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Carbon–nitrogen bond cleavage in pyridine ring systems mediated by organometallic thorium(IV) complexes†

Jaime A. Pool, Brian L. Scott and Jaqueline L. Kiplinger*

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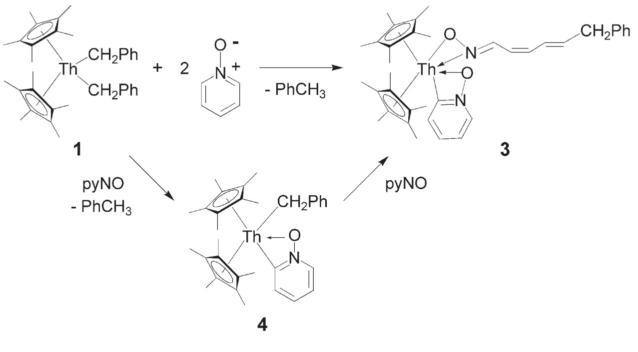
Thorium(IV) alkyl and aryl complexes of the type $(C_5Me_5)_2ThR_2$ (R = CH_2Ph, Ph) have been found to mediate the facile ring-opening and dearomatization of the pyridine ring of pyridine *N*-oxide under ambient conditions to afford the first thorium η^2-(*O*,*N*)-oximate complexes.

Out of all the nitrogen compounds subject to hydrodenitrogenation (HDN) catalysis during petroleum refining, the *N*-heterocyclic compounds that contain pyridine, quinoline and indole rings are among those most difficult to process.[1] One crucial question that remains unresolved concerns the manner in which the strong C–N bonds in *N*-heterocyclic arenes are cleaved. Although numerous transition metal, lanthanide, and actinide η^2-(*N*,*C*)-pyridyl complexes have been prepared,[2] examples of metal-mediated C–N activation of aromatic *N*-heterocyclic compounds are exceedingly rare, notably feature η^2-(*N*,*C*)-pyridine ligands and require both reducing conditions and elevated temperatures.[3] Herein we report a facile ring-opening of the pyridine ring of pyridine *N*-oxide (pyNO) under ambient conditions, mediated by the thorium(IV) complexes $(C_5Me_5)_2ThR_2$ (R = CH_2Ph (**1**),[4] Ph (**2**)[5]).

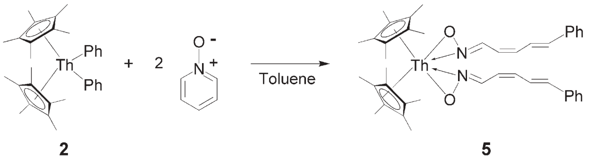
As illustrated in Scheme 1, reaction of $(C_5Me_5)_2Th(CH_2Ph)_2$ (**1**) with 2 equiv. of pyNO at ambient temperature unexpectedly results in a facile C–N bond cleavage and ring-opening of pyNO to give the first thorium oximate complex **3** as an orange–brown solid in 77% isolated yield. Diagnostic NMR spectroscopic data clearly demonstrate that diamagnetic **3** contains both a cyclometallated η^2-(*O*,*C*)-pyNO and an oximate linkage resulting from the ring-opening of a second pyNO molecule. In particular, the ^1H NMR spectrum of **3** exhibits characteristic doublets at 8.98 and 3.17 ppm for the oximate N=C(H) and CH_2 protons respectively. Other notable resonances appear for the four oximate vinyl protons and the four pyridine ring protons on the cyclometallated η^2-(*O*,*C*)-pyNO. Consistent with these structural assignments is the observation, by ^1H NMR spectroscopy, that the addition of HCl or DCl to complex **3** produces one equiv. of free pyNO or pyNO-d_1 respectively, one equiv. of the ring-opened organic oxime fragment and $(C_5Me_5)_2ThCl_2$.[4]



Scheme 1

To the best of our knowledge, the opening of the aromatic ring of pyNO, promoted by a *d*- or *f*-block metal complex, has never before been observed.[6] Previously, we reported that addition of one equiv. of pyNO to a toluene solution of $(C_5Me_5)_2Th(CH_2Ph)_2$ (**1**) results in C–H bond activation, the loss of toluene and the formation of the unusual cyclometallated pyNO complex $(C_5Me_5)_2Th(CH_2Ph)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$ (**4**) (Scheme 1).[7] Addition of another equiv. of pyNO to complex **4** results in the formation of **3**, suggesting that **4** is an isolable intermediate along the pathway to complex **3**. Importantly, reaction of **4** with pyNO-d_5 affords the labeled oximate complex $(C_5Me_5)_2Th[\eta^2\text{-}(O,C)\text{-}ONC_5H_4][\eta^2\text{-}(O,N)\text{-}ON{=}CD\text{–}(CD{=}CD)_2\text{–}CH_2Ph]$ (**3**-d_5), confirming that ring-opening and C–N bond cleavage only occurs for the second equiv. of pyNO.

