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A General Route to Labile Niobium and Tantalum d^0 Monoimides. Discussion of Metal−Nitrogen Vibrational Modes

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Reaction of $TaCl_5$ with 2 equiv of an amine in the presence of sodium silicate and pyridine affords $Ta(NR)Cl_3(py)_2$ in good yield. Reaction of $NbCl_5$ with $ZnCl_2$ followed by addition of an amine RNH_2 and pyridine affords $M(NR)Cl_3(dme)$ (dme is 1,2-dimethoxyethane). For niobium this reaction proceeds smoothly regardless of the amine but is ineffective with tantalum and alkyl amines. An alternative route involves reaction of $TaCl_5$ with 3 equiv of RNH_2 to form $[RNH_3]_2[Ta(NR)Cl_5]$, followed by reaction of this salt with $ZnCl_2$ in the presence of dme. The molecular structure of $Nb(N^tBu)Cl_3(dme)$ (formula $C_8H_{19}Cl_3NNbO_2$) was determined by X-ray crystallography (monoclinic space group Cc with $a = 30.565(4)$ Å, $b = 7.2406(13)$ Å, $c = 13.915(2)$ Å, $\beta = 90.626(7)°$, $V = 3079.4(8)$ Å^3, $Z = 8$). The Nb−N bond length is 1.72 Å with a Nb−N−C bond angle of 177° in a distorted octahedral structure. In order to characterize the M−N stretching frequencies in these compounds, IR data for each compound are compared with calculated stretching frequencies using the commercially available Spartan calculation package. These experiments reveal that there is no real M−N stretching frequency in these imidos. Rather, the M−N modes are strongly coupled to N−C and C−H or C−C modes in these imidos. IR active modes are observed at ~1260 cm^{-1} for tantalum alkyl imidos and ~1350 cm^{-1} for tantalum aryl imidos. These correspond to a Ta−(N−C) stretch coupled to the CR_3 umbrella deformation.

Introduction

Transition metal compounds containing imido ligands (RN^{2-}) have become extremely important in inorganic chemistry.[1] These divalent ligands potentially provide a total of three bonds to a metal center, one σ and two π, depending on the ability of the metal to form a total of three bonds to any given imido ligand.[1] Early routes to Ta and Nb imido compounds involved reduction of acetonitrile with MCl_4 and zinc[2] or reaction of tantalum neopentylidenes with imines in a Wittig-like reaction.[3,4] This method could be fairly general since a variety of imines could be used, but the expense of preparing $Ta(CH^tBu)Cl_3(thf)_2$, the precursor, is undesirable.

Somewhat later, Nielson reported that silated alkylamines react with MCl_5 (M = Nb, Ta) to give the dimeric (bridging halide) compounds shown:[5]

$$\mathrm{NbCl_5 + xs\ Me_3SiNHCMe_3 \longrightarrow [(Me_3CN)NbCl_2(NH_2CMe_3)(\mu\text{-}Cl)]_2} \tag{2}$$

The coordinated amine in these compounds can be replaced with small phosphines, but the resulting species were not isolated due to their oily, tacky nature. This is particularly problematic since exchange of the amine with other bases is often difficult, and its presence obviously detracts from the usefulness of these materials in the synthesis of alkylated compounds. A similar reaction with silylarylamines in the presence of thf or dme (1,2-dimethoxyethane), however, affords the etherated compounds.[6] In this case, the aniline derivative produced is labile enough to be replaced with the weakly coordinating dme. These materials are much more useful for subsequent derivatization.[4,6,7]

$$\mathrm{TaCl_5 + 2\ Me_3SiNHAr \xrightarrow{tol/dme} (ArN)TaCl_3(dme) + ArNH_2} \tag{3}$$

Finally, some clever reactions involving hexamethyldisilazane with the metal halides afford silylimidos.[8] This result is directly analogous to the above reactions and valuable due to the instability of Me_3SiNH_2,[9] making it impossible to prepare the imido compound using the methods described below.

$$\mathrm{NbCl_5 + 2\ (Me_3Si)_2NH \longrightarrow [(Me_3SiN)NbCl_2(NH_2SiMe_3)(\mu\text{-}Cl)]_2} \tag{4}$$

Our interest in group 5 monoimido compounds stems from the extremely interesting properties of their photoexcited states.[7,10−12] Examples of luminescence from solutions of these compounds at room temperature have been reported recently, with emission quantum yields ranging from 0.25 to 0.0001 and emission lifetimes from 20 μs to 20 ns.[10,11] We have found that the alkyl substituent has a substantial effect on the absorption and emission energies in these compounds.[10,11,13]

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Therefore access to a variety of these imidos is important in probing electronic structure. In our search for labile, electronically simple materials, we sought routes other than those above which lead to monoimido compounds containing simple, labile ligands, specifically, $M(NR)Cl_3(dme)$, directly from RNH_2. We were also interested in modifying the Wigley procedure, eq 3, in order to avoid generation of the relatively expensive $Me_3SiNHAr$ prior to reaction with the metal halide. Additionally, the usefulness of the above methods will be limited by our ability to prepare silated amines. We have found a surprisingly simple reaction sequence that avoids these problems and is effective for each amine we have investigated.

Finally, we are interested in establishing the metal−nitrogen stretching frequency in these compounds in order to judge the variation of the metal−nitrogen interaction; there has been significant controversy over the location of these absorptions in IR spectra.[1] A number of assignments on group 5 imido compounds report two absorptions that can be attributed to M−N modes.[1,14] There is reportedly[1] a low-frequency mode in the range 900−1000 cm^{-1} and a higher energy mode between 1100 and 1350 cm^{-1}. Strähle[14] showed that the M−N stretch moved from 1107 to 963 cm^{-1} upon changing X from Cl to I in the series $(XN)VCl_3$.[15] The lower frequency mode changed from 510 to 390 cm^{-1} in the same comparison. Furthermore, Strähle predicts higher energy MN modes in alkylimido compounds.[14] Several papers corroborate this conclusion; however, Osborne makes an opposite assignment in $(PhN)VCp_2$, based on ^{15}N labeling experiments. The NC mode is assigned to a 1330 cm^{-1} absorption, while the 934 cm^{-1} absorption is assigned to the MN absorption (Cp_2M compounds may be anomalous). We hope to clarify this argument.

Results

The reaction of interest, eq 5, is a simple one, but the relatively poor solubility these $M(NR)Cl_3L_2$ compounds makes purification difficult, even though conversion is generally high.

$$TaCl_5 + RNH_2 + 2\,L \longrightarrow Ta(NR)Cl_3L_2 + 2\,HCl \quad (5)$$

We report two general ways of preparing these compounds by reaction of primary amines with MCl_5 (M = Nb, Ta). One approach is to use an insoluble inorganic base to remove the byproduct HCl. The other is to use a combination of a soluble organic base and zinc chloride for the same task. In each case, precipitation of the salt byproducts from the reaction mixture is key to purification of the imido product.

Synthesis of Tantalum Imides. Generally, results for the alkylamines were fairly consistent and somewhat different from the aniline derivatives. As examples, three compounds will be discussed, $Ta(NR)Cl_3L_2$ (R = CMe_2Et (tA), L = py (**1a**), L = $^1/_2$ dme (**1c**); R = C_6H_5, L = $^1/_2$ dme (**7**)).

Inorganic Bases as Proton Acceptors. Addition of anhydrous Na_2SiO_3 to a solution of $TaCl_5$ in Et_2O/toluene followed by 1 or 2 equiv of *tert*-amyl amine ($tANH_2$) results in a pale yellow to yellow-green solution. Pyridine is then added to give a yellow solution. After the mixture is stirred overnight at ambient temperature, the product is filtered from the insoluble salts, and excess amine is readily removed after concentration *in vacuo* with a pentane wash. This procedure yields $Ta(NtA)Cl_3(py)_2$ (**1a**) as a pure, slightly yellow powder. Consistently, use of only 1 equiv of amine results in yields of 40−50%, but using 2 equiv increases the yield to ~70%. We tried a number of inorganic bases, including K_2CO_3, $Na_2B_4O_7$, and CaH_2, but these reactions result in yields of 50% or less. Each of the tantalum alkylimido bis(pyridine)s, with the exception of compounds **5a** and **6a** (R = $CMe_2CH_2CMe_3$ and *n*-Bu), can be prepared directly from the amine and $TaCl_5$ in reasonable isolated yields using Na_2SiO_3. Unfortunately, attempts at preparation of the dme adducts of alkylimidos using this method were unsuccessful (<20% yield).

$$TaCl_5 + 2\,RNH_2 + 2.5\,Na_2SiO_3 + 2\,py \longrightarrow \underset{60\text{ - }80\,\%\text{ yield}}{Ta(NR)Cl_3py_2} \quad (6)$$

Use of Amines as Proton Acceptors. On the basis of the related syntheses of groups 6[16,17] and 7[18,19] imidos, it seemed reasonable that pyridine or triethylamine could be used as an external base in these reactions. Addition of, for example, a solution of aniline ($PhNH_2$; 1 equiv) and pyridine to $TaCl_5$ in Et_2O/toluene does not result in formation of the imido. However, pretreatment of the tantalum solution with 2 equiv of $ZnCl_2$ results in formation of a fine white precipitate which dissolves upon addition of the amine mixture and a high yield of $Ta(NPh)Cl_3(dme)$ (**7**) after filtration and recrystallization (eq 7). This method also affords compounds **8**−**12** (R = 2,6-$^iPr_2C_6H_3$ (Ar), 2,6-$Me_2C_6H_3$ (Ar′), 4-CNC_6H_4, 2-naphthyl, 2-anthryl) in high yield.

$$TaCl_5 + ArylNH_2 + 2\,ZnCl_2 + 2\,py \xrightarrow{dme} Ta(NAryl)Cl_3(dme) \quad (7)$$

Perhaps the most valuable success of this route is in the synthesis of compounds **11** and **12**. Thus, 2-aminonaphthalene ($NapNH_2$) and 2-aminoanthracene ($AnthNH_2$) can be readily converted into the corresponding imidos **11** and **12**, respectively in good yield. On the basis of these observations, this method should smoothly provide arylimidos of the form Ta(NAryl)-Cl_3(dme) regardless of the amine. Importantly, the lability of the dme ligand makes these compounds valuable starting materials for synthesis of other monoimido compounds.[4,6,7] For example, addition of py to $Ta(NAr)Cl_3(dme)$ (**8**)[12] affords $Ta(NAr)Cl_3(py)_2$ quantitatively.

Unfortunately, this method is unsuccessful for synthesis of the corresponding alkylimidos using dme as the Lewis base, $Ta(NR)Cl_3(dme)$, **1c**−**6c**. In some cases, the desired compound could be isolated in low yields (<20%). Fortunately, addition of 3 equiv of $tANH_2$ to a solution of $TaCl_5$ in Et_2O/toluene quantitatively affords the salt $[tANH_3]^+{}_2[Ta(NtA)Cl_5]^{2-}$ (**1b**), eq 8. A related transformation has been observed recently for arylamines.[20] This salt can then be treated with $ZnCl_2$ in the presence of dme to afford $Ta(NtA)Cl_3(dme)$ (**1c**) in 86% yield, eq 9. Reactions with other alkylamines also proceed in high

$$MCl_5 + 3\,RNH_2 \longrightarrow [RNH_3]^+{}_2\,[M(NR)Cl_5]^{2-} \quad (8)$$

$$[RNH_3]^+{}_2\,[M(NR)Cl_5]^{2-} + ZnCl_2 + dme \longrightarrow M(NR)Cl_3(dme) \quad (9)$$

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yield to form the pentachloride salts (**2b**−**6b**) and, subsequently, the corresponding dme adducts (**2c**−**6c**).

