# Metallapyrimidines and Metallapyrimidiniums from Oxidative Addition of Pyrazolate N−N Bonds to Niobium(III), Niobium(IV), and Tantalum(IV) Metal Centers and Assessment of Their Aromatic Character

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S *Supporting Information*

ABSTRACT: Treatment of $MCl_4(4\text{-}tBupy)_2$ (M = Nb, Ta) with 3 equiv of potassium 3,5-di-*tert*-butylpyrazolate afforded (2,2,6,6-tetramethyl-5-ketimidehept-3-en-3-imide)bis(3,5-di-*tert*-butylpyrazolate)chloroniobium(V) (**1**; 24%) and (2,2,6,6-tetramethyl-5-ketimidehept-3-en-3-imide)bis(3,5-di-*tert*-butylpyrazolate)-chlorotantalum(V) (**2**; 27%) as deep red and yellow crystalline solids, respectively. Analogous treatment of $NbCl_4(THF)_2$ with 3 equiv each of 4-*tert*-butylpyridine and potassium 3,5-di-*tert*-butylpyrazolate and excess Na/Hg in diethyl ether afforded (2,2,6,6-tetramethyl-5-ketimidohept-3-en-3-imide)bis(3,5-di-*tert*-butylpyrazolate)niobium(V) (**3**, 32%) as deep red crystals. X-ray crystallography established that **1** and **3** each contain two intact η^2-3,5-di-*tert*-butylpyrazolate ligands as well as one 3,5-di-*tert*-butylpyrazolate ligand that has undergone N−N bond oxidative addition to the niobium center. In **1**, one of the nitrogen atoms abstracted a hydrogen atom from tetrahydrofuran solvent, whereas no hydrogen atom abstraction occurred in **3**. These complexes represent rare examples of pyrazolate N−N bond cleavage. NICS calculations suggest that the niobacycles are weakly aromatic, in comparison to the highly aromatic 3,5-di-*tert*-butylpyrazolate ligands and pyrimidine.
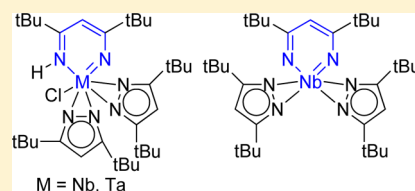
Complexes containing pyrazolate ligands have been extensively investigated.[1] The pyrazolate ligand can adopt terminal coordination modes such as η^2 and η^5 and bridging coordination modes that include μ-η^1:η^1, μ-η^2:η^2, and many others.[1,2] Pyrazolate ligands are remarkably unreactive and generally serve as ancillary ligands. Oxidative addition of pyrazolate N−N bonds could afford metallapyrimidines, which are metal-containing analogues of the aromatic nitrogen heterocycle pyrimidine. Metallapyrimidines fall into the general class of metallaaromatics. Metallabenzene complexes are the most widely studied metallaaromatics and contain planar or nearly planar, conjugated six-membered rings with six delocalized π electrons.[3] There is continuing interest in these compounds, due to their structural resemblance to benzene, potential aromaticity, and interesting reactivity.[3,4] Nitrogen-containing metallabenzene analogues are restricted to an osmapyridine, an osmapyridinium, and a tantalapyridine.[5] The only report of pyrazolate N−N bond cleavage involved a series of tetranuclear uranium complexes that were obtained upon treatment of $UI_3(THF)_4$ with potassium 3,5-dimethylpyrazolate (KMe₂pz).[6] These uranium clusters contain Me₂pz and 4-ketimidopent-2-en-2-imide ligands, the latter of which arises from pyrazolate N−N bond activation.[6]

In the course of our research relating to atomic layer deposition (ALD) film growth precursors containing pyrazolate ligands[7] and the ALD growth of mid-valent transition-metal oxide and nitride films,[8] we sought to prepare mid-oxidation-state niobium and tantalum compounds that contain pyrazolate ligands and that might serve as ALD precursors for M_2O_3 and

MO_2 films. Herein, we report the unexpected finding that 3,5-di-*tert*-butylpyrazolate (tBu₂pz) N−N bonds undergo two-electron oxidative addition on a putative niobium(III) center to afford a niobium(V) complex that contains the 2,2,6,6-tetramethyl-5-ketimidohept-3-en-3-imide (tmkh³⁻) ligand (Chart 1). On niobium(IV) and tantalum(IV) ions, tBu₂pz

Chart 1. Structures of tmkh³⁻ and tmkh²⁻ Ligands
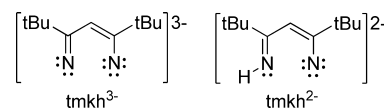
N−N bond cleavage is also observed, along with hydrogen atom abstraction by the 5-ketimide nitrogen atom, to afford hydrogen-substituted tmkh²⁻ ligands (Chart 1) supported on niobium(V) and tantalum(V) centers. These new complexes provide the first examples of pyrazolate N−N bond cleavage at single metal centers and also constitute the first examples of planar metallapyrimidines and metallapyridiniums. The aromaticity of the metallacycles is probed by variable-temperature NMR spectroscopy and theoretical calculations.

