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Mapping the Basicity of Selected 3d and 4d Metal Nitrides: A DFT Study

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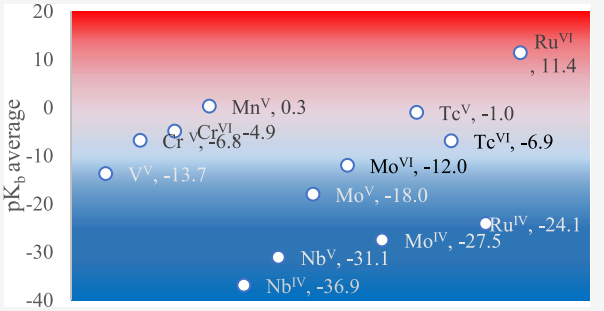
ABSTRACT: Nitride complexes have been invoked as catalysts and intermediates in a wide variety of transformations and are noted for their tunable acid/base properties. A density functional theory study is reported herein that maps the basicity of 3d and 4d transition metals that routinely form nitride complexes: V, Cr, Mn, Nb, Mo, Tc, and Ru. Complexes were gathered from the Cambridge Structural Database, and from the free energy of protonation, the $pK_b(N)$ of the nitride group was calculated to quantify the impact of metal identity, oxidation state, coordination number, and supporting ligand type upon metal-nitride basicity. In general, the basicity of transition metal nitrides decreases from left to right across the 3d and 4d rows and increases from 3d metals to their 4d congeners. Metal identity and oxidation state primarily determine basicity trends; however, supporting ligand types have a substantial impact on the basicity range for a given metal. Synergism of these factors in determining the overall $pK_b(N)$ values is discussed, as are the implications for the catalytic reactivity of metal nitrides.



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INTRODUCTION

Research on transition metal nitride (TMN) complexes has led to several breakthroughs in inorganic chemistry since the 1960s, especially given their intermediacy in catalytic reactions such as nitrogen fixation,[1] amination, group or atom transfer,[2,3] ammonia syntheses,[4,5] ammonia oxidation,[6,7] or ammonia decomposition,[8] generally, as well as their distinctive reactivity compared to other terminal metal−ligand multiply bonded complexes.[9] The reactivity of transition metal nitrides is a reflection of their unique electronic properties and structural features.[10,11] It has been shown that it is possible to tune the reactivity of the nitride ligand—*via* its bonding with the transition metal—from nucleophilic to electrophilic.[11] In the present research, we seek to quantify the extent to which the basicity of a metal nitride active site can be tuned by alteration of inner coordination sphere components. Previous research from our and other groups shows that the basicity of the metal-nitride moiety and other metal-element multiple bonds is a key parameter in dictating their reactivity, particularly concerning activating strong C−H and N−H bonds and in reactions relevant to the reduction of dinitrogen.[12,13]

Assuming the usual coordinates of crystal field theory, the triple bond by which nitride (N^{3-}) typically bonds to d-block metals results from the formation of one σ bond between an sp-hybridized orbital from N and a d_{z^2} orbital from the metal, plus two π bonds from overlap between $p_{x,y}$ (N) and $d_{xz,yz}$ (M) orbitals. In octahedral and related ligand fields, there is also a non-bonding orbital d_{xy} and a highly anti-bonding $d_{x^2-y^2}$. As such, stable transition metal-nitride complexes typically have metal ions whose formal d-counts are low—d^{0-2}—which tends to result in basic/nucleophilic nitrides given the Lewis acidity expected of high-valent transition metal ions.

To some extent, the nitride basicity is offset by the covalency of the MN interactions. The nature and occupancy of the metal-nitride orbitals determine M≡N stability and reactivity, in particular the occupation of the (N pπ−M dπ)* molecular orbitals. If the π* molecular orbital has mostly metal character, it results in a strongly nucleophilic nitride (Figure 1A), while if the π* orbital has predominantly N p character, the nitride exhibits electrophilic properties (Figure 1B).[11]

Nitride reactivity is expected to be sensitive to metal identity (*e.g.*, 3d *vs.* 4d), formal oxidation state, and the nature of any supporting ligands. However, quantification of this sensitivity is lacking in the literature. Generally, nucleophilic nitride complexes are expected to result from high oxidation states in early or middle series transition metals, while later d-block metals yield more electrophilic/less nucleophilic nitrides or nitridyls.[11] Geometries typically observed in nitride complexes are those such as tetrahedral or square pyramidal in which there are no ligands trans to the nitride, although octahedral nitride

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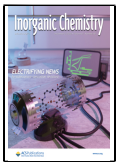

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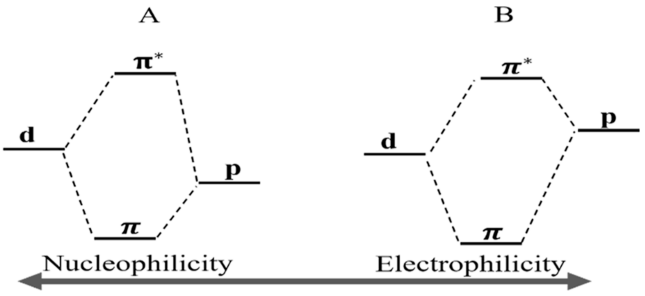

Figure 1. Metal nitride M dπ and N pπ bonding and anti-bonding molecular orbital characteristics can be manipulated to alter nitride reactivity. Adapted from ref 11.

complexes are known particularly for heavier 4d and 5d metals (Figure 2). Such geometric features about the central metal ion—coordination geometry, trans effect/influence, and so forth—will impact M≡N reactivity, but the magnitude of such effects is unknown. Supporting ligands can tune the acidity/basicity of the nitride ligand depending on their inherent donor/acceptor properties relative to the nitride ligand.[14] What is less clear from the literature, and which is thus a central question of this research, is how much support ligands impact nitride basicity using pK_b(N) as a quantifying parameter?

