Tetrahydroquinolinyl Amido and Indolinyl Amido Complexes of Tantalum as Models for Substrate−Catalyst Adducts in Hydrodenitrogenation Catalysis

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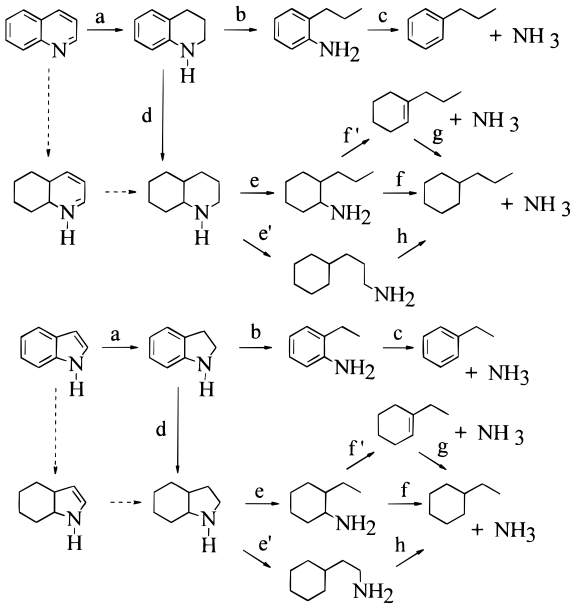
The reactions of $TaCl_5$ with $Me_3SiNC_9H_{10}$ or $LiNC_9H_{10}$, where $[NC_9H_{10}]^-$ = tetrahydroquinolinyl (the amido anion of tetrahydroquinoline), afford selective preparative routes to the complete series of amido halide complexes of tantalum(V) $Ta(NC_9H_{10})_nCl_{5-n}$ for $n = 1-5$ (compounds **1**−**5**, respectively). The monokis(tetrahydroquinolinyl) complex is isolated as an ether adduct $Ta(NC_9H_{10})Cl_4(OEt_2)$ while the complexes $Ta(NC_9H_{10})_nCl_{5-n}$ ($n = 2-5$) are found to be base-free, monomeric species. The related complexes of indolinyl $[NC_8H_8]^-$ (the amido anion of indoline), $Ta(NC_8H_8)_nCl_{5-n}(THF)$ for $n = 1$ (**6**) or 2 (**7**), have been prepared from $TaCl_5$, $Me_3SiNC_8H_8$, and THF. An X-ray structural determination of $Ta(NC_9H_{10})_2Cl_3$ (**2**) reveals that it adopts a trigonal bipyramidal geometry with equatorial amido ligands that are closer to lying parallel (within) than perpendicular to the TBP equatorial plane. Routes to mixed-ligand aryloxide−amide complexes have been developed from either aryloxide or amido precursors but not from both. Thus, $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (**8**), where Ar = 2,6-$C_6H_3{}^iPr_2$, and $Ta(NC_8H_8)(OAr)Cl_3(OEt_2)$ (**9**) are available from reacting $Ta(OAr)Cl_4(OEt_2)$ with $Me_3SiNC_9H_{10}$ and $Me_3SiNC_8H_8$, respectively, while $Ta(NC_9H_{10})_2(OAr)_2Cl$ (**10**) is available from $Ta(NC_9H_{10})_2Cl_3$ (**2**) and excess $LiOAr{\cdot}OEt_2$. The alkyl derivatives $Ta(NC_9H_{10})(OAr)Me_2Cl$ (**11**), $Ta(NC_9H_{10})(OAr)Et_2Cl$ (**12**), $Ta(NC_9H_{10})_2(OAr)_2Me$ (**13**), and $Ta(NC_9H_{10})Me_2Cl_2$ (**14**) are prepared from AlR_3 or ZnR_2 reagents and the appropriate precursor. Thermolyzing compounds **4**, **5**, and **11**−**14** in solution afforded no evidence for the formation of any $\eta^2(N,C)$-heterocyclic complexes arising from metalation of a NC_9H_{10} ligand.

Introduction

The catalytic removal of nitrogen from petroleum is necessary to reduce NO_x emissions upon combustion of its fuel products and to reduce organonitrogen compounds, which can poison re-forming and hydrocracking catalysts used in petroleum refining.[1−6] Under standard hydrodenitrogenation (HDN) conditions (300−450 °C, up to 200 atm of H_2), N-heterocycles are readily hydrogenated, although they are slow to undergo C−N bond hydrogenolysis reactions.[7−10] A generalized HDN reaction scheme for the model substrates quinoline and indole is presented in Scheme 1.[3,11,12] The most efficient and selective method of quinoline HDN involves the a → b → c pathway in which the carbocyclic ring is not hydrogenated, however most of the quinoline follows the a → d → e → f pathway (perhaps involving f′) where the carbocycle is also hydrogenated *before* C−N bonds are cleaved. In either case, the most facile step is hydrogenation of the heterocycle (step a); therefore, quinoline HDN invariably involves the intermediacy of tetrahydroquinoline, just as indole HDN proceeds *via* indoline, Scheme 1.

Scheme 1



While there are several reports of quinoline complexes,[13−17] and catalytic HDN studies invariably examine quinoline and

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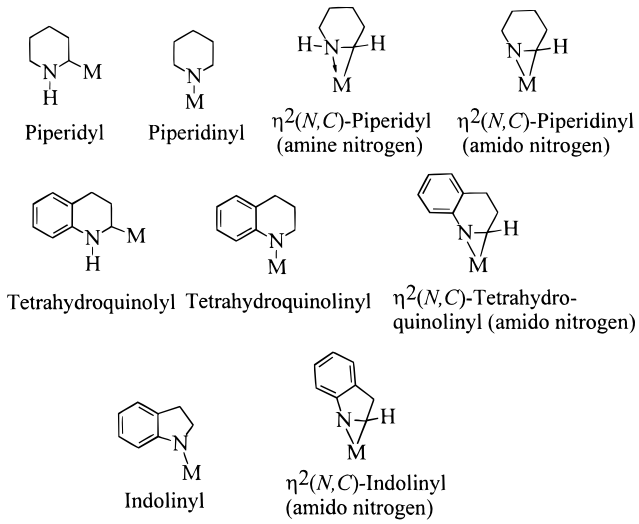
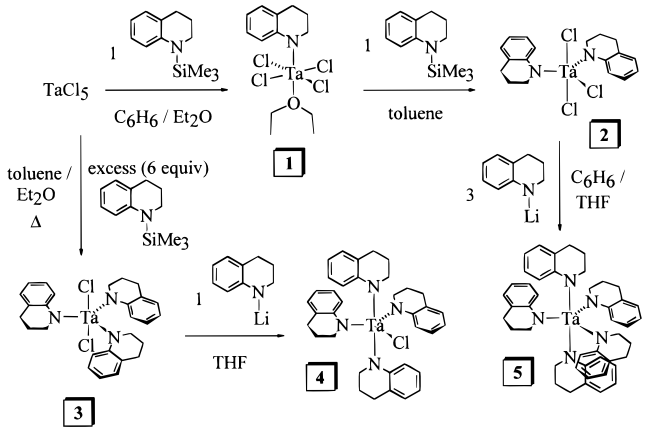