This final method is highly desirable since the amine substituent does not seem to affect the course of the reaction and the product, formed in good yield, is a labile, useful starting material for further syntheses.

Synthesis of Niobium Imides. Our results for the Nb compounds differ somewhat. We have been successful in preparing all of the niobium imidos according to eq 7. Both the pyridine and dme adducts are thus available directly from $NbCl_5$, the amine, pyridine or NEt_3, and $ZnCl_2$ in high yield. Reaction of alkylimido pentachloride salts with $ZnCl_2$ and dme also results in good yields of $Nb(NtA)Cl_3(dme)$ (**13c**) and the other alkylimides. This method affords the desired compounds in somewhat better yield. Finally, attempts at using inorganic bases to prepare the niobium imidos generally fail, particularly using CaH_2 as base. We attribute this to the greater tendency for Nb to reduce compared to Ta and to the greater lability of second-row elements compared to their heavier congeners.

Spectroscopic Properties. The geometry of these species is clear from ^1H NMR and consistent with previous observations by Wigley.[6] In **1a**, for example, the tA geminal methyl groups are equivalent as are the geminal protons on the methylene carbon, indicating a plane of symmetry containing the Ta−N−C axis. The pyridine ligands are inequivalent, however, and one of the pyridines exchanges rapidly on the NMR time scale with free pyridine in solution. It seems clear then that the chlorides are all *cis* to the imido group and that the pyridines are *cis*. Presumably, the pyridine *trans* to the imido is the one which exchanges with free pyridine. NMR data for all of the bis(pyridine) adducts are similar. Furthermore, data for the dme adducts are also consistent with the *cis*,*mer*-$M(NR)Cl_3L_2$ geometry.

Molecular Structure of $Nb(N^tBu)Cl_3(dme)$. One of the earliest structural studies on a transition metal imido compound involved the dimeric diimido Nb^V compound $[Nb_2Cl_8(NCMe)_2(\eta^2\text{-}NC(Me)C(Me)CN)]^{2-}$, which was prepared by reduction of $NbCl_4$ in acetonitrile.[2] This was taken advantage of in a later paper on synthesis of bridging imidos from imines using Nb^{IV}.[21] A small number of other structures of group 5 imido compounds exist formulated as $[M(NR)Cl_4L]^-$, where R is an alkyl substituent. Structures of compounds with weakly coordinating Lewis bases, such as THF or dme, are rare. Also, we are interested in structural effects on excited state properties. Therefore, we crystallographically characterized the molecular structure of $Nb(N^tBu)Cl_3(dme)$ (**14**), shown in Figure 1. There are two chemically identical molecules (see Experimental Details), of which molecule A is discussed. Crystallographic data and relevant bond lengths and angles are listed in Tables 1 and 2, respectively. The structure is intriguing in a number of ways. The niobium−nitrogen bond length is 1.722(7) Å, short for an imido ligand, but within ∼0.04 Å of the average (∼1.76 Å).[1] As expected, the Nb−N−C angle is essentially linear, 176.8(7)°. Also typical of compounds containing multiply bonded ligands, the equatorial ligands are "pushed back" from the equatorial plane by the electronic influence of the imido, resulting in N−Nb−L angles of between 95 and 100°. The halides are slightly distorted from perfect octahedral geometry in the plane as well; Cl(1)−Nb−Cl(2) and Cl(3)−Nb−Cl(2) angles are 94.92(10) and 92.93(11)°, respectively. This occurs even though the equatorial Nb−O bond is significantly shorter (by 0.2 Å) than the Nb−O bond *trans* to the imido. The latter may be attributed to a *trans* influence and has been observed in the structure of closely related $Mo(N)Cl_3(dme)$.[22]

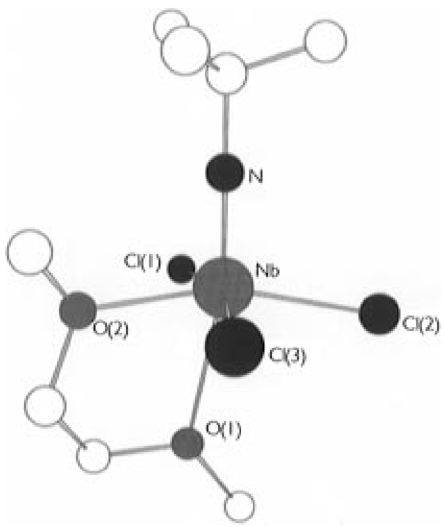

Figure 1. Molecular structure of $Nb(NCMe_3)Cl_3(dme)$ (**14**).

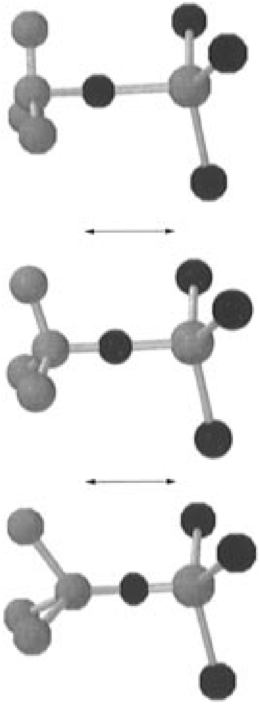

Figure 2. Assigned [Ta−*N*−*C*] medium frequency vibrational mode (ν = 1171 cm^{-1}) calculated for $Ta(NCMe_3)Cl_3$. The magnitude of the vibration is exaggerated for clarity.

Table 1. Crystallographic Data for $Nb(NCMe_3)Cl_3(dme)$ (**14**)

formula	$C_8H_{19}NO_2Cl_3Nb$
fw	360.50
cryst system	monoclinic
space group	*Cc*
$a-c$, Å	30.565(4), 7.2406(13), 13.915(2)
β, deg	90.626(7)
V, Å^3	3079.4(8)
Z	8
D_x, g cm^{-3}	1.555
μ(Mo Kα), cm^{-1}	12.9
λ, Å	0.710 73
T, K	249
$R(F)$, $R(wF^2)$,[a] %	3.92, 10.25

[a] Quantity minimized = $R(F) = \sum\Delta/\sum(F_o)$; $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $\Delta = |F_o - F_c|$.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $Nb(NCMe_3)Cl_3(dme)$ (**14**)

	molecule A	molecule B
Lengths		
Nb−N	1.722(7)	1.730(8)
Nb−Cl(1)	2.400(3)	2.385(3)
Nb−Cl(2)	2.366(3)	2.361(3)
Nb−Cl(3)	2.424(3)	2.421(3)
Nb−O(1)	2.389(6)	2.375(7)
Nb−O(2)	2.187(6)	2.208(6)
N−C(5)	1.463(1)	1.463(1)
Angles		
Cl(1)−Nb−Cl(2)	94.9(1)	95.7(1)
Cl(1)−Nb−Cl(3)	162.2(1)	162.4(1)
Cl(2)−Nb−Cl(3)	92.9(1)	92.1(1)
Cl(1)−Nb−N	95.8(3)	95.9(3)
Cl(1)−Nb−O(1)	81.4(2)	81.7(2)
Cl(1)−Nb−O(2)	85.4(2)	85.7(2)
Cl(2)−Nb−N	100.8(3)	100.6(3)
Cl(2)−Nb−O(1)	91.0(2)	90.4(2)
Cl(2)−Nb−O(2)	161.7(2)	161.6(2)
N−Nb−O(1)	168.1(3)	169.0(3)
N−Nb−O(2)	97.4(3)	97.5(3)
O(1)−Nb−O(2)	70.9(2)	71.7(2)
Nb−N−C	176.8(7)	176.5(7)

Table 3. Calculated Energies in cm^{-1} for Ta−N−C Modes in $Ta(N)Cl_3$, $Ta(NH)Cl_3$, $Ta(NMe)Cl_3$, $Ta(NCMe_3)Cl_3$, $Ta(NPh)Cl_3$, and $Ta(NCMe_3)Cl_3(dme)$

compound	Ta−N	sym stretch	alkyl deformation	antisym stretch	N−C−R bending
$Ta(N)Cl_3$	1120				
$Ta(NH)Cl_3$			1083	3569	
$Ta(NCH_3)Cl_3$		661	1296	1508	989 (E)
$Ta(NPh)Cl_3$		710	1211	1475, 1645	993, 1076
$Ta(NCMe_3)Cl_3$		634	1171	1500	1292, 1292
$Ta(NCMe_3)Cl_3(dme)$		635	1171	1499	

Infrared Data and the Metal−Nitrogen Stretching Frequency. There has been significant controversy over metal−nitrogen stretching frequencies in transition metal imido compounds.[1,23] The main problem is that this mode is strongly coupled to the N−C stretching frequency in these compounds.[14] A secondary problem that we have discovered is significant coupling to carbon−carbon or carbon−hydrogen modes in the alkyl group.[13] In order to gain insight into this problem, we have carried out semi-empirical calculations using the Spartan calculation package[24] on a Silicon Graphics Indigo computer (PM3(tm) parameters) and compared the calculated vibrational modes with the observed absorptions. A simple series was constructed: $Ta(N)Cl_3$, $Ta(NH)Cl_3$, $Ta(NCH_3)Cl_3$, $Ta(NCMe_3)Cl_3$, and $Ta(NPh)Cl_3$. Finally, a calculation was carried out for $Ta(NCMe_3)Cl_3(dme)$ for comparison with actual spectra acquired in a Nujol mull. The molecular geometries were optimized, molecular orbitals calculated, and vibrational frequencies (normal modes) estimated with a frequency calculation. These modes are typically assumed to be overestimated by 10%, so values quoted here are followed parenthetically with the calculated frequency scaled by 0.9. We consider these values as upper and lower estimates of the vibrational frequencies.

The results are tabulated in Table 3. There is a significant change in the mode which is mainly Ta−N in character as one proceeds from nitride to the imides. This mode was selected from the tabulated data (available as Supporting Information) of the normal coordinate analysis. Visual inspection of the animated vibrational modes more clearly shows the atomic motions involved in each predicted vibrational mode. Modes in which both Ta and N atoms are significantly distorted from their equilibrium positions were taken as (Ta−N)-containing modes. These modes are fairly unambiguous since, in the 1000−1400 cm^{-1} region of the spectrum, few modes involve the Ta atom, and only one to three involve both Ta and N to a significant degree, depending on the molecule.

As the group bonded to nitrogen changes, a noticeable change in the frequency of the mode which is mainly Ta−N in character occurs. For the nitride, the Ta−N stretching mode is observed at 1120 (1008) cm^{-1}, where one would predict on the basis of previous literature.[14] In the protioimide, this stretching frequency decreases to 1083 (975) cm^{-1}, closer to that expected for an oxo and consistent with what should be a (slight) bond weakening upon protonation of the nitride. This mode mainly involves a Ta and N symmetric stretch, coupled with a small contribution from the N−H stretch.

In the methylimido, however, this mode drastically increases in energy to ∼1300 (1170) cm^{-1}. This is due to coupling with modes which are mainly N−C and C−H in character and close to what is observed experimentally (*vide infra*). This mode is now best visualized as an umbrella deformation of the CH_3 group coupled with the Ta−N mode. At higher frequency is predicted a mainly N−C stretching mode which involves some tantalum character—this can be thought of as an asymmetric [Ta−*N*−C] stretching mode, in which significant nitrogen motion occurs along the Ta−N−C axis. Finally, a symmetric [*Ta*−N−*C*] mode, in which the Ta and C atoms distort along this axis, is predicted to occur at 661 (595) cm^{-1}. On the basis of these results, there are three main stretching modes predicted for an alkyl imido: a low-energy symmetric vibration *Ta*−N−*C*, a medium energy *Ta*−(*N*−*C*) mode, and a higher energy asymetric Ta−*N*−C mode, using italics to indicate atomic motion.