Treatment of $NbCl_4(THF)_2$ with 2 equiv of 4-*tert*-butylpyridine (4-tBupy) in THF, followed by addition of 3 equiv of KtBu₂pz, led to the isolation of **1** as deep red crystals (Scheme 1). Presumably, the 4-tBupy displaces the coordinated

Scheme 1. Synthetic Approach to 1 and 2
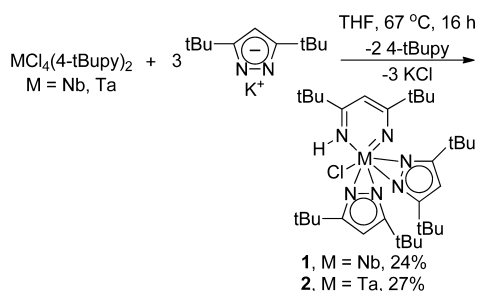

THF ligands from $NbCl_4(THF)_2$ to afford $NbCl_4(4\text{-}tBupy)_2$, which is more soluble and facilitates the reaction. Analogous treatment of $TaCl_4(4\text{-}tBupy)_2$[9] with 3 equiv of $KtBu_2pz$ afforded **2** upon workup as yellow crystals (Scheme 1). Treatment of $MCl_4(4\text{-}tBupy)_2$ with 4 equiv of $KtBu_2pz$ in refluxing THF for 7 days did not lead to displacement of the remaining chloride ion, and only **1** and **2** were isolated in yields similar to those observed with 3 equiv of $KtBu_2pz$. Treatment of $NbCl_4(THF)_2$ with Na/Hg in the presence of 4-tBupy (3 equiv) and $KtBu_2pz$ (3 equiv) in diethyl ether for 48 h afforded **3** as deep red crystals upon workup (Scheme 2). This reaction

Scheme 2. Synthetic Approach to 3
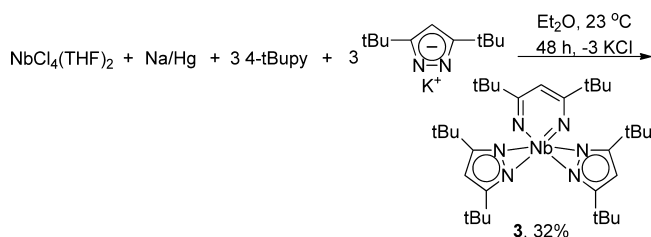
may proceed by formation of $NbCl_3(4\text{-}tBupy)_3$ and subsequent $KtBu_2pz$ salt metathesis or via Nb(IV) pyrazolate species that are reduced by Na/Hg. Complex **3** differs formally from **1** by addition of HCl. Hence, **3** is a metallapyrimidine, whereas **1** and **2** are metallapyrimidiniums. Complexes **1−3** were identified by ^{1}H NMR, ^{13}C{^{1}H} NMR, and infrared spectroscopy, CHN microanalyses, and X-ray crystallography, as described below. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1−3** showed the expected resonances for two η^2-tBu_2pz ligands and one tmkh[2−] (**1**, **2**) or tmkh[3−] (**3**) ligand. In the ^{1}H NMR spectra, **1−3** each exhibit one *tert*-butyl singlet for two equivalent tBu_2pz ligands between δ 1.33 and 1.42 and also show a singlet between δ 6.17 and 6.52 for two chemically equivalent pyrazolate ring core hydrogen atoms. The tmkh[2−] (**1**, **2**) and tmkh[3−] (**3**) ligands in **1−3** each show two resonances between δ 0.97 and 1.17 for the two types of *tert*-butyl groups and singlets between δ 5.86 and 5.97 for the ligand core hydrogen atoms. Additionally, **1** and **2** have N−H resonances at δ 9.85 and 9.28, respectively. To probe the origin of the N-bound hydrogen atom in **1** and **2**, the synthesis of **1** was repeated in 99.8% THF-d_8. Workup, followed by ^{1}H NMR analysis, indicated an 81% reduction in the integration of the N−H hydrogen atom resonance at δ 9.85. This experiment is consistent with the THF solvent as the predominant source of the nitrogen-bound hydrogen atoms in **1** and **2**. The infrared spectra of **1** and **2** show weak N−H stretches at 3337 and 3347 cm^{-1}, respectively. A similar N−H stretch is absent in the infrared spectrum of **3**.