Figure 1. Binding modes and metalated forms of piperidine, tetrahydroquinoline, and indoline.

indole substrates,[14,18−23] complexes of their hydrogenated derivatives tetrahydroquinoline or indoline are scarce.[14,24,25] In this report, we describe the preparation and properties of tantalum aryloxide complexes containing the *amido* ligands of tetrahydroquinoline and indoline, namely tetrahydroquinolinyl ($[NC_9H_{10}]^-$, the anion of tetrahydroquinoline) and indolinyl ($[NC_8H_8]^-$, the anion of indoline), Figure 1. (The amide of indoline, indolinyl $[NC_8H_8]^-$, is not to be confused with the amide of indole, the $[NC_8H_6]^-$ ligand.) These compounds were deemed worthy synthetic targets for two reasons. First, in an effort to closely model substrate−catalyst complexes at the active site in HDN, early transition metal complexes[26] of these partially hydrogenated ligands should be examined. Second, because the $\eta^2(N,C)$ binding mode provides excellent reactivity models for fundamental HDN reactions of pyridines,[27−30] we wanted to determine whether η^1 complexes of tetrahydroquinoline, or of its amide, might serve as precursors to related η^2 species. We note that one mechanistic proposal for piperidine HDN includes an $\eta^2(N,C)$-*piperidyl* ligand, Figure 1.[8,9] (Our terminology for *metalated* forms of selected ligands is also presented in Figure 1.)

Scheme 2



Results

Preparation and Properties of Tetrahydroquinolinyl Complexes of Tantalum(V). By the reaction of $TaCl_5$ with 1 equiv of $Me_3SiNC_9H_{10}$ in C_6H_6/Et_2O, intense burgundy-colored, almost black crystalline rods of compound **1** can be isolated in nearly quantitative yield, Scheme 2. Analytical and spectroscopic data are consistent with the formulation of **1** as the monokis(amido) complex $Ta(NC_9H_{10})Cl_4(OEt_2)$. On the basis of the structures observed or proposed for $Ta[OSi(2\text{-}C_6H_4Me)_3]Cl_4(OEt_2)$,[31] $Ta(OAr)Cl_4(OEt_2)$,[32] and $M(NR_2)Cl_4(OEt_2)$ (M = Nb, Ta),[33] we formulate $Ta(NC_9H_{10})Cl_4(OEt_2)$ (**1**) as the *trans* isomer. The ^1H and ^{13}C NMR data for **1** are entirely consistent with the simple $\eta^1(N)$ mode of amido bonding to the d^0 metal; e.g., the ^1H NMR resonances attributed to the H2 and H8 protons of the NC_9H_{10} ligand are shifted downfield with respect to those of the free tetrahydroquinoline (C_6D_6, probe temperature). This shift appears to be a manifestation of these protons' proximity to the electrophilic d^0 metal when the heterocycle is coordinated in this fashion.[13] However, the ^{13}C chemical shifts do not consistently track the proton shifts, as demonstrated by the HETCOR spectrum of **1** (see Experimental Section).

When $Ta(NC_9H_{10})Cl_4(OEt_2)$ (**1**) reacts with 1 equiv of $Me_3SiNC_9H_{10}$ in toluene, burgundy-colored, microcrystalline $Ta(NC_9H_{10})_2Cl_3$ (**2**) is observed to precipitate in moderate yield, Scheme 2. While samples of $Ta(NC_9H_{10})_2Cl_3$ (**2**) collected in this fashion were found to be analytically pure, the dark red filtrate obtained from isolating these microcrystals contains a mixture of $Ta(NC_9H_{10})Cl_4(OEt_2)$ (**1**), $Ta(NC_9H_{10})_2Cl_3$ (**2**), and $Ta(NC_9H_{10})_3Cl_2$ (**3**) (*vide infra*). The last compound is obtained in high yield from reacting $TaCl_5$ with *excess* $Me_3SiNC_9H_{10}$ (toluene, 100 °C), suggesting that the tris(amido) complex $Ta(NC_9H_{10})_3Cl_2$ (**3**) is a thermodynamic product that arises from maximizing the total bond energies in the $Ta(NC_9H_{10})_nCl_{5-n} + (5-n)Me_3SiNC_9H_{10} + nMe_3SiCl$ mixtures. This feature is confirmed by reacting $Ta(NC_9H_{10})_5$ (*vide infra*) with 5 equiv of Me_3SiCl, which affords the same mixture of $Ta(NC_9H_{10})_3Cl_2$ (**3**), Me_3SiCl, and $Me_3SiNC_9H_{10}$ as that obtained from $TaCl_5$ and 5 equiv of $Me_3SiNC_9H_{10}$ under identical conditions. These observations demonstrate the kinetic accessibility of $Ta(NC_9H_{10})_3Cl_2$ from either direction and suggest the series of facile metathesis reactions shown in eq 1. This kinetic feature has found considerable synthetic utility in early metal alkoxide and amide chemistry.[32−39]

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$$TaCl_5 + 5Me_3SiNC_9H_{10} \rightleftarrows$$
$$Ta(NC_9H_{10})Cl_4 + Me_3SiCl + 4Me_3SiNC_9H_{10} \rightleftarrows$$
$$Ta(NC_9H_{10})_2Cl_3 + 2Me_3SiCl + 3Me_3SiNC_9H_{10} \rightleftarrows$$
$$Ta(NC_9H_{10})_3Cl_2 + 3Me_3SiCl + 2Me_3SiNC_9H_{10} \rightleftarrows$$
$$Ta(NC_9H_{10})_4Cl + 4Me_3SiCl + Me_3SiNC_9H_{10} \rightleftarrows$$
$$Ta(NC_9H_{10})_5 + 5Me_3SiCl \quad (1)$$

Both $Ta(NC_9H_{10})_2Cl_3$ (**2**) and $Ta(NC_9H_{10})_3Cl_2$ (**3**) display equivalent NC_9H_{10} amido ligands in their ^1H and ^{13}C NMR spectra, suggesting either the static structures shown in Scheme 2, presumably with free rotation about $Ta-NR_2$ bonds, or fluxional five-coordinate molecules. The solid state structure of $Ta(NC_9H_{10})_2Cl_3$ (**2**) has been determined to be that shown in Scheme 2; *vide infra*.