In the *tert*-butylimido, the predicted umbrella/*Ta*−(*N*−*C*) stretching frequency drops again to 1171 (1054) cm^{-1}, somewhat lower than actually observed. This may be due in part to geometric considerations; the Ta−N bond length is predicted to be ∼1.77 Å, significantly longer than that observed in **14** and in $Ta(NAr)Ph_3(THF)$ (1.71 Å).[7] Predicted modes at 634 (571) cm^{-1} for the symmetric [*Ta*−N−*C*] mode and 1500 (1350) cm^{-1} for the asymmetric [Ta−*N*−C] mode are again observed.

In our model of an actual compound, $Ta(NCMe_3)Cl_3(dme)$, the Ta−N mode is predicted to be 1171 (1054) cm^{-1}, unchanged as the coordination number increases from 4 to 6. The geometry of this compound is predicted to be very similar to that observed in the structure of **14**. In the phenylimido trichloride, the picture is more complicated. There are a number of modes in the region 1000−1500 cm^{-1} that have varying degrees of N and Ta contributions, but there are two main contributors to Ta−N stretches, one at 1211 (1090) cm^{-1} and another at 1475 (1327) cm^{-1}. Results for $Ta(NPh)Cl_3$ are similar, with coupling of aryl C−C stretches and the Ta−N stretch being the main distortions in the medium-frequency analog to the umbrella mode in the alkylimidos.

With these results in mind, infrared data for the imido compounds were scrutinized in order to find evidence for these three modes, Table 4. Observation of a strong absorption at ∼1250−1280 cm^{-1} in otherwise fairly bleak spectra of the salts $[Ta(NR)Cl_5]^{2-}$ (**1b**−**6b**) is perhaps the most convincing evidence for the medium frequency *Ta*−(*N*−*C*) mode in these compounds. This value is close to that predicted for the

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Table 4. Observed Infrared Absorptions for "Ta−N−CR$_3$" (in cm^{-1}) in the Ta and Nb Imido Compounds[a]

no.	compound	medium	high
1a	$Ta(NCMe_2Et)Cl_3(py)_2$	1255	
1b	$[Ta(NCMe_2Et)Cl_5]^{2-}$	1263	1589
1c	$Ta(NCMe_2Et)Cl_3(dme)$	1255	1589
2a	$Ta(NCMe_3)Cl_3(py)_2$	1283	
2c	$Ta(NCMe_3)Cl_3(dme)$	1275	1586
3a	$Ta(NCH(CHMe_2)_2)Cl_3(py)_2$	1263	
3b	$[Ta(NCH(CHMe_2)_2)Cl_5]^{2-}$	1268	1592
3c	$Ta(NCH(CHMe_2)_2)Cl_3(dme)$	1266	1603
4a	$Ta(NAda)Cl_3(py)_2$	1286	
4c	$Ta(NAda)Cl_3(dme)$	1281	1585
5a	$Ta(N^tOct)Cl_3(py)_2$	1255	
5b	$[Ta(N^tOct)Cl_5]^{2-}$	1263	1589
5c	$Ta(N^tOct)Cl_3(dme)$	1261	1599
6b	$[Ta(NBu)Cl_5]^{2-}$	1300	1585
6c	$Ta(NBu)Cl_3(dme)$	1306	1580
7	$Ta(NPh)Cl_3(dme)$	1359	1583
8	$Ta(NAr)Cl_3(dme)$	1354	1606
9	$Ta(NAr')Cl_3(dme)$	1336	1608
10	$Ta(NPhCN)Cl_3(dme)$	1370	1593
11	$Ta(NNap)Cl_3(dme)$	1322	1591
13a	$Nb(NCMe_2Et)Cl_3(py)_2$	1218	
13b	$[Nb(NCMe_2Et)Cl_5]^{2-}$	1236	
13c	$Nb(NCMe_2Et)Cl_3(dme)$	1225	1594
14	$Nb(NCMe_3)Cl_3(dme)$	1241	1599
16	$Nb(NPh)Cl_3(dme)$	1327	1606
17	$Nb(NAr)Cl_3(dme)$	1332	1584
18	$Nb(NPhCN)Cl_3(dme)$	1336	1591
19	$Nb(NNap)Cl_3(dme)$	1308	1590

[a] In Nujol mulls. Abbreviations: Ada = 1-adamantyl, ^{t}Oct = $CMe_2CH_2CMe_3$, Ar = 2,6-$^iPr_2C_6H_3$, Ar′ = 2,6-$Me_2C_6H_3$, PhCN = 4-CNC_6H_4, Nap = 2-naphthyl, Anth = 2-anthryl.

methylimido trichloride and somewhat higher than the calculated value for the *tert*-butylimido. Previously, Schrock reported that only one absorption in the IR of $Ta(NPh)Cl_3(thf)_2$ (at 1360 cm^{-1}) shifted upon ^{15}N labeling. In agreement with this, the midenergy Ta−N stretch in **9** is observed at 1359 cm^{-1}, and the energy of this mode is predicted to be ~1475 (1327) cm^{-1}. A mode is observed in this region of the spectrum for all the arylimido compounds, while the lowest energy absorption occurs for **11**, the least electron-donating arylimido, at 1322 cm^{-1}. Another feature that we are able to establish is a weak absorption for all of these compounds at approximately 1600 cm^{-1}. The energy of this absorption appears to be invariant with metal, and it corresponds to the higher energy (mainly) N−C mode in these compounds. We were unable to reliably pick out a low frequency mode predicted by the calculations in the 600−750 cm^{-1} region, corresponding to a low energy symmetric [*Ta*−N−*C*] stretch. Similar data were obtained for a series of vanadium, molybdenum, tungsten, and rhenium halo imido compounds.[15]

The niobium compounds show similar trends, with the aryl compounds having higher energy stretching frequencies than their alkyl analogues. The Nb−N stretching frequencies are consistently observed ~30 cm^{-1} red of their heavier congeners. In conclusion, these observed stretching frequencies appear to vary as a function of vibrational mode energies rather than bond strength, for which we have, at this point, little accurate measure.

Discussion

Our primary interest in this work was to find a high yield route to alkylimido compounds of the form $M(NR)Cl_3L_2$, where L is a labile Lewis base. These materials are highly desirable for a number of reasons. The most obvious is their utility as starting materials for group 5 imido chemistry. Known examples of $M(NR)Cl_3L_n$ (R is alkyl) contain the corresponding amine RNH_2 as a Lewis base ligand.[5,25] Replacement of RNH_2 in these compounds with weakly coordinating ligands such as pyridine does not occur smoothly.[5] Coordinated dme is highly desirable due to its ready loss in further reaction chemistry, such as in Grignard reactions.[7,16,17] Of more immediate interest to us is the simplicity of the electronic structure of these compounds.[10−12] The imido ligand is the dominant factor, while the chlorides and simple Lewis base ligands essentially serve to fill out the coordination sphere.

There are a variety of six-coordinate Nb and Ta imidos of the form $M(NR)Cl_3L_2$ where L is RNH_2 or PR_3.[1,5] On the basis of the previous literature, it appeared difficult to avoid incorporation of the amine when more than 1 equiv was added to the metal halide, so we attempted to use nitrogen bases as HCl scavengers. None of these preparations met with reasonable success in the absence of $ZnCl_2$. However, addition of $ZnCl_2$ to MCl_5 prior to amine and py results in good to excellent yields of the arylimidos. For preparation of the alkylimidos, best results are obtained by reaction of the halide with 3 equiv of amine and isolation of $[RNH_3]^+{}_2[M(NR)Cl_5]^{2-}$ followed by treatment with $ZnCl_2$ in the presence of Lewis base. Niobium alkylimidos may also be prepared in a one-pot reaction between MCl_5, $ZnCl_2$, RNH_2, and NEt_3 in somewhat lower yield.

We tried a variety of insoluble inorganic bases such as K_2CO_3, $Na_2B_4O_7$, and $LiBO_2$. Use of these bases results in only modest (< 50%) yields. However, Na_2SiO_3 works well in the presence of pyridine, giving 60−80% yields of $M(NR)Cl_3(py)_2$ when 2 equiv of amine is used, but only 40% or so in the presence of 1 equiv of amine. Even in the presence of excess base, 1 equiv of amine is apparently lost as the ammonium salt. It is possible that some significant concentration of a soluble base is necessary to deprotonate the initially formed amine ($M(NH_2R)Cl_5$) and amide ($M(NHR)Cl_5^-$) complexes, but it is not clear why the resulting ammonium salt is not efficiently deprotonated by the insoluble base.

Syntheses of Imidos Using Amines as Starting Materials. There are now simple, high-yield syntheses for *labile* adducts of d^0 imido chloride compounds of Nb, Ta, Mo,[16] W,[17] and Re[18,19] for almost any alkyl or aryl substituent. It is interesting to compare these syntheses since they are so similar. For Mo, W, and Re, the most readily available starting materials are oxides, and $ClSiMe_3$ is used as an oxygen scavenger. The simplest synthesis involves rhenium bis- and tris(imidos). Rhenium heptoxide reacts with 6 equiv of an aniline derivative in the presence of either pyridine or triethylamine to afford $Re(NAr)_2Cl_3py$[18] or $Re(NAr)_3Cl$,[19] respectively. In reactions with alkyl amines, the amine serves as base to give $Re(NR)_3(OSiMe_3)$, which can be isolated or reacted *in situ* with 3 equiv of HCl to give $Re(NR)_2Cl_3$.[18] The generality of these reactions is not known but is probably similar to those described here (^{t}Bu, Ar, and Ar′ were used previously).

$$\mathrm{Re_2O_7} + 6\,\mathrm{ArNH_2} + 17\,\mathrm{Me_3SiCl} + 14\,\mathrm{NEt_3} \longrightarrow \underset{95\ \%}{\mathrm{Re(NAr)_3Cl}}$$

$$14\,\mathrm{py} \longrightarrow \underset{75\text{ - }85\ \%}{\mathrm{Re(NAr)_2Cl_3py}} \qquad (10)$$

$$\begin{tikzcd} \mathrm{Re_2O_7} + 20\ t\text{-}\mathrm{BuNH_2} + 17\,\mathrm{Me_3SiCl} \arrow[r] & 2\ \mathrm{Re(N}t\text{-}\mathrm{Bu)_3(OSiMe_3)}\ 83\ \% \arrow[d, "6\,\mathrm{HCl}"'] \\ & 2\ \mathrm{Re(NR)_2Cl_3}\ \ 79\ \% \end{tikzcd} \qquad (11)$$

Synthesis of molybdenum bis(imido)s is somewhat more general.[16] Reaction of $[NH_4]_2[Mo_2O_7]$ with a variety of aniline

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[25] Jones, T. C.; Nielson, A. J.; Rickard, C. E. *J. Chem. Soc., Chem. Commun.* **1984**, 205.

derivatives in the presence of NEt_3 in refluxing dme affords high to excellent yields (75−99%) of $Mo(NAr)_2Cl_2(dme)$. For t-$BuNH_2$, again no additional base is required, and yields are somewhat lower (∼60%).

$$(NH_4)_2Mo_2O_7 + 4\ ArNH_2 + 8\ NEt_3 + 17\ Me_3SiCl \longrightarrow \underset{75 - 99\ \%}{2\ Mo(NAr)_2Cl_2(dme)} \tag{12}$$

Tungsten is perhaps the most complicated. $WOCl_4$ is used as the starting material with otherwise similar conditions to those for molybdate.[17,26] This reaction is somewhat more variable, since precise reflux times seem more important for high-yield reactions.[26] Additionally, the noncoordinating base 2,6-lutidine must be used, since NEt_3 does not give good yields.

$$WOCl_4 + 2\ ArNH_2 + 5\ \text{2,6-lutidine} + 5\ Me_3SiCl \longrightarrow \underset{75\ \%}{W(NAr)_2Cl_2(dme)} \tag{13}$$

By contrast, for tantalum and niobium we use the halides as starting materials. We have found that aniline derivatives react smoothly with niobium or tantalum pentachloride in the presence of pyridine, $ZnCl_2$, and dme to give good to excellent yields of $M(NAr)Cl_3(dme)$, eq 7. Alkyl amines react similarly with $NbCl_5$, giving somewhat lower yields. The best way to make mono(alkylimido)niobium and tantalum compounds (eqs 8 and 9) is to react the pentachloride with 3 equiv of amine, generating $[RNH_3]_2[M(NR)Cl_5]$, and treating this salt with $ZnCl_2$ in the presence of dme. This affords the compounds $M(NR)Cl_3(dme)$ in high yields.