Addition of 2 equiv. of pyNO to a toluene solution of $(C_5Me_5)_2ThPh_2$ (**2**) at ambient temperature affords the novel bis(oximate) complex $(C_5Me_5)_2Th[\eta^2\text{-}(O,N)\text{-}ON{=}CH\text{–}(CH{=}CH)_2\text{–}Ph]_2$ (**5**) as a brown crystalline solid in 67% isolated yield (eqn. 1). It is remarkable that *two* pyNO ring systems have been dissected by *one* thorium metal center under mild conditions. Monitoring the reaction mixture by ^1H NMR spectroscopy reveals quantitative formation of a single isomer of **5** within a few min. Similar to complex **3**, the ^1H NMR spectrum of **5** shows a diagnostic doublet at 9.08 ppm for the oximate N=C(H) proton and four down-field resonances, attributed to the vinyl protons of the ring-opened pyNO. The phenyl group appears as a multiplet centered at 7.37 ppm.



(1)

Cleavage of the N–C bonds in the pyridine rings of complex **5** was unambiguously ascertained by a single-crystal X-ray diffraction study (Fig. 1).‡ The molecular structure of **5·pyNO** reveals a typical bent-metallocene framework with two bidentate oximate ligands and a coordinated pyNO molecule contained within the metallocene wedge. The most striking aspects of the structure are the two oximate ligands, which originate from the unprecedented

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data for all compounds. See http://www.rsc.org/suppdata/cc/b5/b502439k/

*kiplinger@lanl.gov

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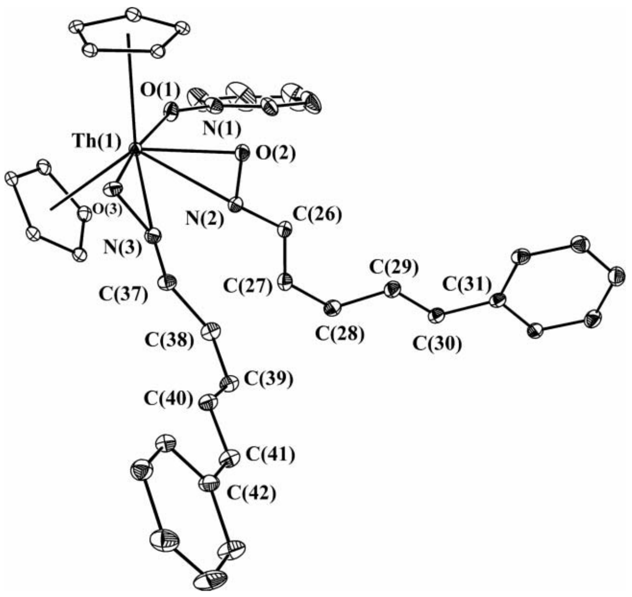
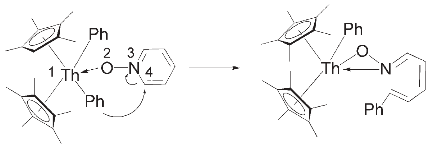


Fig. 1 The molecular structure of complex **5·pyNO** with thermal ellipsoids at the 25% probability level. The methyl substituents on the pentamethylcyclopentadienyl ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): Th(1)–O(2) = 2.332(3), Th(1)–N(2) = 2.577(4), Th(1)–O(3) = 2.334(4), Th(1)–N(3) = 2.519(5), O(2)–N(2) = 1.372(5), O(3)–N(3) = 1.365(5), N(2)–C(26) = 1.280(6), C(26)–C(27) = 1.431(7), C(27)–C(28) = 1.341(8), C(28)–C(29) = 1.444(8), C(29)–C(30) = 1.332(7), C(30)–C(31) = 1.463(8), N(3)–C(37) = 1.280(7), C(37)–C(38) = 1.445(8), C(38)–C(39) = 1.346(8), C(39)–C(40) = 1.431(8), C(40)–C(41) = 1.344(8), C(41)–C(42) = 1.471(8); N(2)–Th(1)–O(2) = 31.98(12), N(3)–Th(1)–O(3) = 32.39(12).