Implicit in the present research is the assumption that metal-nitride nucleophilicity, a kinetic concept, is correlated with nitride basicity, a related thermodynamic parameter. Recently, the Chirik group studied the reduction of MnN to form NH_3 by light-driven proton-coupled electron transfer. They calculated N−H bond dissociation free energies (BDFEs) of nitride, nitrene, amide, and ammine complexes by utilizing the B3LYP functional.[15] We hypothesize that evaluating metal nitride basicity can be a useful metric to assess their potential as catalysts for processes involving C−H and N−H bond activation. Recent trends in C−H activation research have sought to control C−H bond acidity [*i.e.*, pK_a(C−H)] to lower kinetic barriers for catalytic hydrocarbon functionalization.[10,11] By similar reasoning, it is posited that controlling the basicity of the metal-nitride active site—and indeed any metal−ligand catalytic site—can also be an effective strategy for tailoring catalytic reactivity.

COMPUTATIONAL METHODS

Accurate pK_a values of hydrocarbon C−H bonds in DMSO were obtained from B3LYP and BMK simulations, which were reported to reproduce experimental pK_a(C−H) values[16] to a precision of ±1 pK_a units[17] after application of a linear correction to account for the basis set and electron correlation effects, as well as the nature of the acid/base conjugate pair used to compute pK_a. Accordingly, the calculated free energies of metal nitrides, its conjugate base (a cationic metal imide), protonated acetonitrile, and acetonitrile in eq 1 were calculated using density functional theory—B3LYP functional—with the Gaussian 16 software package.[18] The visualization of optimized structures was made by using ChemCraft.[19] No linear corrections were applied as the main focus of the current paper is not absolute pK_b values, given that there is very scant experimental data with which to calibrate theory, but rather trends in metal-nitride basicity among series of complexes.

$$L_nMN + CH_3CNH^+ \rightleftharpoons L_nMNH^+ + CH_3CN \quad (1)$$

An acetonitrile continuum solvation model (SMD[20]) was employed, and free energies were calculated at 1 atm and 298.15 K. Metal nitride complexes and their conjugate bases, cationic metal imide complexes, as well as acetonitrile and protonated acetonitrile as the acid/base conjugate (see eq 1), were geometry optimized; these stationary points were characterized by the possession of no imaginary frequencies. Equation 2 is then used to calculate the metal nitride basicity from its protonation energy, which is defined as the pK_b(N) of the nitride ligand for a given complex.

$$pK_b = \frac{\Delta G}{RT\ \ln 10} \quad (2)$$

ΔG in kcal mol^{-1}, R = 0.00198 kcal/mol·K, T = 298.15 K.

Testing basis sets to calculate pK_b values of 128 nitride complexes of seven different transition metals and a wide range of ligands was challenging; four different basis sets of increasing size [6-31G, 6-311+(d,p), def2-svp, def2-tzvpp] were tested. The results suggest that there is a "best" basis set for each metal insofar as smooth convergence of geometry optimizations for these often large complexes is concerned. However, the def2-svp basis set will be the focus of this work since it is reasonably compact, allowing access to the study of larger complexes, and for most complexes, it afforded well-behaved geometry optimization starting from X-ray crystallographic coordinates after H atom positions were normalized using mercury.[21] As a typical example, calculated pK_b(N) for different basis sets, for example, 28 CrN complexes with the B3LYP functional are plotted and confirm that pK_b trends are not greatly affected by changing basis sets (Figure 3).

As an additional typical test, modestly sized nitrides were modeled with four different basis sets in conjunction with the B3LYP functional.

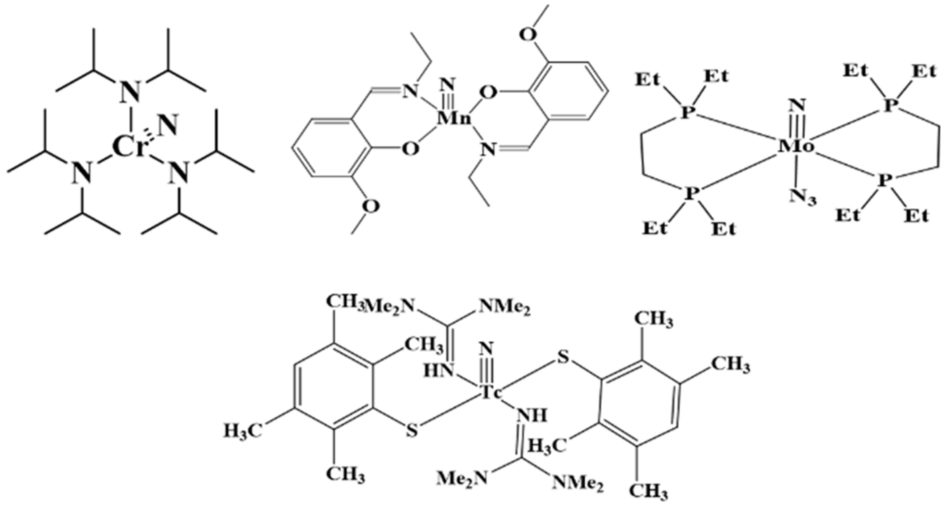

Figure 2. Structurally characterized metal nitride complexes show typical coordination geometries about the reactive MN core.

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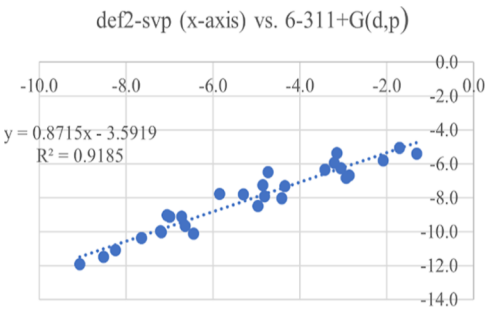

Figure 3. Calculated B3LYP/def2-svp/SMD-acetonitrile (*x*-axis) *vs.* B3LYP/6-311+G(d,p)/SMD-acetonitrile calculated pK_b values for 28 CrN complexes. A least-squares correlation line is plotted, and the equation is given.