Note that, in each of these reactions, an amine, an external base, and a Lewis acid are used to generate the imido. In the oxide reactions,[16−18] Me_3SiCl acts as a Lewis acid to accept the oxygen, forming $(Me_3Si)_2O$. In the halide reactions here, $ZnCl_2$ is the Lewis acid, reacting with the ammonium chloride byproduct to form $[pyH][ZnCl_3(solvent)]$ or $[RNH_3][ZnCl_3(solvent)]$. In either situation, the Lewis acid drives the reaction to completion. This point of view can be extended to the silated amines reacting with the group 5 halides, in which the silyl group is the Lewis acid, removing chloride to form Me_3SiCl.[5,6,25,27]

Finally, we have investigated the infrared spectra of these simple imido compounds in order to determine the observed mode which is mainly M−N in character. The wording is carefully chosen because there is *no* single mode which is solely M−N in character. The mode which is *mainly* M−N in each of these compounds is not observed at energies similar to that of a terminal M−O stretch in an oxo compound, around 1000 cm^{-1}. Substantial mixing of C−N and C−C or C−H modes raises the energy of this mode to ∼1300 cm^{-1} (±50 cm^{-1}). In fact, there are at least three modes in imido compounds which contain a significant degree of metal−nitrogen character.

Experimental Details

General Details. All manipulations were carried out under a dry dinitrogen atmosphere in a Vacuum/Atmospheres drybox. All solvents and liquid reagents were distilled under dry argon over sodium/benzophenone ketyl (THF, ether, pentane), molten sodium (toluene, pyridine), or CaH_2 (dichloromethane, NEt_3). Pentane was washed using 5% HNO_3/H_2SO_4 and dried over $CaCl_2$ prior to distillation, with tetraglyme added to dissolve the ketyl. (2,6-Dimethylphenyl)amine and aniline were distilled from CaH_2 after predrying with solid KOH. *tert*-Amylamine, *tert*-octylamine, *tert*-butylamine, and 2,4-dimethyl-3-aminopentane were dried over CaH_2 for 24 h. Zinc chloride, $TaCl_5$, and $NbCl_5$ (Strem), adamantyl amine (Aldrich), 2-aminonaphtalene, 2-aminoanthracene, and 4-aminobenzonitrile (Acros) were purchased and used as received. All NMR data were recorded in $CDCl_3$ or C_6D_6 at approximately 22 °C on a Varian Gemini 300 MHz spectrometer. All chemical shifts were referenced to internal solvent and reported in ppm downfield from TMS (^{1}H, ^{13}C). $CDCl_3$ was stirred with CaH_2 for 24 h, vacuum transferred, and stored in a black bottle over activated alumina inside the drybox. Activated alumina was prepared by heating at 100 °C on a high vacuum line for 24 h. Deuterated solvents were filtered through Celite immediately before use. Microanalyses (C, H, N) were obtained from Midwest Microlab, 7212 N. Shadeland Ave., Indianapolis, IN, 46250. A number of these compounds were consistently give variable results in combustion analysis. This has been noted previously for other d^0 group 5 compounds, in particular $Ta(CHR)Cl_3L_2$,[28] and a sufficient number of examples analyze satisfactorily.

Preparation of Compounds. $Ta(NCMe_2Et)Cl_3(py)_2$ (1a). Method A. $TaCl_5$ (3.00 g, 8.38 mmol) was dissolved in toluene/ether (30 mL, 5:1 by volume). Anhydrous Na_2SiO_3 (2.05 g, 16.8 mmol) was added to it followed by the dropwise addition of neat H_2NCMe_2Et (1.96 mL, 16.8 mmol). The solution turned yellow-green, lightening to pale-green at the end of the amine addition. Pyridine was added in excess (∼6 mL) producing a yellow solution. The mixture was stirred for 18 h, filtered through Celite, and evaporated *in vacuo*. The resulting solid was washed with pentane and dried *in vacuo* to give 3.18 g of a yellow powder (72%). Analytically pure samples were recrystallized from CH_2Cl_2/pentane.

Method B. $TaCl_5$ (500 mg, 1.40 mmol) was dissolved in toluene/Et_2O (8 mL, 4:1 by volume). Anhydrous Na_2SiO_3 (341 mg, 2.79 mmol) was added to the solution followed by the addition of *tert*-amylamine (163 mL, 1.40 mmol). The solution became colorless and was stirred for 3 min. Pyridine was added (∼1 mL), producing a yellow solution. The mixture was stirred for 30 min, filtered through Celite, and chilled to −40 °C. A white precipitate was filtered off and the solution concentrated *in vacuo* to give a yellow oil which crystallized after standing under pentane, giving 0.342 g (46%) of a yellow solid. ^{1}H NMR ($CDCl_3$) δ 9.01 (d, 2, $\mathrm{py_A}$-H_o), 8.94 (d, 2, $\mathrm{py_B}$-H_o), 7.93 (tt, 1, $\mathrm{py_A}$-H_p), 7.83 (tt, 1, $\mathrm{py_B}$-H_p), 7.41 (m, 4, py-H_m), 1.66 (q, 2, $\mathrm{CMe_2C}H_2$-Me), 1.32 (s, 6, $\mathrm{C}Me_2\mathrm{CH_2Me}$), 1.10 (t, 3, $\mathrm{CMe_2CH_2}Me$); ^{13}C NMR ($CDCl_3$) δ 152.9 ($\mathrm{py_A}$-C_o), 151.4 ($\mathrm{py_B}$-C_o), 140.0 ($\mathrm{py_A}$-C_p), 138.4 ($\mathrm{py_B}C_\mathrm{p}$), 124.5 ($\mathrm{py_A}$-$C_\mathrm{m}$), 124.3 ($\mathrm{py_B}$-$C_\mathrm{m}$), 69.1 ($C\mathrm{Me_2CH_2}$ Me), 37.8 ($\mathrm{CMe_2}C\mathrm{H_2Me}$), 29.2 ($\mathrm{C}Me_2\mathrm{CH_2Me}$), 9.2 ($\mathrm{CMe_2CH_2}Me$). Anal. Calcd for $TaC_{15}H_{21}Cl_3N_3$: C, 33.95; H, 3.99; N, 7.92. Found: C, 33.88; H, 4.23; N, 7.68.

$[H_3NCMe_2Et]_2[Ta(NCMe_2Et)Cl_5]$ (1b). $TaCl_5$ (500 mg, 1.40 mmol) was dissolved in toluene (8 mL) by adding Et_2O (1 mL). H_2NCMe_2Et (489 mL, 4.19 mmol) was added slowly giving a yellow solution which was stirred for 4 h. This produced a small amount of white precipitate. The mixture was evaporated *in vacuo* leaving a pale-yellow powder which was washed with pentane and dried *in vacuo* to give 860 mg (99%) of the product: ^{1}H NMR ($CDCl_3$) δ 7.14 (bs, 6, $H_3\mathrm{NCMe_2Et}$), 1.74 (q, 4, $\mathrm{H_3NCMe_2C}H_2\mathrm{CH_3}$), 1.61 (q, 2, $\mathrm{NCMe_2C}H_2$-$\mathrm{CH_3}$), 1.39 (s, 12, $\mathrm{H_3NC}Me_2\mathrm{CH_2CH_3}$), 1.31 (s, 6, $\mathrm{NC}Me$ $_2\mathrm{CH_2CH_3}$), 1.10 (t, 3, $\mathrm{NCMe_2CH_2C}H_3$), 0.99 (t, 6, $\mathrm{H_3NCMe_2CH_2C}H_3$); ^{13}C NMR ($CDCl_3$) δ 69.5 ($\mathrm{N}C\mathrm{Me_2CH_2CH_3}$), 56.7 ($\mathrm{H_3N}C\mathrm{Me_2CH_2CH_3}$), 37.5 ($\mathrm{NCMe_2}C\mathrm{H_2CH_3}$), 33.3 ($\mathrm{H_3NCMe_2}C\mathrm{H_2CH_3}$), 29.1 ($\mathrm{NC}Me_2\mathrm{CH_2CH_3}$), 25.0 ($\mathrm{H_3NC}Me_2\mathrm{CH_2CH_3}$), 9.1 ($\mathrm{NCMe_2CH_2}C\mathrm{H_3}$), 8.0 ($\mathrm{H_3NCMe_2}$-$\mathrm{CH_2}C\mathrm{H_3}$). Anal. Calcd for $TaC_{15}H_{39}Cl_5N_3$: C, 29.07; H, 6.34; N, 6.78. Found: C, 28.68, H, 6.42; N, 7.06.

$Ta(NCMe_2Et)Cl_3(dme)$ (1c). Compound **1b** (1.00 g, 1.61 mmol) was dissolved in toluene (8 mL) by adding 167 mL (1.61 mmol) of dme. $ZnCl_2$ (660 mg, 4.84 mmol) was added last. The mixture was stirred for 18 h, during which time the pale-yellow solution became colorless. The solution was filtered through Celite and evaporated *in vacuo*. This provided a colorless oil which crystallized upon standing under pentane to give 640 mg (86%) of a white solid: ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 3, $\mathrm{O}Me_\mathrm{A}$), 4.17 (m, 2, $\mathrm{O(C}H_2\mathrm{)_A}$), 4.03 (m, 2, $\mathrm{O(C}H_2\mathrm{)_B}$), 3.91

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(s, 3, OMe_B), 1.62 (q, 2, $CMe_2CH_2CH_3$), 1.30 (s, 6, $CMe_2CH_2CH_3$), 1.11 ($CMe_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 76.0 ($O(CH_2)_A$), 71.0 ($O(CH_2)_B$), 70.6 (OMe_A), 69.7 ($CMe_2CH_2CH_3$), 62.2 (OMe_B), 37.9 ($CMe_2CH_2CH_3$), 29.3 ($CMe_2CH_2CH_3$), 9.1 ($CMe_2CH_2CH_3$). Anal. Calcd for $TaC_9H_{21}Cl_3NO_2$: C, 23.37; H, 4.58; N, 3.03. Found: C, 23.22; H, 4.58; N, 3.07.