ring-opening and dearomatization of two pyNO molecules. As is evident from the geometric parameters, the oximate ligands possess alternating N=C double, C–C single, and C=C double bonds with *trans–cis–trans* orientations respectively. Both oximate ligands are bound to the thorium(IV) metal center in an η^2-(*O*,*N*) fashion with a Th–O σ-bond and a Th–N dative interaction: Th(1)–O(2) = 2.332(3), Th(1)–N(2) = 2.577(4) Å and N(2)–Th(1)–O(2) = 31.98(12)°. Th(1)–O(3) = 2.334(4), Th(1)–N(3) = 2.519(5) Å and N(3)–Th(1)–O(3) = 32.39(12)°. The thorium–oxygen interactions are longer than those reported for thorium alkoxide complexes,[8] but substantially shorter (∼*ca.* 0.2 Å) than expected for a dative interaction.[9] The thorium–nitrogen dative interactions are substantially longer (∼*ca.* 0.3 Å) than those observed for thorium amides.[10] Interestingly, the oximate O–N bond distances (O(2)–N(2) = 1.372(5) and O(3)–N(3) = 1.365(5) Å) are significantly shorter than those reported for structurally related transition metal oximate complexes $Ta(ONMe_2)[OSi(SiMe_3)_3](NMe_2)_3$ (1.466(13)),[11] $MoO_2(ONEt_2)_2$ (1.427(3)),[12] and $Ti(ONEt_2)_4$ (1.402(7) Å)[12]. Combined, these geometrical data suggest electronic delocalization throughout the three-membered Th–O–N metallacycle, as previously noted for transition metal oximate compounds.[11–14]

The cleavage of the C–N bond in these aromatic *N*-heterocyclic systems is most likely facilitated by the neighboring electron-withdrawing oxygen atom. Thus, a plausible mechanism involves initial O-coordination of the pyNO ligand to the oxophilic thorium(IV) metal center, followed by 1,4-migration of the benzyl or phenyl ligand. This results in the formation of a new C–C bond with concomitant C–N bond cleavage to give the observed ring-opened oximate complexes (eqn. 2). For **2** this sequence occurs twice. This supposition is supported by the observation that addition of one equiv. of pyNO to **2** produces complex **5**, along with the single ring-opened compound $(C_5Me_5)_2Th(Ph)[\eta^2$-(*O*,*N*)-ON=CH–(CH=CH)$_2$–Ph] and unreacted **2**. This pathway differs from the chemistry observed for **1** and is consistent with the greater migratory aptitude of a phenyl moiety compared to a benzyl group.[15]



(2)

As noted by Wigley and co-workers, intramolecular 1,2-migration of hydride, alkyl, and aryl ligands in the tantalum complexes $[\eta^2$-(*N*,*C*)-2,4,6-$NC_5{}^tBu_3H_2]Ta(OAr)_2R$ effects C–N bond cleavage in the coordinated η^2-(*N*,*C*) pyridine ligand.[3a,3c] For other pyridine complexes, presumably N-bound intramolecular alkylation results in a disruption of the aromatic π-system, but without C–N bond cleavage.[16] For example, Erker and co-workers reported that the reaction of $(C_5Me_5)_2Th$(butadiene) with pyridine affords an η^3-allyl thorium metallacycle that results from C–C coupling of the diene to the α-carbon of the pyridine ring; however, no intermediate pyridine complex was detected.[16b]

In conclusion, we have found that thorium(IV) alkyl and aryl complexes mediate the facile ring-opening and dearomatization of the pyridine ring of pyNO under ambient conditions to afford the first thorium η^2-(*O*,*N*)-oximate complexes. These unique chemical transformations represent a new entry in the reactivity of pyNO. Extension of this chemistry to other *N*-heterocyclic compounds is currently under investigation in our laboratory.

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Jaime A. Pool, Brian L. Scott and Jaqueline L. Kiplinger*
Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: kiplinger@lanl.gov; Fax: (505)667-9905; Tel: (505)665-9553

Notes and references

‡ Crystal structure data for **5·pyNO**: $C_{57}H_{79}N_3O_3Th$, M = 1086.278, triclinic, a = 13.700(3), b = 14.541(3), c = 15.156(3) Å, α = 103.102(3), β = 110.879(3), γ = 95.230(3)°, U = 2698.1(9) Å^3, T = 203(2) K, space group $P\bar{1}$, Z = 2, μ(Mo–Kα) = 2.806 mm^{-1}, λ = 0.71073 Å, 14366 reflections measured, 7170 unique (R_{int} = 0.0160) which were used in all calculations. Final $wR(F^2)$ = 0.0843 (all data). CCDC 263799. See http://www.rsc.org/suppdata/cc/b5/b502439k/ for crystallographic data in CIF or other electronic format.

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