Since the reaction of any $Ta(NC_9H_{10})_nCl_{5-n}$ ($n = 0-3$) complex with excess $Me_3SiNC_9H_{10}$ affords only $Ta(NC_9H_{10})_3Cl_2$, further amidation of the metal center was attempted using more nucleophilic reagents. When $Ta(NC_9H_{10})_3Cl_2$ is reacted with 1 equiv of $LiNC_9H_{10}\cdot 2THF$ (in THF), orange crystals of the tetrakis(amido) complex $Ta(NC_9H_{10})_4Cl$ (**4**) can be isolated in high yield, Scheme 2. Similarly, reacting $Ta(NC_9H_{10})_2Cl_3$ with 3 equiv of $LiNC_9H_{10}\cdot 2THF$ (in C_6H_6/THF) affords an orange powder that analyzes as the pentakis(amido) complex $Ta(NC_9H_{10})_5$ (**5**). Although samples of $Ta(NC_9H_{10})_5$ (**5**) isolated in this manner are analytically pure, attempts to grow crystals of this compound have failed. The ^1H and ^{13}C NMR spectra of **4** and **5** reveal equivalent NC_9H_{10} ligands, implying fluxional five-coordinate species. Complex **5** is also accessible from reacting $Ta(NC_9H_{10})_3Cl_2$ with 2 equiv of $LiNC_9H_{10}\cdot 2THF$. The reaction of $TaCl_5$ with 5 equiv of $LiNC_9H_{10}\cdot 2THF$ also affords $Ta(NC_9H_{10})_5$ (**5**) in low yield, along with byproducts arising from tantalum reduction; therefore, this direct synthesis is not the preferred route to **5**. Pentakis(amido) complexes of niobium[40,41] and tantalum[41,42] have been reported from reacting MCl_5 with 5 $LiNR_2$, and the structures of $Nb(NMe_2)_5$,[43] $Nb(NC_5H_{10})_5$,[43] and $Ta(NEt_2)_5$[44] have been determined crystallographically.

Preparation and Properties of Indolinyl Complexes of Tantalum(V). Indolinyl analogues of the tetrahydroquinolinyl complexes are also accessible from metathetical reactions using the appropriate (trimethylsilyl)amine. Thus, reacting $TaCl_5$ with 1 equiv of $Me_3SiNC_8H_8$ (in C_6H_6/Et_2O) affords a dark purple, insoluble solid presumed to be either $[Ta(NC_8H_8)Cl_4]_n$ or $Ta(NC_8H_8)Cl_4\cdot OEt_2$. (We note that moderately soluble $[Ta(OAr)Cl_4]_2$ readily forms adducts with THF or Et_2O.[32]) Upon dissolution of this solid in THF, a soluble monokis(amido) complex can be isolated in high yield as the dark purple adduct $Ta(NC_8H_8)Cl_4(THF)$ (**6**), Scheme 3. The ^1H and ^{13}C NMR data for this compound are also consistent with a simple $\eta^1(N)$ mode of amido bonding to the d^0 metal. Further reaction of $Ta(NC_8H_8)Cl_4(THF)$ (**6**) with 1 equiv of $Me_3SiNC_8H_8$ (in C_6H_6) forms $Ta(NC_8H_8)_2Cl_3(THF)$ (**7**) as a brown powder. The inequivalent NC_8H_8 ligands observed in the NMR spectra of $Ta(NC_8H_8)_2Cl_3(THF)$ (**7**) support its formulation as the *cis-mer* isomer as shown in Scheme 3. The observation that $Ta(NC_9H_{10})_2Cl_3$ (**2**) does not coordinate Et_2O (*vide supra*) and appears to only loosely coordinate THF suggests that the isolation of **7** may reflect the slight steric difference between coordinated NC_9H_{10} and NC_8H_8 amido ligands.

Scheme 3

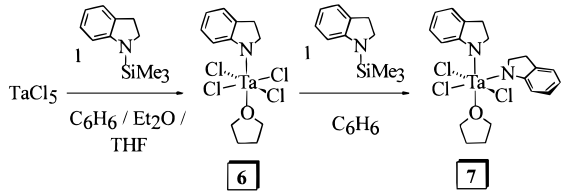

Table 1. Crystallographic Data for $Ta(NC_9H_{10})_2Cl_3$ (**2**)[a]

empirical formula	$C_{18}H_{20}Cl_3N_2Ta$	space group	monoclinic $P2_1/c$ (No. 14)
fw	551.68	T	20 ± 1 °C
a	15.409(1) Å	λ	0.710 73 Å
b	9.946(1) Å	ρ_{calcd}	1.96 g cm^{-3}
c	12.310(1) Å	μ	62.3 cm^{-1}
β	96.62(8)°	R	0.025
V	1874.0(7) Å^3	R_w	0.034
Z	4		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

X-ray Structural Study of $Ta(NC_9H_{10})_2Cl_3$. Red single crystals of $Ta(NC_9H_{10})_2Cl_3$ (**2**) suitable for an X-ray structural determination were grown directly from the toluene reaction solution at −35 °C. A summary of the crystal data and structural analysis is given in Table 1, and relevant bond distances, bond angles, and torsional angles are provided in Table 2. Figure 2 presents two views of $Ta(NC_9H_{10})_2Cl_3$ (**2**) in which the complex can be seen to adopt a trigonal bipyramidal geometry with equatorial NC_9H_{10} amido ligands. The $Cl1_{axial}-Ta-Cl3_{axial}$ linkage is almost linear (170.27(7)°), while the $L_{axial}-Ta-L_{equatorial}$ angles that span a narrow range of 84.92(7)−93.6(2)° (averaging 90.1°) are clearly indicative of a trigonal bipyramid.

The NC_9H_{10} amido ligands are closer to lying parallel (within) than perpendicular to the equatorial plane of the trigonal bipyramid. However, significant tilting of the NC_9H_{10} rings toward a propeller arrangement is apparent, as the phenyl rings of both amido ligands are 35.9(3) and 21.6(4)° out-of-plane with the best equatorial TaN_2Cl plane for the N11 amide and the N21 amide, respectively. The saturated ring of the N21 NC_9H_{10} ligand, however, is twisted more out-of-plane than that of the N11 ligand, as judged from the torsional angles about the Cl−Ta−N−C bonds, Table 2. Although $N(p\pi)\rightarrow Ta(d\pi)$ bonding from *both* amido ligands is possible if they are either parallel or perpendicular to the TBP equatorial plane, a steric preference for *parallel* amido ligands (within the plane) seems more likely, since a nearly perpendicular orientation of these ligands would eclipse the NC_9H_{10} H8 and H2 protons with the axial chloride ligands. However, steric restriction imposed by the neighboring NC_9H_{10} ligand does not allow both amides to lie completely within the equatorial plane, thereby accounting for the observed twisting.