Ta(NCMe$_3$)Cl$_3$(py)$_2$ (2a). Method A. $Ta(NCMe_3)Cl_3(py)_2$ was synthesized in 72% yield using the procedure for **1a** (method A) with *tert*-butylamine.

Method C. $TaCl_5$ (500 mg, 1.40 mmol) was dissolved in of CH_2Cl_2 (10 mL) by adding ~0.3 mL of pyridine. To this solution was added of $ZnCl_2$ (380 mg, 2.79 mmol) producing a white precipitate. The mixture was cooled to −40 °C, and a solution of H_2N^tBu (150 mL, 1.40 mmol) and NEt_3 (0.389 mL, 2.79 mmol) in CH_2Cl_2 was added dropwise, dissolving the precipitate. The reaction mixture was stirred for 18 h and evaporated *in vacuo* leaving yellow oil. This was extracted with toluene/pentane (4:1 by volume), concentrated *in vacuo*, and crystallized from CH_2Cl_2/Et_2O/pentane to give 344 mg (48%) yellow crystals: ^{1}H NMR ($CDCl_3$) δ 9.06 (d, 2, py_A-H_o), 8.97 (d, 2, py_B-H_o), 7.95 (tt, 1, py_A-H_p), 7.85 (tt, 1, py_B-H_p), 7.44 (m, 4, py-H_m), 1.38 (s, 9, CMe_3); ^{13}C NMR ($CDCl_3$) δ 152.9 (py_A-C_o), 151.5 (py_B-C_o), 140.1 (py_A-C_p), 138.5 (py_B-C_p), 124.6 (py_A-C_m), 124.4 (py_B-C_m), 66.3 (CMe_3), 31.6 (CMe_3). Anal. Calcd for $TaC_{14}H_{19}Cl_3N_3$: C, 32.55; H, 3.71; N, 8.13. Found: C, 32.53; H, 3.80; N, 7.97.

[H$_3$NCMe$_3$]$_2$[Ta(NCMe$_3$)Cl$_5$] (2b). Attempts to synthesize this compound using the procedure for **1b** gave the yellow-green powder which was characterized by NMR as a mixture of two products: Ta(N*t*-Bu)Cl_2(HN*t*-Bu)(H_2N*t*-Bu)[20] and the above compound. Several washes of this mixture with pentane/Et_2O yielded the white solid. NMR spectra suggest it to be the mixture of the above compound and *t*-$BuNH_3Cl$. Crystallization from CH_2Cl_2/pentane gave crystals which were characterized by NMR: ^{1}H NMR ($CDCl_3$) δ 7.30 (bs, 6, H_3NCMe_3), 1.48 (s, 18, H_3NCMe_3), 1.36 (s, 9, $NCMe_3$); ^{13}C NMR ($CDCl_3$) δ 54.0 (H_3NCMe_3), 31.4 ($NCMe_3$), 27.9 (H_3NCMe_3); $NCMe_3$, n/a.

Ta(NCMe$_3$)Cl$_3$(dme) (2c). $TaCl_5$ (1.00 g, 2.79 mmol) was dissolved in ~30 mL of toluene/Et_2O mixture (8:1 by volume). *tert*-Butylamine (880 ml, 8.38 mmol) was added to this solution. It was allowed to stir for 15 min, during which time was formed a white precipitate. A 290 mL volume of 1,2-dimethoxyethane was added to this mixture followed by the addition of $ZnCl_2$ (1.52 g, 11.2 mmol). The reaction mixture was stirred for 18 h, filtered through Celite, and evaporated *in vacuo* leaving a yellowish oil which was treated with three 4 mL portions of Et_2O. The extracts were combined, evaporated *in vacuo*, and crystallized under pentane to give 1.06 g (84%) of the white product. Analytically pure samples were obtained by the CH_2Cl_2/pentane recrystallization: ^{1}H NMR ($CDCl_3$) δ 4.23 (s, 3, OMe_A), 4.17 (m, 2, $O(CH_2)_A$), 4.03 (m, 2, $O(CH_2)_B$), 3.91 (s, 3, OMe_B), 1.34 (s, 9, CMe_3); ^{13}C NMR ($CDCl_3$) δ 76.1 ($O(CH_2)_A$), 71.2 ($O(CH_2)_B$), 70.7 (OMe_A), 66.9 (CMe_3), 62.2 (OMe_B), 31.6 (CMe_3). Anal. Calcd for $TaC_8H_{19}NO_2Cl_3$: C, 21.42; H, 4.27; N, 3.12. Found: C, 21.34; H, 4.07; N, 3.27.

Ta(NCH^{i}Pr$_2$)Cl$_3$(py)$_2$ (3a). Method A. This compound was synthesized in 64% yield using the procedure for **1a** (method A), except $H_2NCH(CHMe_2)_2$ was used instead of *tert*-amylamine and the product was purified using hot ether extraction.

Method B. This compound was synthesized in 40% yield using the procedure for **1a** (method B) with $H_2NCH(CHMe_2)_2$.

Method D. This compound was synthesized in 44% yield using the procedure for **1a** (method B) with $H_2NCH(CHMe_2)_2$ and $Na_2B_4O_7$.

Method E. $TaCl_5$ (500 mg, 1.40 mmol) was dissolved in of CH_2Cl_2 (8 mL) by adding ~0.3 mL of pyridine. $H_2NCH(CHMe_2)_2$ (207 mL, 1.40 mmol) was added slowly to give a yellow solution. CaH_2 (58 mg, 1.40 mmol) was added, and the reaction mixture was stirred for 5 h, filtered through Celite, and chilled to −40 °C. A white precipitate was filtered off, and the mother liquor was concentrated *in vacuo* to give a reddish oil and a white precipitate. The oil was dissolved in Et_2O, layered with pentane, and chilled to −40 °C to give 388 mg (50%) of red-yellow crystals: ^{1}H NMR ($CDCl_3$) δ 9.01 (d, 2, py_A-H_o), 8.89 (d, 2, py_B-H_o), 7.93 (tt, 1, py_A-H_p), 7.83 (tt, 1, py_B-H_p), 7.41 (m, 4, py-H_m), 4.56 (t, 1, CHi-Pr_2), 1.96 (m, 2, $CH(CHMe_2)_2$), 1.20 (d, 6, $CH(CHMe'Me)_2$), 1.03 (d, 6, $CH(CHMe'Me)_2$); ^{13}C NMR ($CDCl_3$) δ 152.6 ($py_{A-}C_o$), 151.7 (py_B-C_o), 140.0 (py_A-C_p), 138.3 (py_B-C_p), 124.6 (py_A-C_m), 124.2 (py_B-C_m), 82.7 ($CH(CHMe_2)_2$), 34.0 ($CH(CHMe_2)_2$), 20.9 ($CH(CHMe'Me)_2$), 18.8 ($CH(CHMe'Me)_2$). Anal. Calcd for $TaC_{17}H_{25}Cl_3N_3$: C, 36.55; H, 4.51; N, 7.52. Found: C, 36.38; H, 4.80; N, 7.68.

[H$_3$NCH^{i}Pr$_2$]$_2$[Ta(NCH^{i}Pr$_2$)Cl$_5$] (3b). $TaCl_5$ (0.500 g, 1.40 mmol) was dissolved in toluene (8 mL) by adding Et_2O (1 mL). $H_2NCH(CHMe_2)_2$ (0.622 mL, 4.19 mmol) was added slowly giving a yellow solution which was stirred for 4 h. This produced a small amount of white precipitate. The mixture was evaporated *in vacuo* leaving a pale-yellow powder which was washed with pentane and dried *in vacuo* to give 0.978 g (99%) of the product: ^{1}H NMR ($CDCl_3$) δ 7.06 (bs, 6, $H_3NCH(CHMe_2)_2$), 4.65 (t, 1, $NCH(CHMe_2)_2$), 2.80 (t, 2, $H_3NCH(CHMe_2)_2$), 2.05 (m, 4, $H_3NCH(CHMe_2)_2$), 1.91 (m, 2, $NCH(CHMe_2)_2$), 1.23 (d, 6, $NCH(CHMeMe')_2$), 1.06 (m, 30, $NCH(CHMeMe')_2$ and $H_3NCH(CHMe_2)_2$); ^{13}C NMR ($CDCl_3$) δ 83.4 ($NCH(CHMe_2)_2$), 64.2 ($H_3NCH(CHMe_2)_2$), 34.0 ($NCH(CHMe_2)_2$), 28.2 ($H_3NCH(CHMe_2)_2$), 20.7 ($NCH(CHMeMe')_2$), 19.8 ($H_3NCH(CHMeMe')_2$), 18.7 ($NCH(CHMeMe')_2$), 17.5 ($H_3NCH(CHMeMe')_2$). Anal. Calcd for $TaC_{21}H_{51}N_3Cl_5$: C, 35.83; H, 7.30; N, 5.97. Found: C, 35.29, H, 6.94, N, 5.99.

Ta(NCH^{i}Pr$_2$)Cl$_3$(dme) (3c). Compound **3b** (500 mg, 710 mmol) was dissolved in toluene (8 mL) by adding 74 mL (710 mmol) of dme. $ZnCl_2$ (0.290 g, 2.13 mmol) was added last. The mixture was stirred for 18 h during which time the pale-yellow solution became colorless. The solution was decanted from an oily, sticky solid and evaporated *in vacuo*. This provided a yellow oil which crystallized upon standing under pentane to give 291 mg (83%) of a white solid: ^{1}H NMR ($CDCl_3$) δ 4.32 (t, 1, $CH(CHMe_2)_2$), 4.19 (s, 3, OMe_A, and m, 2, $O(CH_2)_A$), 4.02 (m, 2, $O(CH_2)_B$), 3.90 (s, 3, OMe_B), 1.92 (m, 2, $CH(CHMe_2)_2$), 1.25 (d, 6, $CH(CHMe'Me)_2$), 1.07 (d, 6, $CH(CHMe'Me)_2$); ^{13}C NMR ($CDCl_3$) δ 83.1 ($CH(CHMe_2)_2$), 76.0 ($O(CH_2)_A$), 70.4 ($O(CH_2)_B$), 70.1 (OMe_A), 62.3 (OMe_B), 34.1 ($CH(CHMe_2)_2$), 20.9 ($CH(CHMe'Me)_2$), 18.6 ($CH(CHMe'Me)_2$). Anal. Calcd for $TaC_{11}H_{25}Cl_3NO_2$: C, 26.93; H, 5.14; N, 2.85. Found: C, 26.89; H, 5.20; N, 2.85.

Ta(N-1-adamantyl)Cl$_3$(py)$_2$ (4a). Method A. This compound was synthesized in 66% yield using the procedure for **1a** (method A) with adamantylamine.

Method F. This compound was synthesized in 30% yield using the procedure for **1a** (method B) with adamantylamine and K_2CO_3: ^{1}H NMR ($CDCl_3$) δ 9.04 (d, 2, py_A-H_o), 8.97 (d, 2, py_B-H_o), 7.93 (tt, 1, py_A-H_p), 7.86 (tt, 1, py_B-H_p), 7.43 (m, 4, py-H_m), 2.13 (bs, 3, $C(CH_2CHCH_2)_3$), 1.96 (d, 6, $C(CH_2CHCH_2)_3$), 1.60 (m, 6, $C(CH_2CHCH_2)_3$); ^{13}C NMR ($CDCl_3$) δ 153.0 (py_A-C_o), 151.4 (py_B-C_o), 139.9 (py_A-C_p), 138.6 (py_B-C_p), 124.5 (py_A-C_m), 124.3 (py_B-C_m), 67.1 ($C(CH_2CHCH_2)_3$), 44.7 ($C(CH_2CHCH_2)_3$), 36.2 ($C(CH_2CHCH_2)_3$), 29.5 ($C(CH_2.CH.CH_2)_3$). Anal. Calcd for $TaC_{20}H_{25}N_3Cl_3$: C, 40.39; H, 4.24; N, 7.07. Found: C, 40.95; H, 4.38; N, 6.69.