The differences in calculated pK_b values were not significant (Table 1), especially when discounting the very small 6-31G basis set, which lacks

Table 1. Comparing Calculated pK_b(N) Values for VCl_2(quinuclidine)$_2$(N) with the B3LYP Functional Using 4 Different Basis Sets[a]

CCDC refcode: JACKON	
basis set	pK_b
6-31G	−7.8
6-311+G(d,p)	−10.2
def2svp	−9.3
def2tzvpp	−10.9

[a]For all simulations continuum solvent effects (acetonitrile) were incorporated *via* the SMD model.

polarization functions on main group elements. It is also worth mentioning that the RMSD in atomic positions indicated excellent agreement among optimized geometries with the different basis sets tested (Figure 4).

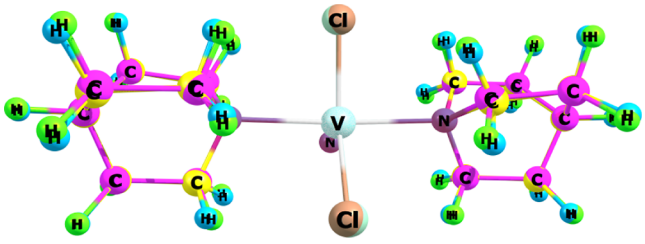

Figure 4. Overlay of optimized geometries of VCl_2(quinuclidine)$_2$(N) with the B3LYP functional and the def2-svp *vs* def2-tzvp basis sets with SMD-acetonitrile solvation. The RMSD in atomic positions is 0.09 Å.

Finally, four VN complexes found in the Cambridge Crystallographic Data Centre (CCDC) were modeled using the def2-svp basis set in conjunction with the BMK functional used in previous studies of organometallic pK_a values.[16,22] This functional showed imaginary frequencies for protonated LUWPUP and predicted a lower basicity for both JACKON and FURHIJ by ∼3 units compared with B3LYP (Table 2) using the same basis set. Thus, considering accuracy, reproduction of trends in nitride basicity, computational run time, and smooth convergence of geometry optimizations, the B3LYP/def2-svp/SMD-MeCN level of theory was deemed suitable to map pK_b trends in the current research.

RESULTS AND DISCUSSION

Although assessment of individual pK_b values for each transition metal nitride was performed in the current research, this paper will focus on pK_b trends for transition metal nitride complexes, which exhibited dependency on two main factors. The first factor was related to the transition metal: metal's identity (*e.g.*, 3d *vs.* 4d or Cr *vs.* Mn), its formal oxidation state, and the metal's coordination number. It will be seen that metal factors dominate basicity trends across the 3d and the 4d rows and also upon going from a 3d nitride to a 4d counterpart. The second factor was tied to supporting ligand properties; please note that only mono-nitride complexes were modeled, and most typically, the nitride is the only multiply bonded ligand present in the complexes studied. The ligand factor determines the pK_b range for a given transition metal for a series of nitrides. It will be seen that supporting ligands have a *substantial* impact on nitride basicity.

Vanadium Nitride Basicity. There are four neutral vanadium nitrides in the CCDC. These VN complexes have the central metal in its highest formal oxidation state (5+), and metal coordination numbers are either four or five. Since the current set of vanadium nitrides has only V^V ions, the range of pK_b is expected to largely reflect the supporting ligand factor. The calculated pK_b range of these VN complexes is −19.0 to −9.3, and the pK_b average (and sample standard deviation) is −13.7 ± 5.1. LUWPUP (Table S1 and Figure 5) is the complex

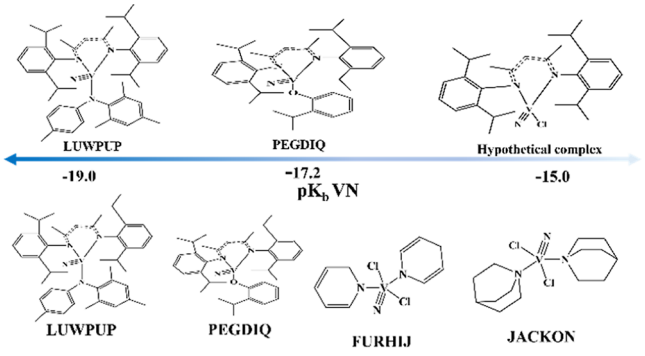

Figure 5. Examining ligand effects upon pK_b(N) of V^V complexes. Changing a single monodentate supporting ligand has major importance on nitride basicity.

Table 2. Computed pK_b Values of PEGDIQ, JACKON, FURHIJ, and LUWPUP (V-Nitrides) Using the def2-svp Basis Set with Two Functionals[a]

	pK_bBMK/def2-svp/SMD-MeCN	pK_bB3LYP/def2-svp/SMD-MeCN
PEGDIQ	−17.1	−17.2
JACKON	−5.9	−9.3
FURHIJ	−5.9	−9.3
LUWPUP[b]	−15.5	−19.0

[a]See Figure 5 for a picture of these complexes. [b]Two small imaginary frequencies, <75 cm^{-1}, persisted for the conjugate acid of LUWPUP despite repeated attempts to remove them.

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with the highest calculated $pK_b(N)$ value of −19.0; it is ligated by β-diketiminate, nitride, and anilide ligands. Interestingly, PEGDIQ shows a decrease in pK_b to −17.2, $\delta pK_b \sim 2$, upon substitution of a single supporting ligand, anilide by phenolate. The last two complexes—FURHIJ and JACKON—show a significant drop in pK_b (*i.e.*, are less basic), each computed to be −9.3; these complexes have a vanadium coordination number of five and possess two chloride ligands each. As such, the coordination environment at the vanadium center is substantially different from the first two cases considered, which is reflected in a substantial drop in basicity ($\delta pK_b > 8$).