Ligand twisting is accompanied by a *smaller* N−Ta−N angle than one might expect: the N11−Ta−N21 angle of 116.8(2)° contrasts with the Cl2−Ta−N angles of 121.4(1) and 121.8-

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Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsional Angles (deg) in $Ta(NC_9H_{10})_2Cl_3$ (**2**)[a]

Bond Distances			
Ta−Cl1	2.381(2)	C17−C18	1.37(1)
Ta−Cl2	2.340(2)	C18−C19	1.392(8)
Ta−Cl3	2.383(2)	N21−C21	1.498(8)
Ta−N11	1.932(5)	N21−C29	1.429(8)
Ta−N21	1.932(5)	C21−C22	1.51(1)
N11−C11	1.493(7)	C22−C23	1.51(1)
N11−C19	1.412(8)	C23−C24	1.49(1)
C11−C12	1.502(9)	C24−C29	1.399(8)
C12−C13	1.52(1)	C24−C25	1.39(1)
C13−C14	1.498(9)	C25−C26	1.39(1)
C14−C19	1.409(9)	C26−C27	1.36(1)
C14−C15	1.391(9)	C27−C28	1.369(9)
C15−C16	1.38(1)	C28−C29	1.395(9)
C16−C17	1.37(1)		
Bond Angles			
Cl1−Ta−Cl2	84.92(7)	Cl3−Ta−N21	92.7(2)
Cl1−Ta−Cl3	170.27(7)	N11−Ta−N21	116.8(2)
Cl1−Ta−N11	92.9(2)	Ta−N11−C11	110.0(4)
Cl1−Ta−N21	90.8(2)	Ta−N11−C19	135.3(4)
Cl2−Ta−Cl3	85.51(7)	C11−N11−C19	114.5(5)
Cl2−Ta−N11	121.4(1)	Ta−N21−C21	112.4(4)
Cl2−Ta−N21	121.8(2)	Ta−N21−C29	132.3(4)
Cl3−Ta−N11	93.6(2)	C21−N21−C29	115.1(5)
Torsional Angles			
Cl1−Ta−N11−C11	100.44(34)	Cl1−Ta−N21−C21	128.82(38)
Cl1−Ta−N11−C19	−84.62(52)	Cl1−Ta−N21−C29	−56.48(50)
Cl2−Ta−N11−C11	14.61(41)	Cl2−Ta−N21−C21	−146.68(33)
Cl2−Ta−N11−C19	−170.45(46)	Cl2−Ta−N21−C29	28.02(57)
Cl3−Ta−N11−C11	−72.32(34)	Cl3−Ta−N21−C21	−60.26(38)
Cl3−Ta−N11−C19	102.62(52)	Cl3−Ta−N21−C29	114.44(50)
N21−Ta−N11−C11	−167.21(34)	N11−Ta−N21−C21	35.16(45)
N21−Ta−N11−C19	7.72(60)	N11−Ta−N21−C29	−150.14(48)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

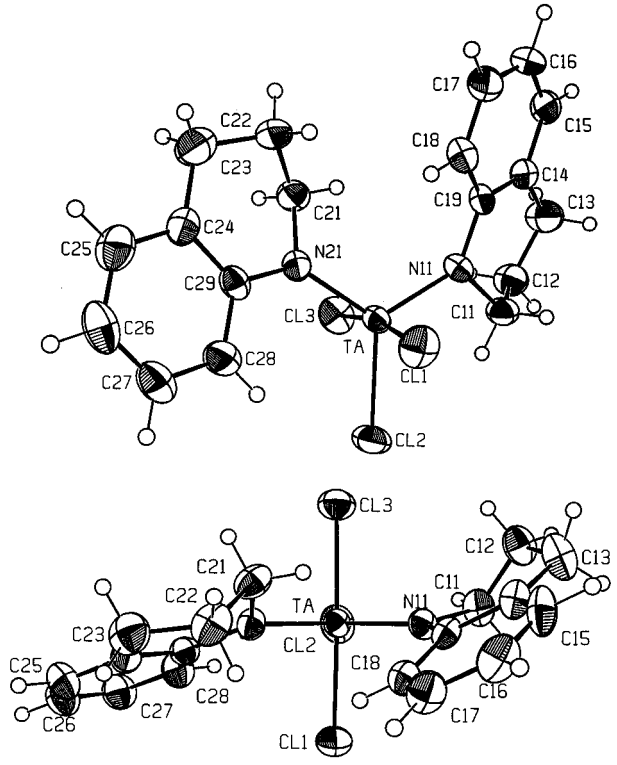
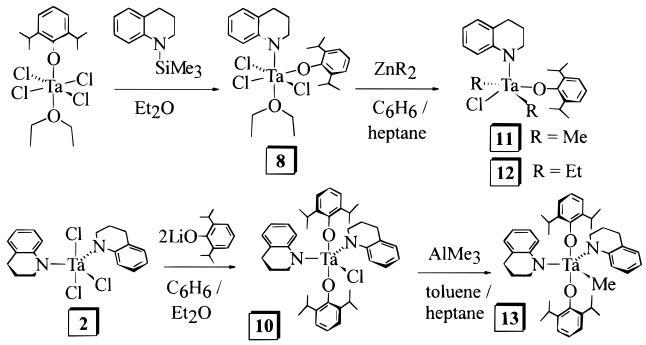


Figure 2. Two views of the molecular structure of $Ta(NC_9H_{10})_2Cl_3$ (**2**) with atoms represented as 50% ellipsoids.

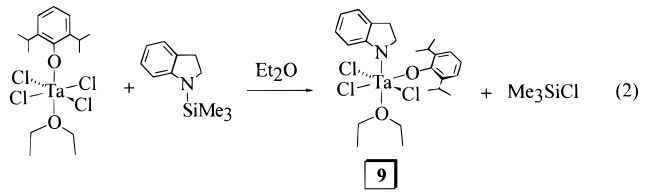
(2)°. This structural feature was also noted in $Ta[N(SiMe_3)_2]_2Cl_3$,[45] the structure of which has been communicated.[46] $Ta[N(SiMe_3)_2]_2Cl_3$ also adopts a trigonal bipyramidal geometry with equatorial $N(SiMe_3)_2$ ligands and a propeller-like twisting of the amido ligands out of the equatorial plane. Likewise, the equatorial N−Ta−N angle in $Ta[N(SiMe_3)_2]_2Cl_3$ measures only 115°. While the small N−Ta−N angle may reflect an enhancement in N(pπ)→Ta(dπ) overlap, the authors suggest that interactions between the equatorial chloride and methyl groups from both $N(SiMe_3)_2$ ligands induce *larger* than expected equatorial Cl−Ta−N angles and simultaneously reduce the equatorial N−Ta−N angle to minimize these interactions.[46]

Scheme 4



Preparation and Properties of Aryloxide and Alkyl Derivatives of $Ta(NC_9H_{10})_nCl_{5-n}$ (n = 1, 2). Recently, we described excellent structural and reactivity HDN model complexes supported by aryloxide ancillary ligands, in particular $[\eta^2(N,C)$-2,4,6-$NC_5{}^tBu_3H_2]Ta(OAr)_2Cl$ (Ar = 2,6-$C_6H_3{}^iPr_2$) that was used to uncover the mechanistic details of C−N bond scission reactions.[27−30] We set out, therefore, to prepare η^1-(N)-NC_9H_{10} compounds containing ancillary O-2,6-$C_6H_3{}^iPr_2$ ligands, with a particular view to develop routes to alkyl complexes of the form $Ta(NC_9H_{10})_x(OAr)_yR_z$. These species would allow us to test whether their thermolysis would lead to NC_9H_{10} cyclometalation and alkane elimination and thereby afford $\eta^2(N,C)$ heterocycles such as those in Figure 1.