[H$_3$N-1-adamantyl]$_2$[Ta(N-1-adamantyl)Cl$_5$] (4b). This compound was synthesized in quantitative yield using the procedure for **1b** with 1-adamantylamine. We were not able to assign both ^{1}H and ^{13}C NMR spectra, partially because of low solubility in NMR solvents ($CDCl_3$, CD_2Cl_2, C_6D_6). However, it was successfully used as a starting material in the further synthesis of Ta(N-1-adamantyl)Cl_3(dme).

Ta(N-1-adamantyl)Cl$_3$(dme) (4c). This compound was synthesized in 78% yield using the procedure for **1c** with [H_3N-1-adamantyl]$_2$[Ta(N-1-adamantyl)Cl_5]: ^{1}H NMR (C_6D_6) δ 3.48 (s, 3, OMe_A), 3.43 (s, 3, OMe_B), 3.03 (bm, 4, OCH_2), 2.00 (d, 6, $C(CH_2CHCH_2)_3$), 1.94 (bs, 3, $C(CH_2CHCH_2)_3$), 1.42 (m, 6, $C(CH_2CHCH_2)_3$); ^{13}C NMR (C_6D_6) δ 75.4 ($O(C\ H_2)_A$), 70.7 ($O(C\ H_2)_B$), 70.2 (OMe_A), 67.7 ($C\ (CH_2CHCH_2)_3$), 61.7 (OMe_B), 45.4 ($C(CH_2CHCH_2)_3$), 36.4 ($C(C\ H_2CHCH_2)_3$), 29.9 ($C(CH_2CHCH_2)_3$). Anal. Calcd for $TaC_{14}H_{25}NO_2Cl_3$: C, 31.93; H, 4.78; N, 2.66. Found: C, 31.41; H, 4.82; N, 2.62.

Ta(NCMe$_2$CH$_2$CMe$_3$)Cl$_3$(py)$_2$ (5a). This compound was synthesized by the ligand exchange reaction of **5c** with pyridine and characterized by NMR: ^{1}H NMR ($CDCl_3$) δ 9.00 (tt, 4, py-H_o), 7.93 (tt, 1, py_A-H_p), 7.83 (tt, 1, py_B-H_p), 7.41 (m, 4, py-H_m), 1.69 (s, 2, $CMe_2CH_2CMe_3$), 1.47 (s, 6, $CMe_2CH_2CMe_3$), 1.05 (s, 9, $CMe_2CH_2CMe_3$); ^{13}C NMR ($CDCl_3$) δ 153.0 (py_A-C_o), 151.5 (py_B-C_o), 139.9 (py_A-C_p), 138.3 (py_B-C_p), 124.5 (py_A-C_m), 124.2 (py_B-C_m), 70.3 ($CMe_2CH_2CMe_3$), 56.1 ($CMe_2CH_2CMe_3$), 31.7 ($CMe_2CH_2CMe_3$ and CMe_2-

CH$_2$C*Me*$_3$), 31.3 (CMe$_2$CH$_2$*C*Me$_3$). Anal. Calcd for TaC$_{18}$H$_{27}$N$_3$Cl$_3$: C, 37.75; H, 4.75; N, 7.34. Found: C, 37.65; H, 4.80; N, 7.35.

[H$_3$NCMe$_2$CH$_2$CMe$_3$]$_2$[Ta(NCMe$_2$CH$_2$CMe$_3$)Cl$_5$] (5b). This compound was synthesized in 96% yield using the procedure for **1b** with *tert*-octylamine: ^{1}H NMR (CDCl$_3$) δ 7.10 (bs, 6, *H*$_3$NCMe$_2$CH$_2$CMe$_3$), 1.75 (s, 4, H$_3$NCMe$_2$C*H*$_2$CMe$_3$), 1.59 (s, 2, NCMe$_2$C*H*$_2$CMe$_3$), 1.52 (s, 12, H$_3$NC*Me*$_2$CH$_2$CMe$_3$), 1.47 (s, 6, NC*Me*$_2$CH$_2$CMe$_3$), 1.09 (s, 9, NCMe$_2$CH$_2$C*Me*$_3$), 1.05 (s, 18, H$_3$NCMe$_2$CH$_2$C*Me*$_3$); ^{13}C NMR (CDCl$_3$) δ 71.1 (N*C*Me$_2$CH$_2$CMe$_3$), 58.2 (H$_3$N*C*Me$_2$CH$_2$CMe$_3$), 55.9 (NCMe$_2$*C*H$_2$CMe$_3$), 52.5 (H$_3$NCMe*C*H$_2$CMe$_3$), 32.1 (NC*Me*$_2$CH$_2$CMe$_3$), 31.8 (NCMe$_2$CH$_2$C*Me*$_3$), 31.3 (H$_3$NC*Me*$_2$CH$_2$CMe$_3$), 27.4 (H$_3$NCMe$_2$CH$_2$C*Me*$_3$); NCMe$_2$CH$_2$*C*Me$_3$ and H$_3$NCMe$_2$CH$_2$*C*Me$_3$, n/a.

Ta(NCMe$_2$CH$_2$CMe$_3$)Cl$_3$(dme) (5c). This compound was synthesized in 75% yield using the procedure for **1c** with [H$_3$NCMe$_2$CH$_2$CMe$_3$]$_2$[Ta(NCMe$_2$CH$_2$CMe$_3$)Cl$_5$]. ^{1}H NMR (CDCl$_3$) δ 4.22 (s, 3, O*Me*$_A$), 4.17 (m, 2, O(C*H*$_2$)$_A$), 4.02 (m, 2, O(C*H*$_2$)$_B$), 3.90 (s, 3, O*Me*$_B$), 1.64 (s, 2, CMe$_2$C*H*$_2$CMe$_3$), 1.45 (s, 6, C*Me*$_2$CH$_2$CMe$_3$), 1.06 (s, 9, CMe$_2$CH$_2$C*Me*$_3$); ^{13}C NMR (CDCl$_3$) δ 76.1 (O(*C*H$_2$)$_A$), 71.0 (O(*C*H$_2$)$_B$), 70.9 (*C*MeCH$_2$CMe$_3$), 70.6 (O*Me*$_A$), 62.2 (O*Me*$_B$), 56.2 (CMe$_2$*C*H$_2$CMe$_3$), 31.8 (C*Me*$_2$CH$_2$CMe$_3$), 31.7 (CMe$_2$CH$_2$C*Me*$_3$), 31.3 (CMe$_2$CH$_2$*C*Me$_3$).

[H$_3$N(CH$_2$)$_3$CH$_3$]$_2$[Ta(N(CH$_2$)$_3$CH$_3$)Cl$_5$] (6b). This compound was synthesized in quantitative yield using the procedure for **1b** with *n*-butylamine: ^{1}H NMR (CDCl$_3$) δ 7.65 (bs, 6, *H*$_3$N(CH$_2$)$_3$CH$_3$), 5.16 (t, 2, NC*H*$_2$(CH$_2$)$_2$CH$_3$), 3.04 (m, 4, H$_3$NC*H*$_2$(CH$_2$)$_2$CMe$_3$), 1.74 (m, 6, H$_3$NCH$_2$C*H*$_2$CH$_2$CH$_3$ and NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.45 (m, 6, H$_3$NCH$_2$CH$_2$C*H*$_2$CH$_3$ and NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.95 (m, 9, H$_3$NCH$_2$CH$_2$C*H*$_3$ and NCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 61.0 (N*C*H$_2$(CH$_2$)$_2$CH$_3$), 40.3 (H$_3$N*C*H$_2$(CH$_2$)$_2$CH$_3$), 34.8 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 29.4 (H$_3$NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.4 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 19.8 (H$_3$NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 13.4 (H$_3$NCH$_2$CH$_2$CH$_2$*C*H$_3$).

Ta(N(CH$_2$)$_3$CH$_3$)Cl$_3$(dme) (6c). This compound was synthesized in 87% yield using the procedure for **1c** with [H$_3$N(CH$_2$)$_3$CH$_3$]$_2$[Ta(N(CH$_2$)$_3$CH$_3$)Cl$_5$]: ^{1}H NMR (CDCl$_3$) δ 4.88 (t, 2, NC*H*$_2$(CH$_2$)$_2$CH$_3$), 4.18 (s, 3, O*Me*$_A$), 4.16 (m, 2, O(C*H*$_2$)$_A$), 4.03 (m, 2, O(C*H*$_2$)$_B$), 3.91 (s, 3, O*Me*$_B$), 1.58 (m, 4, NCH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.93 (t, 3, NCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 75.9 (O(*C*H$_2$)$_A$), 70.7(O(*C*H$_2$)$_B$), 70.3 (O*Me*$_A$), 62.4 (O*Me*$_B$), 61.3 (N*C*H$_2$(CH$_2$)$_2$CH$_3$), 34.7 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.3 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.7 (NCH$_2$CH$_2$CH$_2$*C*H$_3$).

Ta(NC$_6$H$_5$)Cl$_3$(dme) (7). TaCl$_5$ (500 mg, 1.40 mmol) was dissolved in dichloromethane (10 mL) by adding ~0.25 mL of dimethoxyethane. ZnCl$_2$ (380 mg, 2.79 mmol) was added to the solution, forming a white precipitate. This was cooled to −40 °C, and a solution of H$_2$NPh (130 mg, 1.40 mmol) and pyridine (226 mL, 2.79 mmol) in CH$_2$Cl$_2$ was added slowly. This dissolved the precipitate and produced a yellow solution. The mixture was stirred for 17 h. A precipitate formed and was filtered off. The mother liquor was concentrated *in vacuo* to a yellow solid. This was recrystallized from CH$_2$Cl$_2$/pentane to give 610 mg (93%) yellow crystals: ^{1}H NMR (CDCl$_3$) δ 7.35 (t, 2, Ph-*H*$_m$), 7.07 (d, 2, Ph-*H*$_o$), 6.89 (t, 1, Ph-*H*$_p$), 4.20 (m, 2, O(C*H*$_2$)$_A$), 4.13 (s, 3, O*Me*$_A$), 4.11 (m, 2, O(C*H*$_2$)$_B$), 4.02 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ 153.2 (Ph-*C*$_i$), 127.9 (Ph-*C*$_m$), 126.7 (Ph-*C*$_o$), 126.0 (Ph-*C*$_p$), 76.0 (O(*C*H$_2$)$_A$), 71.2 (O(*C*H$_2$)$_B$), 69.9 (O*Me*$_A$), 63.2 (O*Me*$_B$). Anal. Calcd for TaC$_{10}$H$_{15}$NCl$_3$O$_2$: C, 25.63; H, 3.23; N, 2.99. Found: C, 25.29; H, 3.21; N, 3.01.