Since the difference between LUWPUP and PEGDIQ is a single supporting ligand, it was decided to change this to Cl^- to further investigate ligand effects on $pK_b(N)$ values; the calculated pK_b value of this hypothetical complex was −15.0, $dpK_b \sim 4$, *versus* the anilide derivative. It is noteworthy that varied vanadium nitride forms have been used in the electrocatalytic nitrogen reduction reaction (NRR). Xu *et al.* tested vanadium nitride (VN) nanoparticles to catalyze electrochemical NRR.[23] Recent electrocatalytic studies of ammonia formation at vanadium oxynitride surfaces suggested a V-nitride intermediate in NRR;[24] this research also pointed to the acid/base properties of surface V sites as being critical to NRR activity. Finally, Lee *et al.* synthesized and characterized the nitrido-bridged dimeric vanadium(IV) complex.[25] These results provided an early indication that hard Lewis base supporting ligands can substantially decrease VN basicity (see Figure 5).

To evaluate oxidation state effects, hypothetical V^{IV} and V^{III} nitrides were built from FURHIJ, $VCl_2(quinuclidine)_2(N)$, by eliminating first one and then two Cl^- ligands, respectively, while maintaining an overall neutral complex. The $V^{III}N$ model is *substantially* more basic by 30 units, and the $V^{IV}N$ more basic by 20 units *versus* d^0-V^V-FURHIJ (Figure 6). This simple

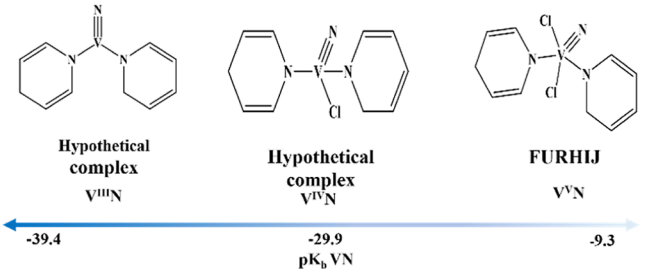

Figure 6. Increasing the basicity of vanadium nitride by lowering the metal's formal oxidation states through alteration of a known complex $VCl_2(quinuclidine)_2(N)$.

computational "experiment" showing markedly increased basicity of metal nitrides by lowering the metal's formal oxidation state inspired us to seek similar trends for other metals for which multiple formal oxidation states can be found for table nitrides.

Chromium Nitride Basicity. Forty five (45) chromium nitrides from the CCDC were modeled to determine their $pK_b(N)$ values. These CrN complexes have two formal oxidation states, corresponding to either +5 or +6. The pK_b range of CrN complexes is −17.4 to −0.4 and the average pK_b = −5.2 ± 3.1 (Figure 7). There are seven chromium(V) nitrides, all of which are five coordinate (Table S2). The average pK_b of Cr^VN complexes is −6.8 ± 5.1. Thirty eight chromium(VI) nitrides are four coordinate (Table S3); the average pK_b of

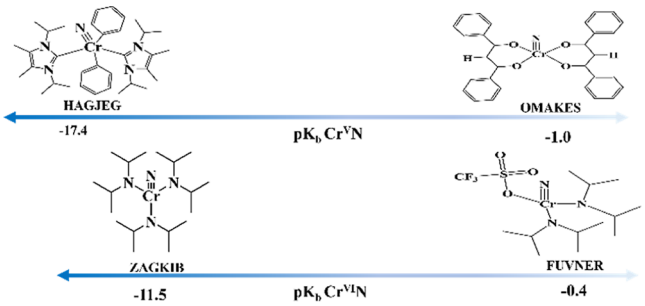

Figure 7. Comparing the calculated $pK_b(N)$ ranges for Cr^VN and $Cr^{VI}N$ complexes. CCDC refcodes are given.

$Cr^{VI}N$ = −5.0 ± 2.6. Analyzing chromium oxidation state effects reveals that Cr^VN has more negative pK_b values than $Cr^{VI}N$, that is, is more basic, $\delta pK_b \sim 2$, although the difference is commensurate with the sample standard deviations.

Analyzing the seven Cr^VN complexes in this study, symmetrical ligand environments around the Cr-nitride active site were typical. HAGJEG, $Cr(NHC)_2(Ph)_2(N)$, is by far the most basic Cr^VN complex studied, $pK_b(N)$ = −17.4 (NHC = N-heterocyclic carbene). The least basic Cr^V-nitride has a calculated $pK_b(N)$ = −1.0 [OMAKES, CrN(1,3-diphenylpropane-1,3-dionate)$_2$] (Figure 8). Interestingly, the series of

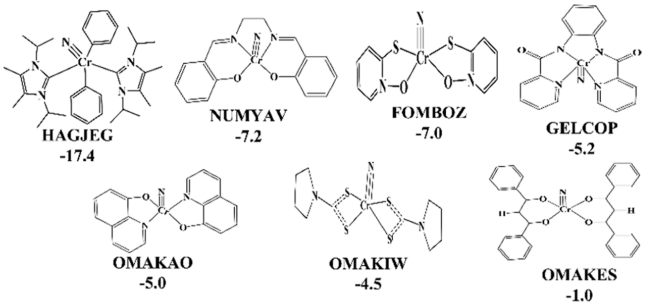

Figure 8. Chemical structures of the seven Cr^VN studied, along with their CCDC reference codes and calculated $pK_b(N)$ values, illustrate significant supporting ligand effects upon nitride basicity.

complexes having similar pK_b are all square pyramidal complexes (nitride in the apical position), with either a dianionic tetradentate or two anionic bidentate ligands, all with O- and N-based donors occupying these basal coordination sites. The more basic $Cr(NHC)_2(Ph)_2(N)$ has softer carbon-based ligands, that is, phenyl and N-heterocyclic carbenes.