The most facile entry into mixed-ligand compounds was determined to be from the aryloxide chlorides. Thus, an Et_2O solution of $Ta(OAr)Cl_4(OEt_2)$[32] reacts with $Me_3SiNC_9H_{10}$ to provide dark red crystals of $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (**8**), one possible structure of which is shown in Scheme 4. $Ta(NC_9H_{10})$-$(OAr)Cl_3(OEt_2)$ (**8**), however, has *not* been prepared from reacting $Ta(NC_9H_{10})Cl_4(OEt_2)$ (**1**) with Me_3SiOAr or $LiOAr\cdot OEt_2$, although this preparative route would seem viable. We previously reported a similar reactivity feature in the preparation of $Ta(NEt_2)(OAr)Cl_3(OEt_2)$, a complex that is accessible from $Ta(OAr)Cl_4(OEt_2)$ and Me_3SiNEt_2 but not from $Ta(NEt_2)Cl_4(OEt_2)$ and Me_3SiOAr or $LiOAr\cdot OEt_2$.[33] Similarly, the indolinyl compound $Ta(NC_8H_8)(OAr)Cl_3(OEt_2)$ (**9**) may be prepared from $Ta(OAr)Cl_4(OEt_2)$ and $Me_3SiNC_8H_8$ in Et_2O, eq 2. Attempts



(2)

to further alkoxylate $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (**8**) using $LiOAr\cdot OEt_2$ led to disproportionation products, since the principal species isolable from this reaction was identified as $Ta(NC_9H_{10})_2(OAr)_2Cl$ (**10**); this complex is readily accessible from its bis(amide) precursor. When $Ta(NC_9H_{10})_2Cl_3$ (**2**) is

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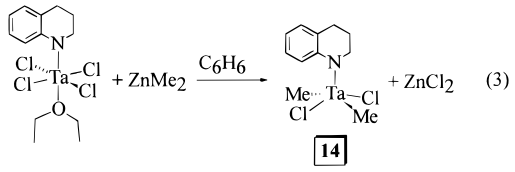
reacted with excess $LiOAr{\cdot}OEt_2$ (in C_6H_6/Et_2O), $Ta(NC_9H_{10})_2(OAr)_2Cl$ (**10**) can be isolated in essentially quantitative yield. When less than 1 equiv of $LiOAr{\cdot}OEt_2$ is employed in this reaction, **10** is simply isolated in lower yield along with unreacted **2**. $Ta(NC_9H_{10})_2(OAr)_2Cl$ (**10**) is also available, but in low yield, from reacting $Ta(OAr)_2Cl_3(OEt_2)$[32] with 2 equiv of $LiNC_9H_{10}{\cdot}2THF$.

The desired alkyl complexes were accessed from reacting compounds **8** and **10** with AlR_3 or ZnR_2 reagents, which afforded more tractable reactions and higher yields than alkyllithium or Grignard reagents. When a benzene solution of $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (**8**) is treated with excess $ZnMe_2$, yellow crystals of $Ta(NC_9H_{10})(OAr)Me_2Cl$ (**11**) can be obtained in 64% yield, Scheme 4. $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ and excess $ZnEt_2$ react to afford $Ta(NC_9H_{10})(OAr)Et_2Cl$ (**12**) in comparable yield. Attempts to either monoalkylate or exhaustively alkylate $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (**8**) led simply to lower yields of the dialkyl complexes. The ^1H and ^{13}C NMR spectra of these compounds reveal equivalent alkyl groups, most likely indicating fluxional species in solution. Treating toluene solutions of $Ta(NC_9H_{10})_2(OAr)_2Cl$ (**10**) with $AlMe_3$ (1 equiv) affords yellow crystals of $Ta(NC_9H_{10})_2(OAr)_2Me$ (**13**) in 77% yield. The ^1H and ^{13}C NMR data for this compound reveal equivalent NC_9H_{10} and equivalent OAr ligands at probe temperature.

An interesting spectroscopic feature of the ethyl derivative $Ta(NC_9H_{10})(OAr)Et_2Cl$ (**12**) is the coincidence of the methylene CH_2 and methyl CH_3 protons of the ethyl ligand at δ 2.11 in its ^1H NMR spectrum (250 MHz, C_6D_6, probe temperature). The ^{13}C NMR spectrum (62.9 MHz, C_6D_6) of **12** clearly shows *inequivalent* methylene *C*H_2 and methyl *C*H_3 carbon atoms (at δ 78.08 and 15.68, respectively), and the HETCOR spectrum of **12** correlates both *C*H_2 and *C*H_3 carbons with the single CH_2CH_3 ^1H NMR resonance. To confirm this assignment, the 500 MHz ^1H NMR spectrum of **12** was obtained where the methylene CH_2 and methyl CH_3 protons are observed at δ 2.112 and 2.104, respectively (C_6D_6, probe temperature).

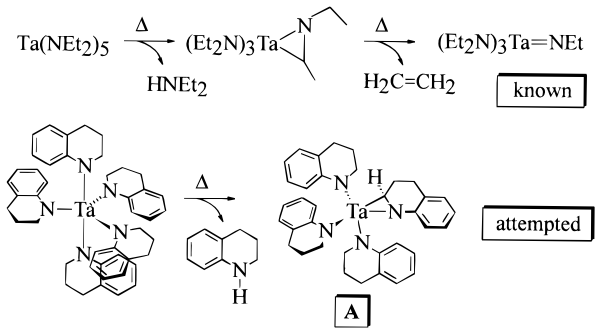
We additionally prepared one amido alkyl complex without aryloxide ancillary ligands. $Ta(NC_9H_{10})Cl_4(OEt_2)$ (**1**) can be smoothly alkylated with 2 equiv of $ZnMe_2$ in benzene solution to provide high yields of orange, crystalline $Ta(NC_9H_{10})Me_2Cl_2$ (**14**), eq 3. Attempts to prepare the ethyl analog of **14** from



$Ta(NC_9H_{10})Cl_4(OEt_2)$ and $ZnEt_2$ afforded a thermally unstable complex that could not be completely characterized.