Ta(N-2,6-*i*-Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (8). This compound was synthesized in 99% yield using the procedure for **7** with 2,6-diisopropylphenylamine: ^{1}H NMR (CDCl$_3$) δ 7.18 (d, 2, Ar-*H*$_m$), 6.83 (t, 1, Ar-*H*$_p$), 4.32 (m, 2, C*H*Me$_2$), 4.23 (m, 2, O(C*H*$_2$)$_A$), 4.12 (m, 2, O(C*H*$_2$)$_B$), 4.10 (s, 3, O*Me*$_A$), 4.02 (s, 3, O*Me*$_B$), 1.31 (d, 12, CH*Me*$_2$); ^{13}C NMR (CDCl$_3$) δ Ar-*C*$_i$ was not observed, 148.7 (Ar-*C*$_m$), 126.0 (Ar-*C*$_o$), 121.9 (Ar-*C*$_p$), 76.0 (O*C*H$_2$)$_A$), 70.8 (O(*C*H$_2$)$_B$), 69.9 (O*Me*$_A$), 62.9 (O*Me*$_B$), 27.4 (*C*HMe$_2$), 24.7 (CH*Me*$_2$). This compound has been reported previously.[6]

Ta(N-2,6-Me$_2$C$_6$H$_3$)Cl$_3$(dme) (9). This compound was synthesized in 68% yield using the procedure for **7** with 2,6-dimethylaniline: ^{1}H NMR (CDCl$_3$) δ 7.03 (d, 2, Ar-*H*$_m$), 6.63 (t, 1, Ar-*H*$_p$), 4.22 (m, 2, O(C*H*$_2$)$_A$), 4.12 (s, 3, O*Me*$_A$), 4.11 (m, 2, O(C*H*$_2$)$_B$), 4.01 (s, 3, O*Me*$_B$), 2.82 (s, 6, Ar-*Me*); ^{13}C NMR (CDCl$_3$) δ *C*$_i$ n/a, 138.5 (Ar-*C*$_o$), 126.8 (Ar-*C*$_m$), 125.4 (Ar-*C*$_p$), 76.0 (O(*C*H$_2$)$_A$), 70.9 (O(*C*H$_2$)$_B$), 70.2 (O*Me*$_A$), 62.9 (O*Me*$_B$), 19.1 (Ar-*C*H$_3$). Anal. Calcd for TaC$_{12}$H$_{19}$Cl$_3$NO$_2$: C, 29.02; H, 3.86; N, 2.82. Found: C, 28.83; H, 3.81; N, 2.96.

Ta(N-4-CNC$_6$H$_4$)Cl$_3$(dme) (10). This compound was synthesized in 86% yield using the procedure for **7** with 4-aminobenzonitrile: ^{1}H NMR (CDCl$_3$) δ 7.64 (d, 2, Ar-*H*$_m$), 7.14 (d, 2, Ar-*H*$_o$), 4.24 (m, 2, O(C*H*$_2$)$_A$), 4.17 (m, 2, O(C*H*$_2$)$_B$), 4.14 (s, 3, O*Me*$_A$), 4.09 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ *C*$_i$, *C*$_p$, *C*N, n/a, 132.3 (Ar-*C*$_m$), 127.4 (Ar-*C*$_o$), 76.1 (O(*C* H$_2$)$_A$), 71.3 (O(*C* H$_2$)$_B$), 69.9 (O*Me*$_A$), 63.6 (O*Me*$_B$). Anal. Calcd for TaC$_{11}$H$_{14}$Cl$_3$N$_2$O$_2$: C, 26.77; H, 2.86; N, 5.68. Found: C, 26.25; H, 2.86; N, 5.51.

Ta(N-2-naphthyl)Cl$_3$(dme) (11). This compound was synthesized in 90% yield using the procedure for **7** with 2-aminonaphthalene. ^{1}H NMR (CDCl$_3$) δ 7.81 (d, 1, Ar-*H*$_4$), 7.77 (d, 1, Ar-*H*$_5$), 7.69 (d, 1, Ar-*H*$_3$), 7.46 (m, 2, Ar-*H*$_7$, *H*$_1$), 7.31 (m, 2, Ar-*H*$_6$,*H*$_8$), 4.22 (m, 2, O(C*H*$_2$)$_A$), 4.17 (s, 3, O*Me*$_A$), 4.15 (m, 2, O(C*H*$_2$)$_B$), 4.07 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ 150.7 (Ar-*C*$_2$), 132.5 (Ar-*C*$_{10}$), 131.7 (Ar-*C*$_9$), 128.0 (Ar-*C*$_4$), 127.9 (Ar-*C*$_5$), 127.2 (Ar-*C*$_3$), 126.0 (Ar-*C*$_7$), 125.9 (Ar-*C*$_1$), 125.7 (Ar-*C*$_6$), 124.7 (Ar-*C*$_8$), 75.9 (O(*C* H$_2$)$_A$), 71.1 (O(*C* H$_2$)$_B$), 69.8 (O*Me*$_A$), 63.2 (O*Me*$_B$). Anal. Calcd for TaC$_{14}$H$_{17}$NO$_2$Cl$_3$: C, 32.42; H, 3.30; N, 2.70. Found: C, 31.77; H, 3.12; N, 3.17.

Ta(N-2-anthryl)Cl$_3$(dme) (12). This compound was synthesized in 96% yield using the procedure for **7** with 2-aminoanthracene: ^{1}H NMR (CDCl$_3$) δ 8.36 (s, 1, Ar-*H*$_{10}$), 8.21 (s, 1, Ar-*H*$_1$), 7.98 (m, 2, Ar-*H*$_4$, *H*$_5$), 7.92 (d, 1, Ar-*H*$_3$), 7.53 (s, 1, Ar-*H*$_9$), 7.47 (m, 1, Ar-*H*$_7$), 7.37 (m, 2, Ar-*H*$_6$,*H*$_8$). Anal. Calcd for TaC$_{18}$H$_{19}$NO$_2$Cl$_3$: C, 38.02; H, 3.37; N, 2.46. Found: C, 36.90; H, 3.35; N, 2.45.

Nb(NCMe$_2$Et)Cl$_3$(py)$_2$ (13a). This compound was synthesized in 19% yield using the procedure for **1a** (method A) with NbCl$_5$. ^{1}H NMR (CDCl$_3$) δ 9.02 (dt, 2, py$_A$-*H*$_o$), 8.86 (dt, 2, py$_B$-*H*$_o$), 7.89 (tt, 1, py$_A$-*H*$_p$), 7.82 (tt, 1, py$_B$-*H*$_p$), 7.39 (m, 4, py-*H*$_m$), 1.74 (q, 2, CMe$_2$C*H*$_2$Me), 1.40 (s, 6, C*Me*$_2$CH$_2$Me), 1.13 (t, 3, CMe$_2$CH$_2$*Me*); ^{13}C NMR (CDCl$_3$) δ 152.7 (py$_A$-*C*$_o$), 151.2 (py$_B$-*C*$_o$), 139.7 (py$_A$-*C*$_p$), 138.2 (py$_B$-*C*$_p$), 124.3 (py$_A$-*C*$_m$), 124.1 (py$_B$-*C*$_m$), MeCH$_2$Me$_2$*C*, n/a, 35.9 (CMe$_2$*C* H$_2$Me), 26.9 (C*Me*$_2$CH$_2$Me), 9.2 (CMe$_2$CH$_2$ *Me*). Anal. Calcd for NbC$_{15}$H$_{21}$N$_3$Cl$_3$: C, 40.70; H, 4.78; N, 9.49. Found: C, 39.55; H, 4.86; N, 9.13.

[H$_3$NCMe$_2$Et]$_2$[Nb(NCMe$_2$Et)Cl$_5$] (13b). This compound was synthesized in quantitative yield using the procedure for **1b** with NbCl$_5$: ^{1}H NMR (CDCl$_3$) δ 6.53 (bs, 6, *H*$_3$NCMe$_2$Et), 1.77 (q, 4, H$_3$NCMe$_2$C*H*$_2$CH$_3$), 1.68 (q, 2, NCMe$_2$C*H*$_2$CH$_3$), 1.43 (s, 12, H$_3$NC*Me*$_2$CH$_2$CH$_3$), 1.38 (s, 6, NC*Me*$_2$CH$_2$CH$_3$), 1.11 (t, 3, NCMe$_2$CH$_2$C*H*$_3$), 1.00 (t, 6, H$_3$NCMe$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ N*C*Me$_2$CH$_2$CH$_3$, n/a, 56.6 (H$_3$N*C*Me$_2$CH$_2$CH$_3$), 35.6 (NCMe$_2$*C*H$_2$CH$_3$), 33.3 (H$_3$NCMe$_2$*C*H$_2$CH$_3$), 26.7 (NC*Me*$_2$CH$_2$CH$_3$), 25.0 (H$_3$NC*Me* $_2$CH$_2$CH$_3$), 9.1 (NCMe$_2$CH$_2$*C*H$_3$), 8.1 (H$_3$NCMe$_2$CH$_2$*C*H$_3$). Anal. Calcd for C$_{15}$H$_{39}$N$_3$Cl$_5$Nb: C, 33.89; H, 7.39; N, 7.90. Found: C, 33.87; H, 7.41; N, 7.89.

Nb(NCMe$_2$Et)Cl$_3$(dme) (13c). NbCl$_5$ (500 mg, 1.85 mmol) was dissolved in 10 mL of toluene by adding dimethoxyethane (192 mL, 1.85 mmol). To this yellow colored solution was slowly added *tert*-amylamine (649 mL, 5.55 mmol). The solution became foggy in 3 min. An excess of ZnCl$_2$ (1.01 g, 7.40 mmol) was added, and the reaction mixture was stirred for 4 h. It was then chilled to −40 °C for 3 h, filtered through Celite, and concentrated *in vacuo*. The resulting powder was washed with pentane and dried *in vacuo* to give 651 mg (94%) of a yellow solid: ^{1}H NMR (CDCl$_3$) δ 4.08 (m, 2, O(C*H*$_2$)$_A$), 4.05 (s, 3, O*Me*$_A$), 4.02 (m, 2, O(C*H*$_2$)$_B$), 3.87 (s, 3, O*Me*$_B$), 1.69 (q, 2, CMe$_2$C*H*$_2$CH$_3$), 1.37 (s, 6, C*Me*$_2$CH$_2$CH$_3$), 1.14 (CMe$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 75.5 (O(*C*H$_2$)$_A$), 70.4 (O(*C*H$_2$)$_B$), 69.6 (O*Me*$_A$), 61.9 (O*Me*$_B$), *C*Me$_2$CH$_2$CH$_3$ not observed, 36.0 (C(Me)$_2$*C*H$_2$CH$_3$), 27.1 (C*Me*$_2$CH$_2$CH$_3$), 9.1 (CMe$_2$CH$_2$*C*H$_3$). Anal. Calcd for NbC$_9$H$_{21}$NO$_2$Cl$_3$: C, 28.86; H, 5.65; N, 3.74. Found: C, 26.83; H, 5.54; N, 4.04.

Nb(NCMe$_3$)Cl$_3$(dme) (14). NbCl$_5$ (1.00 g, 3.70 mmol) was dissolved in dichloromethane (30 mL) by adding dimethoxyethane (384 mL, 3.70 mmol). ZnCl$_2$ (1.01 g, 7.40 mmol) was added to the solution, forming a white precipitate. This was cooled to −40 °C, and a solution of *tert*-butylamine (389 mL, 3.70 mmol) and triethylamine (1.03 mL, 7.40 mmol) in CH$_2$Cl$_2$ (10 mL) was slowly added. The precipitate dissolved, and the yellow solution was stirred for 18 h, during which time it darkened. It was concentrated *in vacuo* to a dark green oil, which was extracted with toluene, filtered through Celite, and concentrated *in vacuo*. The resulting yellow oil crystallized after standing with pentane to give 933 mg (70%) of a yellow solid. ^{1}H NMR (CDCl$_3$) δ 4.08 (m, 2, O(C*H*$_2$)$_A$), 4.06 (s, 3, O*Me*$_A$), 4.02 (m, 2, O(C*H*$_2$)$_B$), 3.89

(s, 3, O*Me*$_B$), 1.42 (C*Me*$_3$); ^{13}C NMR (CDCl$_3$) δ 75.4 (O*C*H$_2$)$_A$), 70.5 (O*C*H$_2$)$_B$), 69.7 (O*Me*$_A$), 61.9 (O*Me*$_B$) *C*Me$_3$, n/a, 29.4 (C*Me*$_3$).