To more methodically assess the impact of changing supporting ligand basicity upon MN basicity, a fixed motif was chosen for the $Cr^{VI}(N)(X)_3$ family of complexes. To control variation among supporting ligands in the examples from the CCDC, modeled complexes were built, differing only in a single, univalent X ligand (Figure 9). The basicity trend indicates that for main group supporting ligands, the pK_b values decrease from right to left and from higher to lower within the p-block. The displayed CrN pK_b trends agreed with similar calculations on VN complexes, that is, hard Lewis base supporting ligands tend to decrease nitride pK_b values. What is perhaps more important is that the overall impact on nitride basicity by changing a single ligand is huge, $\delta pK_b \sim 16$, from the most basic (X = PMe_2) to the least basic (X = Br^-). Such sensitivity in $pK_b(N)$ is commensurate with computed substituent effects in organic

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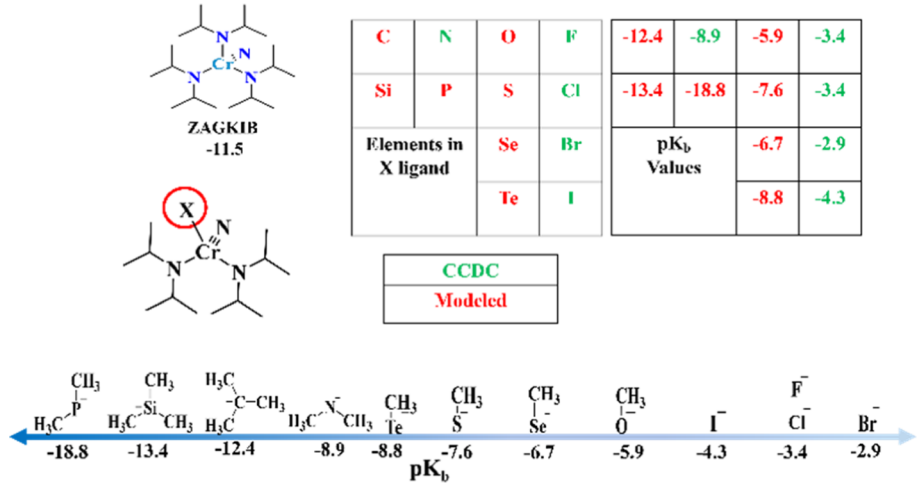

Figure 9. Calculated $pK_b(N)$ values for a series of $Cr^{VI}N$ complexes, examining the effect of modifying a single supporting ligand upon nitride basicity.

systems, for example, acetonitrile *versus* CF_3-CN, which yields a $\delta pK_b \sim 13$ at the level of theory employed herein.

Manganese Nitride Basicity. Fourteen complexes were found in the CCDC that contain Mn and one nitride group (Table S4). All of these complexes have Mn in the 5+ (d^2) formal oxidation state and four co-ligands, most typically anionic O- and N-based ligands. The calculated pK_b range is quite narrow for this set of MnN complexes, −5.5 to +4.9, with a sample average and standard deviation of 0.3 ± 2.5. Figure 10

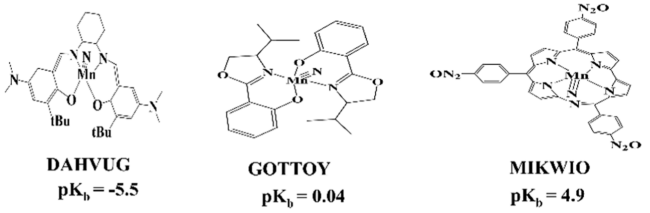

Figure 10. Chemical structures, CCDC refcodes, and calculated $pK_b(N)$ values of the most, neutral, and least basic Mn^VN complexes.

shows the most and least basic MnN complexes and one that is intermediate between the extremes. DAHVUG, a substituted MnN(salophen) complex, has a computed $pK_b(N)$ of −5.5. Approximately 10 units less basic is a MnN−porphyrin complex (refcode MIKWIO) (Figure 10). Despite the superficial structural similarity among the manganese-nitrides, there are still substantial differences in basicity within this series of complexes. In light of the work of Chirik *et al.*,[15] this suggests substantial scope to tune these and related earth-abundant metal nitrides for catalytic and electrocatalytic reactivity through the appropriate choice of supporting ligands.

The effect of metal upon nitride basicity was further tested in two ways. First, a hypothetical Mn^VN complex from a known Cr^V nitride, GELCOP, was generated (Figure 11). For the Cr^VN complex, the computed $pK_b = -5.2$, replacing the d^1-Cr^V with a d^2-MnN yielded $pK_b = +1.4$ (Figure 11), $\delta pK_b \sim 7$. Second, hypothetical V^VN and Cr^VN complexes were generated from MIKWIO, a Mn^VN−porphyrin complex with $pK_b = +4.9$, and GOTTOY [$Mn^VN(N-O)_2$] with $pK_b = +0.04$ (see Figure 10). The pK_b values shifted to negative values for the earlier metal ions (Figure 12). Thus, these calculations indicate metal identity/d-count as a dominant driver of nitride basicity with

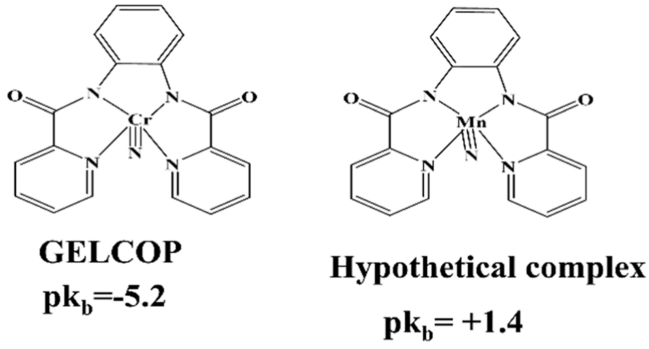

Figure 11. Modeling metal identity influence upon MN basicity. A hypothetical Mn^V complex derived from known GELCOP (Cr^VN) showed significantly reduced nitride basicity.