Attempts To Prepare η^2(*N*,*C*)-Heterocyclic Ligands by Cyclometalation. The alkyl derivatives $Ta(NC_9H_{10})(OAr)Me_2Cl$ (**11**), $Ta(NC_9H_{10})(OAr)Et_2Cl$ (**12**), and $Ta(NC_9H_{10})_2(OAr)_2Me$ (**13**), as well as the amido derivatives $Ta(NC_9H_{10})_4Cl$ (**4**), $Ta(NC_9H_{10})_5$ (**5**), and $Ta(NC_9H_{10})Me_2Cl_2$ (**14**), were all thermolyzed in an attempt to cyclometalate a NC_9H_{10} ligand and eliminate alkane or HNC_9H_{10}, much in the way that $Ta(NEt_2)_5$ undergoes thermolysis to form the *N*-ethylethanimine complex $Ta(\eta^2\text{-EtN=CHCH}_3)(NEt_2)_3$, Scheme 5.[41,42,47,48] The proposed complex arising from cyclometalation of an amido ligand in $Ta(NC_9H_{10})_5$ (**5**), *viz.* $Ta(\eta^2\text{-}NC_9H_9)(NC_9H_{10})_3$ (**A**), is presented

Scheme 5



in Scheme 5 for comparison. Similar amido cyclometalations were observed more recently in η^5-C_5Me_5-supported tantalum complexes; for example, $Cp^*Ta(\eta^2\text{-MeN=CH}_2)Me_2$ is isolated when solutions of $Cp^*Ta(NMe_2)Me_3$ are warmed to room temperature,[49] and $Cp^*_2Ta(\eta^2\text{-MeN=CH}_2)H$ is formed as the kinetic product from $[Cp^*_2Ta(NMe_2)]$.[50,51] Moreover, Gambarotta and co-workers have found a similar cyclometalation reaction in the preparation of $Nb[\eta^2\text{-CyN=C}_6H_{10}](NCy_2)_2Cl$ (Cy = C_6H_{11}) from $NbCl_4(THF)_2$ and $LiNCy_2$[52] and in the preparation of its tantalum analog $Ta[\eta^2\text{-CyN=C}_6H_{10}](NCy_2)_2Cl$ from $TaCl_5$ and $LiNCy_2$.[53]

Unfortunately, thermolyzing **11**−**14** in C_6D_6 solution (80 °C, up to 24 h) afforded no evidence for the formation of any η^2-(*N*,*C*) heterocycles; intractable mixtures that included paramagnetic species were slowly formed. While thermolysis of $Ta(NC_9H_{10})_4Cl$ (**4**) and $Ta(NC_9H_{10})_5$ (**5**) under similar conditions (C_6D_6, ≥80 °C) produced free tetrahydroquinoline, HNC_9H_{10}, no evidence for the formation of an η^2(*N*,*C*) complex was obtained in either case; intractable, paramagnetic products were again obtained. In order to test whether a *reversible* metalation of a NC_9H_{10} ligand occurs under these conditions,[54,55] a sample of $Ta(NC_9H_{10})_5$ (**5**) was thermolyzed in the presence of excess DNC_9H_{10} and examined by ^1H and ^{13}C NMR.[56] No incorporation of deuterium into either H2 or H8 (or any position) of the coordinated NC_9H_{10} amide ligand was observed. When the reaction mixture was hydrolyzed with aqueous base (which exchanged any N-bound deuterium), a GC/mass spectral analysis of the organic phase revealed that no significant deuterium incorporation into HNC_9H_{10} occurred, thereby precluding a reversible C−H activation of this ligand.

Discussion

We recently prepared niobium and tantalum complexes (M = Nb, Ta) of the form $M(NEt_2)Cl_4(OEt_2)$, $[M(NEt_2)_2Cl_3]_2$, $Ta(NEt_2)_2Cl_3L$ (L = OEt_2, THF, py), and $[Nb(NEt_2)_2Cl_3]_2$ directly from the halides and Me_3SiNEt_2 under the appropriate conditions.[33,57] This synthetic procedure allows selective formation of the mixed amido halides and circumvents any reduction

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(51) We note that most η^2-imine compounds of tantalum are prepared from C≡NR insertions into metal−alkyl bonds. See: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.
(52) Berno, P.; Gambarotta, S. *Organometallics* **1995**, *14*, 2159.
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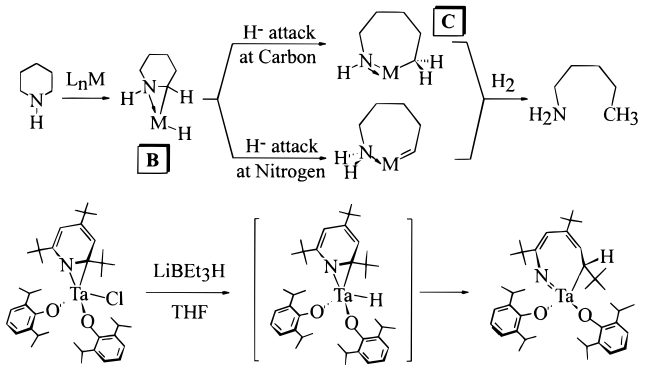
Scheme 6



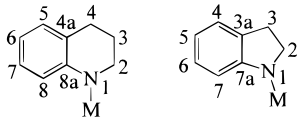
problems or the formation of product mixtures that can arise when the more powerful alkali metal amidating agents are used. The viability of this approach is evident in the present work since the entire series of mixed-ligand complexes are selectively prepared; thus, sequential amidation of $TaCl_5$ using $Me_3SiNC_9H_{10}$ affords the $Ta(NC_9H_{10})_nCl_{5-n}$ for $n = 1-3$ complexes and subsequent reaction with $LiNC_9H_{10}$ provides selective routes to the $n = 4$ and 5 species.

The impetus for preparing these complexes is suggested in Scheme 1, where quinoline HDN is shown to proceed *via* the intermediacy of tetrahydroquinoline. The motivation for attempting the cyclometalation reactions suggested in Scheme 5 is realized by examining the Laine proposal for C−N bond cleavage in piperidine, outlined in Scheme 6.[8,9] An important feature of this proposal is the initial formation of an $\eta^2(N,C)$-piperidyl *amine* complex (**B** of Scheme 6) that arises from metalation of a piperidine ligand. If the subsequent C−N bond cleavage results from hydride transfer to C_α, then formation of a ring-opened *amido* complex (**C**) occurs. In our model studies, we have observed that an $\eta^2(N,C)$-pyridine complex, containing a formal *amido* nitrogen, can be transformed to a formal *imido* complex upon C−N scission. Specifically, we observed that hydride can attack the metal and migrate to C_α of $[\eta^2(N,C)$-2,4,6-$NC_5{}^tBu_3H_2]Ta(OAr)_2Cl$ to afford the C−N bond scission product $Ta(=NC{}^tBu=CHC{}^tBu=CHCH{}^tBu)(OAr)_2$ (**2**), shown in Scheme 6.[29,30] A complex such as $Ta(\eta^2\text{-}NC_9H_9)(NC_9H_{10})_3$ (**A**) of Scheme 5 was desired to test whether nucleophilic addition would cleave the C−N bond of the η^2-NC_9H_9 ligand in a substrate more relevant to HDN. Furthermore, the likelihood of *protonating* the heterocycle nitrogen of an η^2-NC_9H_9 complex like **A** (Scheme 5) to afford a direct analog of the Laine intermediate **B** (Scheme 6) was an attractive prospect. Unfortunately, in our hands, the initial cyclometalation step was not realized and therefore reactions of η^2-NC_9H_9 complexes with electrophiles and nucleophiles could not be carried out.