Nb(N-1-adamantyl)Cl$_3$(py)$_2$ (15a). Compound **15c** (250 mg, 57.0 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL). Pyridine was added (~0.3 mL) and the solution stirred for 3 h. It was concentrated *in vacuo* to give a yellow oil which crystallized upon standing under pentane to a yellow solid quantitative yield: ^{1}H NMR (CDCl$_3$) δ 9.04 (d, 2, py$_A$-*H*$_o$), 8.88 (d, 2, py$_B$-*H*$_o$), 7.87 (m, 2, py-*H*$_p$), 7.41 (m, 4, py-*H*$_m$), 2.13 (s, 9, C(CH$_2$C*H*CH$_2$)$_3$ and C(C*H*$_2$CHCH$_2$)$_3$), 1.63 (m, 6, C(CH$_2$CHC*H*$_2$)$_3$); ^{13}C NMR (CDCl$_3$) δ 152.8 (py$_A$-*C*$_o$), 151.1 (py$_B$-*C*$_o$), 139.7 (py$_A$-*C*$_p$), 138.3 (py$_B$-*C*$_p$), 124.3 (py$_A$-*C*$_m$), 124.2 (py$_B$-*C*$_m$), *C*(CH$_2$CHCH$_2$)$_3$ not observed, 42.2 (C(CH$_2$*C*HCH$_2$)$_3$), 36.0 (C(*C*H$_2$CHCH$_2$)$_3$), 29.1 (C(CH$_2$CH*C*H$_2$)$_3$). Anal. Calcd for NbC$_{20}$H$_{25}$N$_3$Cl$_3$: C, 47.39; H, 4.98; N, 8.29. Found: C, 46.85; H, 5.18; N, 8.12. This compound consistently analyzed low in carbon.

Nb(N-1-adamantyl)Cl$_3$(dme) (15c). NbCl$_5$ (500 mg, 1.85 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) by adding ~0.3 mL of dimethoxyethane. ZnCl$_2$ (504 mg, 3.70 mmol) was added, and a white precipitate formed. This was cooled to −40 °C, and a solution of adamantylamine (280 mg, 1.85 mmol) and triethylamine (516 mL, 3.70 mmol) in CH$_2$Cl$_2$ (5 mL) was slowly added. The reaction mixture was stirred for 16 h, during which time the precipitate dissolved and a yellow-brown solution formed. This was evaporated *in vacuo* to give a yellow solid and a black oil which was treated two times with 5 mL of toluene/CH$_2$Cl$_2$ (4:1 by volume) in order to extract the product. The extracts were combined, concentrated *in vacuo*, and recrystallized from CH$_2$Cl$_2$/pentane to give 578 mg (71%) of a yellow solid: ^{1}H NMR (CDCl$_3$) δ 4.09 (s, 3, O*Me*$_A$), 4.07 (m, 2, O(C*H*$_2$)$_A$), 4.01 (m, 2, O(C*H*$_2$)$_B$), 3.88 (s, 3, O*Me*$_B$), 2.09 (bs, 3, C(CH$_2$C*H*CH$_2$)$_3$), 2.06 (s, 6, C(C*H*$_2$CHCH$_2$)$_3$), 1.61 (m, 6, C(CH$_2$CHC*H*$_2$)$_3$); ^{13}C NMR (CDCl$_3$) δ 75.4 (O(*C*H$_2$)$_A$), 70.4 (O(*C*H$_2$)$_B$), 70.1 (O*Me*$_A$), 61.8 (O*Me*$_B$), *C*(CH$_2$CHCH$_2$)$_3$ not observed, 42.5 (C(CH$_2$*C*HCH$_2$)$_3$), 35.8 (C(*C*H$_2$CHCH$_2$)$_3$), 29.1 (C(CH$_2$CH*C*H$_2$)$_3$). Anal. Calcd for NbC$_{14}$H$_{25}$NCl$_3$O$_2$: C, 38.33; H, 5.75; N, 3.19. Found: C, 37.34; H, 5.66; N, 3.19. This compound consistently analyzed low in carbon.

Nb(NC$_6$H$_5$)Cl$_3$(dme) (16). This compound was synthesized in quantitative yield using the procedure for **7** with NbCl$_5$. ^{1}H NMR (CDCl$_3$) δ 7.35 (m, 4, Ph-*H*$_o$,*H*$_m$), 7.11 (tt, 1, Ph-*H*$_p$), 4.12 (m, 4, OC*H*$_2$), 4.02 (s, 3, O*Me*$_A$), 4.00 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ Ph-*C*$_i$ not observed, 128.4 (Ph-*C*$_o$), 127.4 (Ph-*C*$_p$), 125.2 (Ph-*C*$_m$), 75.3 (O(*C* H$_2$)$_A$), 70.9 (O(*C* H$_2$)$_B$), 68.6 (O*Me*$_A$), 62.8 (O*Me*$_B$).

Nb(N-2,6-*i*-Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (17). This compound was synthesized in quantitative yield using the procedure for **8** with NbCl$_5$: ^{1}H NMR (CDCl$_3$) δ 7.11 (d, 2, Ar-*H*$_m$), 7.00 (t, 1, Ar-*H*$_p$), 4.40 (m, 2, C*H* Me$_2$), 4.16 (m, 2, O(C*H*$_2$)$_A$), 4.10 (m, 2, O(C*H*$_2$)$_B$), 3.97 (s, 3, O*Me*$_A$), 3.96 (s, 3, O*Me*$_B$), 1.32 (d, 12, CH*Me*$_2$); ^{13}C NMR (CDCl$_3$) δ Ar-*C*$_i$ not observed, 148.6 (Ar-*C*$_m$), 127.3 (Ar-*C*$_o$), 122.7 (Ar-*C*$_p$), 75.6 (O*C*H$_2$)$_A$), 70.6 (O(*C*H$_2$)$_B$), 68.7 (O*Me*$_A$), 62.5 (O*Me*$_B$), 27.9 (*C*HMe$_2$), 24.7 (CH*Me*$_2$). This compound has been reported previously.[12]

Nb(N-4-CNC$_6$H$_4$)Cl$_3$(dme) (18). This compound was synthesized in 75% yield using the procedure for **10** with NbCl$_5$: ^{1}H NMR (CDCl$_3$) δ 7.63 (d, 2, Ar-*H*$_m$), 7.43 (d, 2, Ar-*H*$_o$), 4.15 (bs, 4, OC*H*$_2$), 4.04 (s, 3, O*Me*$_A$), 3.97 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ 155.9 (Ar-*C*$_i$), 132.7 (Ar-*C*$_m$), 125.8 (Ar-*C*$_o$), 118.2 (Ar-*C* N), 110.0 (Ar-*C*$_p$), 75.4 (O(*C*H$_2$)$_A$), 71.1 (O(*C*H$_2$)$_B$), 68.7 (O*Me*$_A$), 63.2 (O*Me*$_B$). Anal. Calcd for NbC$_{11}$H$_{14}$N$_2$O$_2$Cl$_3$: C, 32.58; H, 3.48; N, 6.91. Found: C, 31.66; H, 3.33; N, 6.82.

Nb(N-2-naphthyl)Cl$_3$(dme) (19). This compound was synthesized in quantitative yield using the procedure for **11** with NbCl$_5$: ^{1}H NMR (CDCl$_3$) δ 7.78 (m, 4, Ar-*H*$_4$,*H*$_5$,*H*$_3$, *H*$_1$), 7.54 (dd, 1, Ar-*H*$_8$), 7.49 (m, 1, Ar-*H*$_7$), 7.40 (m, 1, Ar-*H*$_6$), 4.13 (m, 4, OC*H*$_2$), 4.03 (s, 3, O*Me*$_A$), 4.01 (s, 3, O*Me*$_B$); ^{13}C NMR (CDCl$_3$) δ Ar-*C*$_2$, n/a, 132.6 (Ar-*C*$_{10}$), 132.2 (Ar-*C*$_9$), 128.5 (Ar-*C*$_4$), 128.2 (Ar-*C*$_5$), 127.6 (Ar-*C*$_3$), 126.73 (Ar-*C*$_7$), 126.66 (Ar-*C*$_1$), 124.0 (Ar-*C*$_6$), 123.2 (Ar-*C*$_8$), 75.3 (O(*C*H$_2$)$_A$), 70.9 (O(*C*H$_2$)$_B$), 68.6 (O*Me*$_A$), 62.8 (O*Me*$_B$). Anal. Calcd for NbC$_{14}$H$_{17}$NO$_2$Cl$_3$: C, 39.05; H, 3.98; N, 3.25. Found: C, 38.87; H, 3.94; N, 3.21.

Nb(N-2-anthryl)Cl$_3$(dme) (20). This compound was synthesized in quantitative yield using the procedure for **12** with NbCl$_5$: ^{1}H NMR (CDCl$_3$) δ 8.36 (s, 1, Ar-*H*$_{10}$), 8.33 (s, 1, Ar-*H*$_1$), 7.96 (m, 4, Ar-*H*$_4$,*H*$_5$,*H*$_3$,*H*$_9$), 7.47 (m, 1, Ar-*H*$_7$), 7.37 (m, 2, Ar-*H*$_6$,*H*$_8$), 4.16 (s, 4, OC*H*$_2$), 4.06 (s, 6, O*Me*).

Crystallographic Structure Determination. Crystallographic data are collected in Table 3. Yellow-green rod-shaped crystals were photographically characterized and determined to belong to the monoclinic crystal system. Systematic absences in the diffraction data indicated that space group was either *C*2/*c* or *Cc*. The noncentrosymmetric alternative was ultimately chosen on the basis of the absence of either inversional or 2-fold rotational relationships between molecules in the unit cell. The asymmetric unit consists of two uncorrelated chemically identical molecules. An empirical correction for absorption was applied to the diffraction data ($T_{\mathrm{max/min}} = 1.11$). The structure was solved by direct methods, completed from difference Fourier maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms except for carbon to conserve data. Hydrogen atoms were idealized. All computations used SHELXTL 4.2 software (G. Sheldrick, Siemens XRD, Madison, WI).

Spartan Calculations. The molecules were constructed in the builder application of Spartan 4.0 on a Silicon Graphics Indigo workstation. The molecules were then geometry-optimized using the PM3(TM) parameter set. An MO calculation was then performed (not necessary), followed by a frequency calculation to obtain the predicted normal vibrational modes. These were tabulated and examined with the animated modes using the Spartan graphical interface.

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Supporting Information Available: Tables of output files for the frequency calculations of Ta(N)Cl$_3$, Ta(NH)Cl$_3$, Ta(NMe)Cl$_3$, Ta(NCMe$_3$)Cl$_3$, Ta(NPh)Cl$_3$, and Ta(NCMe$_3$)Cl$_3$(dme) (40 pages). An X-ray crystallographic file in CIF format for complex **14** is available on the Internet only. Ordering and access information is given on any current masthead page.

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