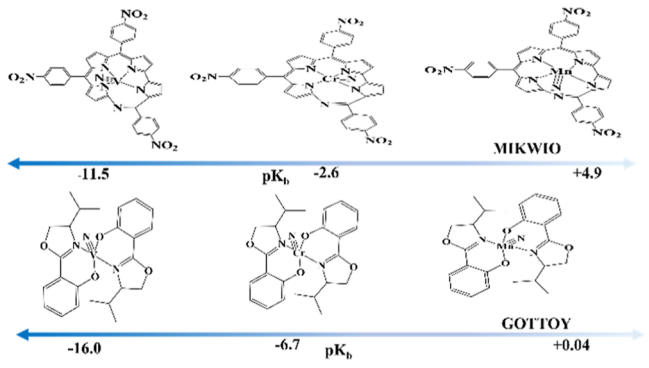

Figure 12. Modeling metal identity influence upon MN basicity; hypothetical V^V and Cr^V complexes derived from known manganese nitride complexes MIKWIO and GOTTOY. Earlier metal ions with the same formal oxidation state (5+ in the present case) yield a substantial increase in nitride basicity.

respect to other variations in the formal oxidation state and supporting ligand effects.

Trends in 3d Metal Nitride Basicity. From studying 3d transition metal nitrides, it seems clear that each has a different pK_b sensitivity, although the small sample size, particularly for *vanadium*, is limited by structurally characterized examples. Table 3 summarizes the calculated basicity of 3d nitrides as quantified by $pK_b(N)$, and in combination with the metal-replacement computations, shows that nitride basicity decreases

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Table 3. Summary of Calculated 3d Basicity Trends for 3d Metal Nitride Complexes; Stdev = Sample Standard Deviation in pK_b(N)

transition metal	sample size	pK_b (average)	stdev
V	4	−13.7	5.1
Cr	45	−5.2	3.1
Mn	14	0.3	2.5

from left to right in the 3d series. From the 63 samples and modeled hypothetical derivatives thereof, the metal identity factor emerges as a deciding factor in nitride basicity, with supporting ligand and formal oxidation state (and d-count) as secondary but still significant factors, by which one may be able to tune the acid/base properties of these important catalytic active sites *via* changing the hard/soft base character of the supporting ligands.

Niobium Nitride Basicity. In the CCDC, a neutral niobium nitride was not found using the search criteria employed; hence, five MoN complexes (*vide infra*) were transmuted to their niobium congeners in order to at least clearly elucidate niobium nitride basicity trends. The five complexes were selected to assess metal oxidation state impact and to probe supporting ligand effects. The results support the proposal that niobium nitrides are more basic, by ∼13 pK_b units, than the corresponding Mo nitrides, further confirming that metal identity dictates nitride basicity (Figure 13, Tables S5−S7).

Molybdenum Nitride Basicity. Thirty seven molybdenum nitrides, having three metal formal oxidation states (4+, 5+, and 6+), were modeled: pK_b(N) = −15.8 ± 8.7, with a wide range of nitride basicities from −32.3 to 4.5. Specifically, there were eight Mo^{IV} nitrides having either coordination number four or five, two Mo^{V} nitrides one with coordination number five and the other with coordination number six , and 27 Mo^{VI} nitrides with metal coordination numbers of four to seven, but for which six coordination was most prevalent. Table 4 collects the pK_b values for the various subsets of the large MoN dataset. As can be deduced from Table 4, average pK_b values decrease with increasing oxidation states of molybdenum, $\delta pK_b \sim 8$ units for one unit change in the formal oxidation state! Looking at the eight Mo^{IV} nitride pK_b values indicated that the presence of phosphine co-ligands—soft Lewis bases—keep nitride basicity high even in the presence of halide ligands (Table S6). It is

Table 4. Summary of Nitride Basicity for 42 Mo-Nitrides Extracted from the CCDC; Stdev = Sample Standard Deviation in pK_b(N)

metal/metal ion	sample size	pK_b (average)	stdev	range
Mo	37	−15.9	8.2	−32.3 to +4.5
Mo^{IV}	8	−27.5	3.3	−32.3 to −24.3
Mo^{V}	2	−18.0	2.6	−19.8 to −16.1
Mo^{VI}	27	−12.0	6.1	−22.7 to +4.5

interesting to note that SECRUO and BULXOV differ only in the phosphine substituents, which resulted in a change in MoN basicity of $\delta pK_b \sim 3$ (Figure 14). The more electron-donating alkyl phosphine yields a more basic nitride *versus* the relatively electron-withdrawing aryl phosphine.

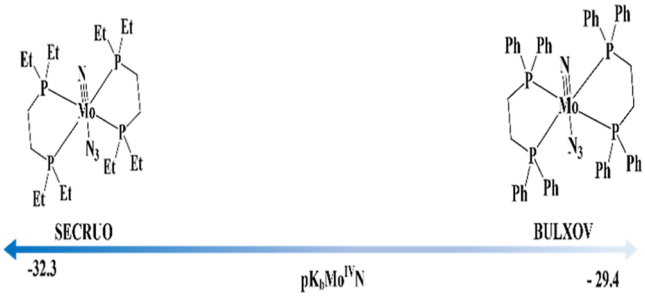

Figure 14. SECRUO the most basic $Mo^{IV}N$ and BULXOV calculated pK_b(N) values highlight the sensitivity of the acid/base properties of the metal nitride active site to phosphine substitution.

Technetium Nitride Basicity. Seventeen Tc nitrides with metal oxidation states of either +5 or +6 were modeled, pK_b = −5.8 ± 4.4 and a wide pK_b range from −13.8 to +6.0. There were 15, five-coordinate Tc^{V} nitrides with average pK_b = −6.9 ± 3.8 (Table S9). The most basic Tc-nitride (VERGEE) had a calculated pK_b = −13.8 with imine and thiolate supporting ligands; the least basic $Tc^{V}N$ possessed phosphine, thiocyanate, and acetonitrile co-ligands [CETKUH, pK_b(N) = −1.6] (Figure 15).