Finally, we note that Gambarotta and co-workers recently described the preparation of $Nb[\eta^2(N,C)\text{-}CyN{=}C_6H_{10}](NCy_2)_2Cl$ ($Cy = C_6H_{11}$) from $NbCl_4(THF)_2$ and $LiNCy_2$, containing one metalated cyclohexyl ring.[52] The proposal is made that intermediate $Nb(NCy_2)_3Cl$ is formed, which undergoes a formal elimination of hydrogen; therefore, under the appropriate conditions, these cyclometalations are facile.[52] Gambarotta has also described the tantalum analog $Ta[\eta^2(N,C)\text{-}CyN{=}C_6H_{10}](NCy_2)_2Cl$ from $TaCl_5$ and $LiNCy_2$, which could form by $HNCy_2$ elimination from the intermediate $Ta(NCy_2)_4Cl$.[53] These reactions are perhaps facilitated by the greater steric congestion of the NCy_2 amides relative to NC_9H_{10}, as well as possible one-electron pathways that are operative in the niobium system.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[58] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[59] and were transferred to the drybox without exposure to air. NMR solvents were passed down a short (5−6 cm) column of activated alumina prior to use. The "cold" solvents used to wash isolated products were typically cooled to −35 °C before use. In all preparations Ar = 2,6-$C_6H_3{}^iPr_2$, $[NC_8H_8]^-$ = the amido anion of indoline (indolinyl), and $[NC_9H_{10}]^-$ = the amido anion of tetrahydroquinoline (tetrahydroquinolinyl). Ring numbering:



Physical Measurements. ^1H and ^{13}C NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker AM-250, Varian Gemini 200, or Varian Unity 300 spectrometer in C_6D_6, $CDCl_3$, or toluene-d_8 solvent. Chemical shifts are referenced to protio impurities (δ: 7.15, C_6D_6; 7.24, $CDCl_3$; 2.09, toluene-d_8) or solvent ^{13}C resonances (δ: 128.0, C_6D_6; 77.0, $CDCl_3$; 20.4, toluene-d_8) and are reported downfield of $SiMe_4$. Routine coupling constants are not reported. NMR assignments were assisted by COSY, APT, HETCOR, or gated $^{13}C\{^1H\}$ decoupled spectra. The ^1H NMR multiplet signals for H2 and H3 of both NC_9H_{10} and NC_8H_8 ligands often appear as pseudotriplets but are nominally recorded as multiplets throughout. Electron ionization mass spectra (70 eV) were recorded to $m/z = 999$ on a Hewlett Packard 5970 mass selective detector and RTE-6/VM data system. For GC mass spectra, the sample was introduced into the mass spectrometer by a Hewlett Packard Model 5890 gas chromatograph equipped with an HP-5 column. Microanalytical samples were handled under nitrogen and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Starting Materials. $TaCl_5$ was obtained from Cerac and used as received. Tetrahydroquinoline, HNC_9H_{10}, indoline, HNC_8H_8, and chlorotrimethylsilane, Me_3SiCl, were obtained from Aldrich and distilled prior to use. *n*-Butyllithium (1.6 M in hexanes) was obtained from Aldrich and used as received. $ZnMe_2$ (Alfa), $ZnEt_2$ (Aldrich), and $AlMe_3$ (Aldrich) were obtained from commercial sources and prepared as either 1.0 or 2.0 M solutions in heptane. $[Ta(OAr)Cl_4]_2$[32] and $LiOAr{\cdot}OEt_2$[57] were prepared as previously described.

Ligand Preparations. $LiNC_9H_{10}{\cdot}2THF$. A solution of tetrahydroquinoline (40.2 mL, 42.6 g, 0.320 mol) in 500 mL of pentane was prepared and cooled to 0 °C. This cold solution was stirred rapidly while 1 equiv of *n*-butyllithium (1.6 M in hexanes, 200 mL, 0.320 mol) was added slowly. After this mixture was stirred at room temperature for 21 h, the reaction volatiles were removed under reduced pressure to afford a pale yellow powder that was dissolved in THF (ca. 500 mL), and the solution was stirred for an additional 2 h. The reaction volatiles were removed from this solution under reduced pressure, and the resulting light yellow solid was placed on a frit, washed with pentane (ca. 125 mL), and dried in vacuo to yield 71.16 g of $LiNC_9H_{10}{\cdot}2THF$ as a pale yellow, almost white solid. An additional 5.61 g of product was obtained by concentrating the filtrate to ca. 25 mL in volume, adding minimal THF (ca. 2 mL) to redissolve the precipitate that formed during concentration of the solution, and cooling to −35 °C for a total yield of 76.77 g (0.271 mol, 85%) of $LiNC_9H_{10}{\cdot}2THF$. Analytically pure compound was obtained as large white crystals by recrystallization from THF/pentane solutions at −35 °C. ^1H NMR (C_6D_6): δ 7.06, 7.00 (overlapping t and d, 1 H each, H6 and H8), 6.42, 6.40 (overlapping t and d, 1 H each, H7 and H5), 3.69

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(m, 2 H, H2), 3.38 (m, 8 H, Hα THF), 2.97 (t, 2 H, H4), 1.95 (m, 2 H, H3), 1.25 (m, 8 H, Hβ THF). ^{13}C NMR (C_6D_6): δ 159.05 (C8a), 130.53 (C8 or C6), 127.68 (C6 or C8), 120.77 (C4a), 112.88, 109.41 (C5, C7), 68.11 (Cα THF), 48.40 (C2), 30.29 (Cβ THF), 25.43 (C4), 24.82 (C3). Anal. Calcd for $C_{17}H_{26}LiNO_2$: C, 72.07; H, 9.25; N, 4.93. Found: C, 72.03; H, 8.89; N, 5.58.