Perspective views of **1** and **3** are shown in Figures 1 and 2. The structure of **2** is very similar to that of **1** and is not
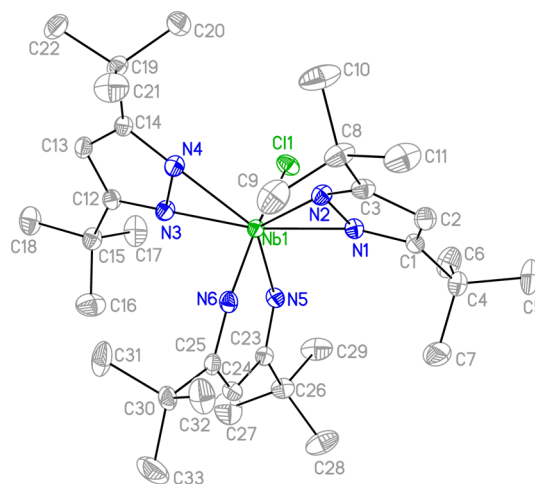

Figure 1. Perspective view of **1**, with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Nb−Cl = 2.5076(4), Nb−N1 = 2.121(1), Nb−N2 = 2.142(1), Nb−N3 = 2.124(1), Nb−N4 = 2.155(1), Nb−N5 = 2.159(1), Nb−N6 = 1.817(1), N1−N2 = 1.374(2), N3−N4 = 1.379(2), N5−C23 = 1.310(2), N6−C25 = 1.346(2), C23−C24 = 1.431(2), C24−C25 = 1.380(2); N1−Nb−N2 = 37.62(4), N3−Nb−N4 = 37.58(5), N5−Nb−N6 = 77.85(5).
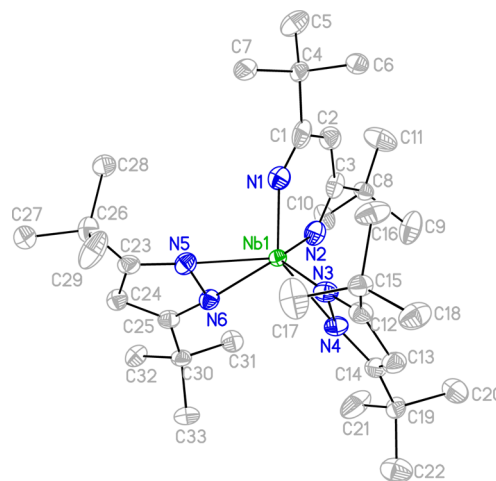

Figure 2. Perspective view of **3**, with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Nb−N1 = 1.927(4), Nb−N2 = 1.841(4), Nb−N3 = 2.146(4), Nb−N4 = 2.143(4), Nb−N5 = 2.156(4), Nb−N6 = 2.146(4), N3−N4 = 1.399(5), N5−N6 = 1.396(6), N1−C1 = 1.306(6), N2−C3 = 1.373(6), C1−C2 = 1.428(6), C2−C3 = 1.354(6); N1−Nb−N2 = 86.5(2), N3−Nb−N4 = 38.1(2), N5−Nb−N6 = 37.9(2).

discussed herein. Both complexes contain two η^2-tBu_2pz ligands and one tmkh[2−] (**1**) or tmkh[3−] (**3**) ligand, and **1** additionally contains a chloride ligand. The Nb−N distances for the tBu_2pz ligands range from 2.121(1) to 2.155(1) Å in **1** and from 2.143(4) to 2.156(4) Å in **3** and are consistent with idealized η^2 bonding. The Nb−N distances for the tmkh[2−] ligand in **1** are 1.817(1) and 2.159(1) Å, while the related values for the tmkh[3−] ligand in **3** are 1.841(4) and 1.927(4) Å. These values suggest one Nb−N imido-like bond within the tmkh[2−] and tmkh[3−] ligands in **1** and **3**, respectively, which are slightly

longer than the Nb—N distances for typical imido linkages (1.73–1.78 Å).[10] The longer Nb—N bond length for the tmkh[2−] ligand in **1** is consistent with a neutral nitrogen donor and the presence of a hydrogen atom on this nitrogen atom. In fact, electron density from a hydrogen atom was observed near N5 in **1** and was refined in the structure solution. In contrast, the longer Nb—N distance in the tmkh[3−] ligand of **3** suggests a formally anionic nitrogen atom. Chart 2 shows the bond

Chart 2. Bond Lengths (Å) in the tmkh[2−] (1) and tmkh[3−] (3) Ligands
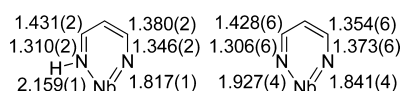
distances within the tmkh[2−] and tmkh[3−] ligand cores of **1** and **3**. The formal single and double bonds within the ligand C_3N_2 cores are shorter and longer, respectively, than those expected for isolated C—N (1.46 Å), C=N (1.21 Å), C—C (1.52 Å), and C=C (1.34 Å) bonds.[11] Since the $Nb_2N_2C_3$ core atoms are coplanar to within 0.151 (**1**) and 0.034 Å (**3**) and formally contain six π electrons, these values may indicate some delocalization and possible aromatic character.