The two Tc(VI) nitrides modeled yielded an average pK_b(N) = −1.0 ± 9.8 (Table S10). This is a significant standard deviation for a sample size of two (FAPTAS, pK_b = −7.9, and

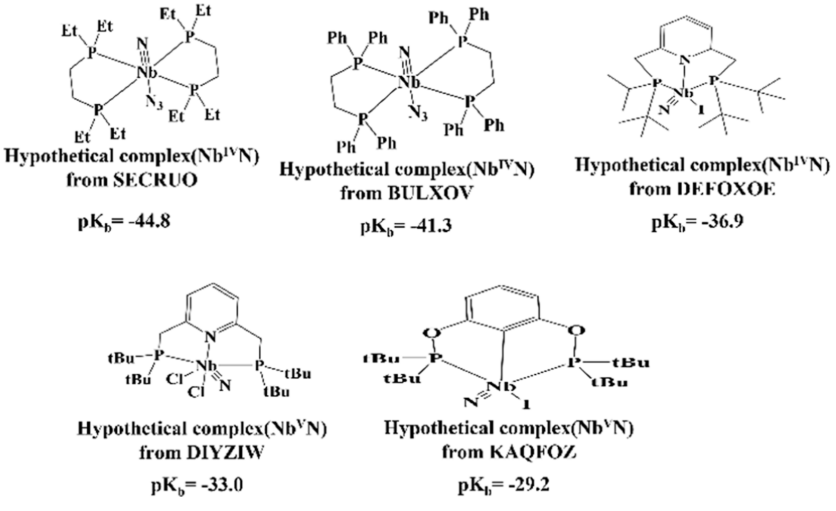

Figure 13. Chemical structures and calculated pK_b(N) values of five hypothetical Nb nitride complexes.

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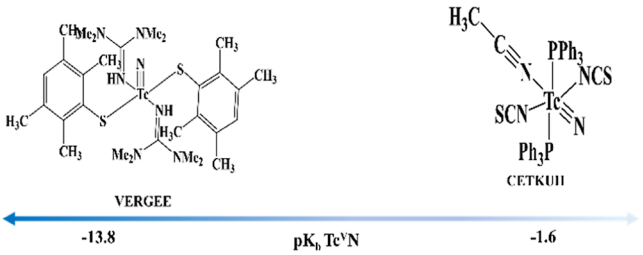

Figure 15. Upper and lower bounds of the calculated Tc(V) nitride pK_b(N) values showed Tc-nitride sensitivity to changing supporting ligands.

WEWNUH, pK_b = 6.0) (Figure 16); Tc^{VI}N showed a negative pK_b value in the presence of phosphine co-ligands and positive

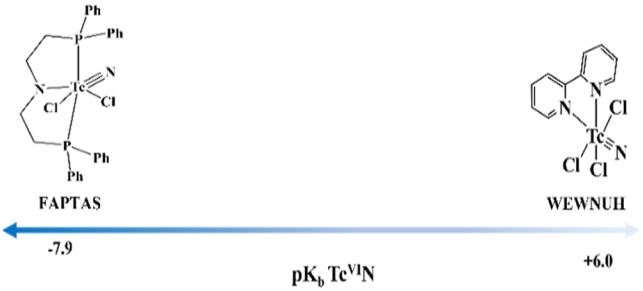

Figure 16. Tc(VI) nitride basicity value showed sensitivity to geometry, coordination, and the supporting ligand environment.

pK_b values in the absence of phosphines (Figure 16). For the most basic Tc^{VI}N modeled, the metal is six-coordinated and the N is trans to the pyridine arm of a bipy ligand. A hypothetical geometric isomer of WEWNUH in which the nitride is trans to a chloride displayed increased basicity (δp$K_b \sim 3$) and produced a calculated pK_b = +2.9. Thus, nitride basicity is sensitive to changing the coordination environment, in the present case the trans influence. Thus, it should be possible to utilize the synergy among metal identity, supporting ligand types and geometric features to tune metal nitride basicity for a specific catalytic application.

Ruthenium Nitride Basicity. Six Ru nitrides with metal formal oxidation states of either 4+ or 6+ were modeled, yielding a calculated pK_b(N) = 1.9 ± 18.1. As with technetium, ruthenium nitrides show a very large calculated pK_b range from −25.9 to +14.7. There were two Ru(IV)-nitrides with four coordination, average pK_b = −24.1 ± 2.5 (Table S11). As before, relatively high pK_b values are computed in the presence of phosphine co-ligands. For the four Ru(VI) nitrides, pK_b = 11.4 ± 4.4 (Table S12). A significantly positive pK_b was exclusive to a Ru(VI) nitride in the current work (Figure 17). Furthermore, we modified MAMVIG Ru^{IV}N to a Ru^{VI}N by the formal oxidative addition of Cl_2 [Ru(pincer)N + Cl_2 → Ru(pincer)$(Cl)_2$N]; the hypothetical Ru^{VI}N complex produced a pK_b(N) = +1.7, δpK_b(N) ∼ 24, which reinforces the strong effect of the metal formal oxidation state upon metal-nitride basicity.

4d Metal Nitrides. Each of the four metals studied in the 4d row displays different pK_b(N) sensitivity insofar as can be judged by the sample standard deviations. Table 5 summarizes the basicity trends of 4d-metal nitride complexes: basicity decreases from left to right, which was the same trend computed for 3d metal nitride complexes. The sample standard deviations are higher than for the corresponding 3d metals, which suggest

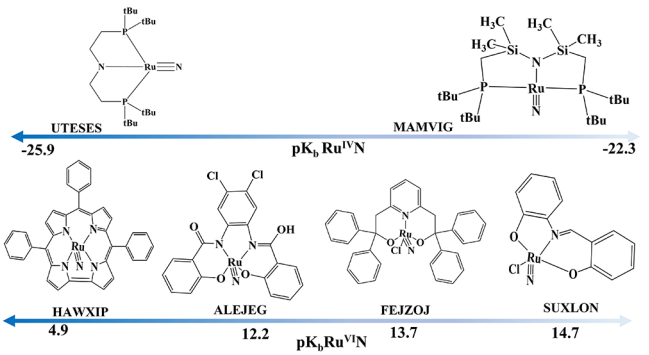

Figure 17. Synergism between metal high formal oxidation state and strong basic supporting ligands generated very weakly basic Ru^{VI}N with positive pK_b(N) values.

