal	NOESY ( <sup>1</sup> H)	HETCOR	HMBC
C1H	C9H, C6H	C1	C2, C3, C5
C3H	C6H, C8H	C3	C1, C2, C4, C5, C7
C6H	C1H, C3H	C6	C2, C5, C6
C8H	C3H	C8	C4, C7, C8
C9H	C1H, C10H	C9	C9, C10
C10H	C9H	C10	C9, C10

<sup>a</sup> In  $\text{C}_6\text{D}_6$  at 25 °C.

One significant question concerning the structure of **5**·**THF** is the extent to which the metallacycle is delocalized [11]. A preliminary X-ray crystallographic study confirms the proposed structure of **5**·**THF** as the metallapyridine monomer  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$ .

While structure refinement is still in progress, the overall features of the metallacycle are evident. Crystal data for  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  (**5**·**THF**,  $\text{C}_{40}\text{H}_{62}\text{NO}_3\text{Ta}$ , the asymmetric unit contains two crystallographically independent molecules) are as follows: orange, triclinic,  $P\bar{1}$  ( $\text{No. } 2$ ),  $a = 13.397(2)$  Å,  $b = 16.925(2)$  Å,  $c = 19.531(1)$  Å,  $\alpha = 108.06(1)^\circ$ ,  $\beta = 103.11(1)^\circ$ ,  $\gamma = 96.86(1)^\circ$ ,  $V = 4013.5(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D(\text{calc}) = 1.30$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 27.4$  cm<sup>-1</sup>, ( $T = -70 \pm 1$  °C); 14739 total reflections (14075 unique) with a maximum  $2\theta$  of 50.0° of which 7928 with  $F_o^2 > 3.0\sigma(F_o^2)^2$  were included in the present refinement for  $R = 0.052$ ,  $R_w = 0.056$ . Selected bond angles (deg) for molecule A of  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  (**5**·**THF**) are:  $\text{Ta-N-C}(4) = 148.0(8)$ ,  $\text{Ta-C}(1)-\text{C}(2) = 127.7(9)$ ,  $\text{C}(1)-\text{C}(2)-\text{C}(3) = 123.1(1)$ ,  $\text{C}(2)-\text{C}(3)-\text{C}(4) = 124.1(1)$ ,  $\text{C}(3)-\text{C}(4)-\text{N} = 117.1(1)$ ,  $\text{N-Ta-C}(1) = 80.6(4)$ ,  $\text{N-Ta-O}(\text{THF}) = 164.8(4)$ .

The metallapyridine monomer  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  adopts a slightly distorted trigonal bipyramidal geometry analogous to the solution structure **5a**. The asymmetric unit contains two crystallographically independent, but virtually identical molecules; preliminary data for one molecule are shown

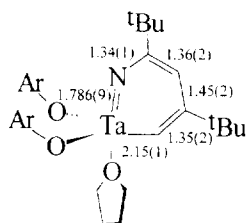
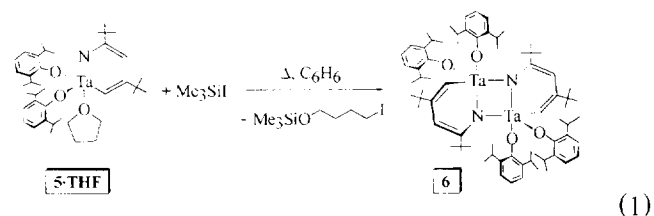


Fig. 2. Selected metallapyridine bond lengths (Å) for molecule A of  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  (**5**·**THF**).

in Fig. 2. The  $\text{TaNC}_4$  metallacycle is very nearly planar (mean deviation from planarity of 0.02 Å), but it is not aromatic, as discrete single and double bonds are evident around the ring. This  $\pi$  electron localization clearly favors the imido form (i.e.  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$ , Scheme 1) rather than the carbene structure, which is especially significant since the metal can dictate that either structure be adopted. Although the imido ligand in **5**·**THF** is strongly bent ( $\text{Ta=N-C}(4) = 148.0(8)^\circ$ ) it is only weakly basic, as attempts to alkylate the imido nitrogen with electrophiles (e.g. MeI) were unsuccessful.

Although base-free **5** is not observed by <sup>1</sup>H NMR spectroscopy during the thermal conversion of **2** to dimer **6**, its intermediacy is supported by the fact that  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2(\text{THF})$  (**5**·**THF**) can be cleanly converted into **6**. Despite the fact that the THF ligand in **5**·**THF** appears to be labile (e.g. the THF is easily displaced by pyridine), heating solutions of **5**·**THF** does not lead to the formation of **6**. However, heating a cherry red solution of **5**·**THF** with  $\text{Me}_3\text{SiI}$  results in the decolorization of the solution and the formation of insoluble red crystals, Eq. (1). The only product observed in solution by <sup>1</sup>H NMR is  $\text{Me}_3\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ , that arises from ring cleavage of the coordinated THF of **5**·**THF** [12]. The insoluble red crystals were identified as dimer **6** by elemental analysis and by comparison of one crystal's unit cell parameters to those of an authentic sample of **6** [7].



In summary, we have demonstrated the formation of a monomeric metallapyridine complex **5**·**THF** from thermolysis of the  $\eta^2(N,C)$ -pyridine complex [ $\eta^2(N,C)$ -2,4,6- $\text{NC}^t\text{Bu}_3\text{H}_2$ ] $\text{Ta}(\text{OAr})_2\text{Me}$  (**2**) in the presence of THF. Nascent  $\text{Ta}(\text{=NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2$  (**5**) is generated by removal of a THF ligand from **5**·**THF** and its conversion into dimeric [ $\text{Ta}(\mu\text{-NC}^t\text{Bu=CHC}^t\text{Bu=CH})(\text{OAr})_2$ ]<sub>2</sub> (**6**) has been established. These observations complete the reaction sequence in Scheme 1, delineate one process by which heterocyclic C–N bonds are cleaved, and offer new insight into how nitrogen heterocycles may be further degraded after C–N bond cleavage. Information on subsequent heterocycle degradation reactions may be relevant to catalytic HDN, since under normal HDN conditions ethane, ethylene, propane, and propylene are the principal products of pyridine HDN with only a minor fraction of  $\text{C}_5$  products being generated [13].

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