Separate ^{1}H NMR resonances were observed for the tmkh[3−] *tert*-butyl groups in **3** up to 90 °C in toluene-d_8, and these resonances remained sharp at all temperatures. Observation of two separate *tert*-butyl resonances for the tmkh[3−] ligand in **3** does not support aromatic character for this fragment, since it implies that π delocalization is not present. To assess the aromaticity quantitatively, nucleus-independent chemical shift (NICS) calculations were performed.[12,13] NICS measures the chemical shifts of ghost atoms placed in the ring plane or above the cyclic π-electron clouds; negative NICS values indicate aromatic fragments, whereas positive NICS values denote antiaromatic species.[12] Both the isotropic and perpendicular chemical shift tensor components were evaluated by placing the ghost atom 1 Å above the centers (NICS(1)) of the pyrazolate and NbN_2C_3 rings. The computed NICS(1)$_{iso}$ and NICS(1)$_{zz}$ values are shown in Table 1 and predict that the pyrazolate

Table 1. Averaged[12] NICS(1) Values

compd	ring	NICS(1)$_{iso}$	NICS(1)$_{zz}$
1	niobapyrimidinium	−1.9	−5.5
	pyrazolates	−9.9	−23.9
3	niobapyrimidine	−4.4	−9.9
	pyrazolates	−10.2	−25.0
pyrimidine		−9.8	−26.6

rings are more aromatic than the NbN_2C_3 rings in **1** and **3** and are in qualitative agreement. The more reliable NICS(1)$_{zz}$ metric,[12,14] however, shows considerably smaller values for the NbN_2C_3 rings (**1**, −5.5; **3**, −9.9) in comparison to the pyrazolate rings (∼−25). For comparison, the NICS(1)$_{zz}$ value for pyrimidine is −26.6, which is similar to the values for the pyrazolate ligands in **1** and **3**. Hence, the pyrazolate ligands in **1** and **3** are about as aromatic as pyrimidine, the NbN_2C_3 rings are only weakly aromatic, and the NbN_2C_3 ring in **1** is less aromatic than that in **3**, consistent with the observation of more bond localization in **1** in comparison to **3**. In the osmapyridine complex Os(CHC(PPh$_3$)CPhCMeN)Cl$_2$(PPh$_3$)$_2$, the Os—C and Os—N bond lengths (1.968(8), 1.974(6) Å) are similar and

the C—C and C—N bond lengths within the ligand core are between single- and double-bond lengths, consistent with an aromatic ring.[5a] In addition, NICS calculations suggested that the osmapyridine fragment is similar to pyridine in its aromatic character.[5a]

In conclusion, we have demonstrated the oxidative addition of tBu$_2$pz N—N bonds to niobium(III), niobium(IV), and tantalum(IV) ions to afford complexes that contain planar metallapyrimidine and metallapyrimidinium groups. In the case of **3**, direct two-electron oxidative addition may occur to afford the tmkh[3−] ligand in **3**, although the mechanistic path is not clear at this point. With niobium(IV) and tantalum(IV), one-electron oxidative addition is coupled with hydrogen atom abstraction from THF solvent to afford tmkh[2−] ligands. Pyrazolate oxidative addition reactions should occur at many other low- and mid-valent single metal centers, and this approach may constitute a general method for the preparation of complexes containing metallapyrimidine and metallapyrimidinium groups. Additionally, oxidative addition reactions employing other anionic nitrogen heterocycles such as 1,2,4-triazolate, 1,2,3-triazolate, and tetrazolate ions may lead to thus far unknown examples of metallatriazines, metallatetrazines, and protonated versions thereof. The present work complements previous studies describing the cleavage of aromatic bonds in several neutral nitrogen heterocycles by low- and mid-valent early- to middle-transition-metal complexes.[5c−e,15] Finally, we note that metal complexes containing β-diketiminate ligands formally resemble doubly alkylated pyrimidinium ions.[16] However, most of the β-diketiminate MN_2C_3 rings are nonplanar and lack a formal metal—nitrogen double bond, and NICS calculations of late-transition-metal complexes with related chelates suggest that few metallacyclic structures are aromatic.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, a table, and CIF files giving synthetic procedures and analytical and spectroscopic data for **1**−**3**, X-ray crystallographic data for **1**−**3**, and details of the computational study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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