Table 5. Summary of 4d Basicity Trends for Mo, Tc, and Ru Nitrides; Stdev = Sample Standard Deviation in pK_b(N)

transition metal	sample size	pK_b (average)	stdev
Nb	5	−37.6	6.3
Mo	37	−15.9	8.2
Tc	17	−5.9	4.4
Ru	6	−0.4	18.7

greater sensitivity of 4d-nitrides to their chemical environment, which may be a reflection of the greater covalency of 4d-ligand *versus* 3d-ligand bonds and hence more effective communication of inductive effects from the supporting ligands to the metal-nitride active site.

SUMMARY AND CONCLUSIONS

The vital role of nitride complexes in the activation and functionalization of C−H and N−H bonds and other catalytically important transformations depends implicitly on the ability to tune the nitride ligand's acidity/basicity and electrophilicity/nucleophilicity accordingly. To this end, a map of 3d and 4d metal-nitride basicity was developed using computed pK_b values for structurally characterized complexes to quantify metal and ligand effects in determining the properties of metal-nitride active sites.

In the current research, the pK_b(N) values of 128 transition metal nitride complexes containing 7 different transition metals were computed to determine nitride basicity trends across the 3d and 4d rows and upon going from lighter to heavier metals. From analyzing the calculated pK_b values of known, structurally characterized complexes as well as those of hypothetical complexes derived from them, this research demonstrates that the main determining factors are the metal primarily and the supporting ligands secondarily. Exploiting these factors should allow one to tune metal nitride basicity within a specific regime for a particular chemical or catalytic application.

The present results showed that metal identity—and especially the d-count of the metal—yields decreasing nitride basicity across the 3d and 4d rows from left to right and increasing basicity going from a 3d metal-nitride to its 4d counterpart (*e.g.*, V → Cr for the former and V → Nb for the latter). The formal oxidation state of the metal also significantly affects basicity; it is seen that nitride basicity [as measured by pK_b(N)] decreases by between 2 and 9 units by making the metal's formal oxidation state more positive (Table 6).

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Table 6. Summary of Calculated pK_b Data for Cr, Mo, Tc, and Ru Complexes in Different Oxidation States[a]

metal	formal oxidation state	# complexes	pK_b average ± stdev	range pK_b
Cr	+5	7	−6.8 ± 5.1	−17.4 to −1.0
	+6	38	−4.9 ± 2.6	−11.5 to −0.4
Mo	+4	8	−27.5 ± 3.3	−32.3 to −24.3
	+5	2	−18.0 ± 2.6	−19.8 to −16.1
	+6	27	−12.0 ± 6.1	−22.7 to +4.5
Tc	+5	15	−6.9 ± 3.8	−13.8 to −1.6
	+6	2	−1.0± 9.8	−7.9 to +6.0
Ru	+4	2	−24.1 ± 2.5	−25.9 to −22.3
	+6	4	11.4 ± 4.4	+4.9 to +14.7

[a]Their pK_b average, sample standard deviation, and pK_b ranges show the significant impact of the transition metal formal oxidation state in determining the basicity of transition metal nitrides.

Although caution is necessary given the differences in sample sizes studied, 4d metal nitrides (Nb, Mo, Tc, and Ru) showed higher sample standard deviations, Table 5, than 3d nitrides, Table 3, which reflects the higher sensitivity of these metals in comparison to their lighter counterparts. One may hypothesize that this is a reflection of the greater covalency inherent in M_{4d}—L bonding than M_{3d}—L bonding. Related to this, 4d metals are generally able to stabilize nitrides in a variety of formal oxidation states, while 3d metal nitrides tend to be dominated by a single formal oxidation state on the metal.

Supporting ligands also significantly impact nitride basicity. It was computed that hard Lewis ligands such as chloride significantly decrease nitride basicity, while softer Lewis bases such as amines/imines and especially phosphines increase nitride basicity. For example, a Cr^V-nitride with a triflate co-ligand (FUVNER, Figure 7) has a calculated pK_b(N) of −0.4, becoming much more basic upon replacement of this single ligand with N^iPr_2 (ZAGKIB, pK_b = −11.5), $\delta pK_b \sim 11$. Nitride basicity is even sensitive to changes in ligand substituents (*e.g.*, Et *.vs* Ph bonded to a phosphine P), *cf.* (Figure 14), $\delta pK_b \sim 3$ less basic upon changing from depe to more electron-withdrawing dppe. Finally, scrutiny of $Tc^{VI}N$ complexes (Figure 16), ($\delta pK_b \sim 14$) suggests that the coordination environment of the metal-nitride fragment can also significantly alter basicity, for example *via* the trans influence.

The datasets in this research provide a useful starting point to address future questions related to tuning nitride basicity and its correlation with reactivity. For example, one may propose that there is a specific metal nitride basicity range to activate specific bonds, for example, the C−H bond of methane or the N−H bond of ammonia. How are the mechanisms by which metal nitrides activate such bonds determined by nitride basicity? Future works will focus on better utilizing metal−ligand active site basicity data to identify improved systems for C−H and N−H bond functionalization by metal nitride and related multiply bonded catalytic intermediates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01812.

Complete data tables of the CCDC refcodes of all the complexes, computed pK_b values, chemical structures, and Cartesian coordinates of all optimized nitride complexes and their conjugate acids (PDF)

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Notes

The authors declare no competing financial interest.

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