$Me_3SiNC_9H_{10}$. (i) A solution of $LiNC_9H_{10}$·2THF (40.0 g, 0.141 mol) in 400 mL of Et_2O was prepared and cooled to 0 °C. A slight excess of neat Me_3SiCl (18.8 mL, 16.09 g, 0.148 mol) was added dropwise to this rapidly stirred solution, whereupon an exothermic yet smooth reaction ensued as the pale yellow solution decolorized and a white precipitate formed. After 17 h, solvent was removed from the mixture in vacuo to form a clear oil and a white solid. The product was extracted from this residue with pentane (ca. 300 mL), the extract was filtered through Celite to remove the large amount of white solid, and the clear, pale yellow filtrate was stripped of solvent to yield a clear yellow oil. This product was distilled under reduced pressure to afford 25.40 g (0.124 mol, 84%) of *N*-(trimethylsilyl)-1,2,3,4-tetrahydroquinoline ($Me_3SiNC_9H_{10}$) as a clear oil with a boiling range of 64−67 °C at *ca.* 10^{-2} Torr.

(ii) A solution of tetrahydroquinoline (40.2 mL, 42.6 g, 0.320 mol) in 500 mL of pentane was prepared and cooled to 0 °C. This cold solution was stirred rapidly while 1 equiv of *n*-butyllithium (1.6 M in hexanes, 200 mL, 0.320 mol) was added slowly. After this mixture was stirred at room temperature for 24 h, the reaction mixture was stripped of solvent to afford a pale yellow powder, which was dissolved in 400 mL of Et_2O and 100 mL of THF. This orange solution was cooled to 0 °C, and a slight excess of Me_3SiCl (45.0 mL, 38.52 g, 0.355 mol) was added dropwise over the course of 30 min, which induced rapid bleaching of the solution and formation of a white precipitate. After 24 h, the solvent was removed from the mixture in vacuo to provide a clear oil and a white solid. The product was extracted from this residue with pentane (ca. 100 mL), the extract was filtered through Celite, and the pale yellow filtrate was stripped of solvent to afford a clear yellow oil. This oil was distilled under reduced pressure as described above to yield 59.84 g (0.291 mol, 91%) of $Me_3SiNC_9H_{10}$ as a clear oil. ^{1}H NMR (C_6D_6): δ 7.03, 6.98 (overlapping t and d, 1 H each, H6 and H8), 6.88, 6.78 (overlapping d and t, 2 H, H5 and H7), 3.01 (m, 2 H, H2), 2.58 (t, 2 H, H4), 1.54 (m, 2 H, H3), 0.20 (s, 9 H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 146.50 (C8a), 130.18, 126.19 (C6 and C8), 125.65 (C4a), 118.35 (coincident C5, C7), 44.73 (C2), 28.14 (C4), 24.28 (C3), 0.97 ($SiMe_3$). One resonance of the C5, C7 pair is not observed and is presumed to be coincident with the δ 118.35 resonance. Anal. Calcd for $C_{12}H_{19}NSi$: C, 70.11; H, 9.25; N, 6.81. Found: C, 70.28; H, 9.26; N, 7.16.

$LiNC_8H_8$·2THF. A solution of 5.00 g (41.9 mmol) of indoline in 40 mL of pentane was prepared and cooled to 0 °C in a ice bath. To this rapidly stirred, cold solution was added over several minutes a 26.2 mL (41.9 mmol) aliquot of *n*-butyllithium solution (1.6 M in hexanes). Within minutes, a white precipitate was observed, and over the next few hours, the mixture became a pasty, off-white suspension. After 3 h, the precipitate was collected by filtration and washed with pentane to remove any unreacted starting materials. This product (base-free $LiNC_8H_8$) was then dissolved in a minimal volume of THF, and the solution was cooled to −35 °C, during which 8.60 g (31.9 mmol, 76%) of white crystals formed, were collected by filtration, and dried in vacuo. ^{1}H NMR (C_6D_6): δ 7.24 (d, 1 H, H7), 7.12 (t, 1 H, H5), 6.48, 6.47 (overlapping t and d, 1 H each, H6 and H4), 3.87 (t, 2 H, H2), 3.44 (m, 8 H, Hα THF), 3.15 (t, 1 H, H3), 1.29 (m, 8 H, Hβ THF). ^{13}C NMR(C_6D_6): δ 147.35 (C7a), 131.86 (C3a), 128.21, 124.19, 110.22, 104.39 (C4, C5, C6, and C7), 67.96 (Cα THF), 53.30 (C2), 33.29 (C3), 25.57 (Cβ THF). Anal. Calcd for $C_{16}H_{24}LiNO_2$: C, 71.32; H, 8.91; N, 5.20. Found: C, 71.50; H, 9.14; N, 5.55.

$Me_3SiNC_8H_8$ (*N*-(Trimethylsilyl)indoline). A large Schlenk tube was charged with 18.70 g (0.157 mol) of indoline (HNC_8H_8) and 200 mL of Et_2O and cooled to −78 °C. To this rapidly stirred solution was slowly added 98.0 mL (0.157 mmol) of *n*-butyllithium solution (1.6 M in hexanes). After this mixture was stirred for 5 min, a solution of Me_3SiCl (20.3 mL, 17.38 g, 0.160 mol) in 100 mL of Et_2O was added over a period of several minutes. When the addition was complete, the solution was removed from the cold bath and allowed to stir at room temperature. Over several minutes, a precipitate was observed to form, and after 18 h, the reaction volatiles were removed under reduced pressure to yield an oily residue. This product was transferred to a short-path distillation apparatus and vacuum distilled (ca. 10^{-2} Torr, 80 °C) to afford the product as a white crystalline solid (27.55 g, 0.144 mol, 90%). ^{1}H NMR (C_6D_6): δ 7.08−7.02 (overlapping m, 2 H total, H7 and H5), 6.74 (t, 1 H, H6), 6.66 (d, 1 H, H4), 3.25 (t, 2 H, H2), 2.70 (t, 2 H, H3), 0.15 (s, 9 H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 142.95 (C7a), 131.91 (C3a), 127.57 (C7), 124.82 (C5), 117.56 (C6), 109.36 (C4), 49.09 (C2), 30.19 (C3), −0.75 ($SiMe_3$). Anal. Calcd for $C_{11}H_{17}NSi$: C, 69.00; H, 8.88; N, 7.32. Found: C, 69.08; H, 8.96; N, 7.53.

Complex Preparations. $Ta(NC_9H_{10})Cl_4(OEt_2)$ (1). Neat $Me_3SiNC_9H_{10}$ (4.60 g, 22.4 mmol) was slowly added to a rapidly stirred solution of $TaCl_5$ (8.00 g, 22.3 mmol) in 70 mL of benzene and 10 mL of Et_2O. The clear $TaCl_5$ solution turned deep red instantly upon $Me_3SiNC_9H_{10}$ addition. The mixture was stirred for 20 h, after which the reaction volatiles were removed under reduced pressure to yield the product as a burgundy-colored powder. This powder was washed with cold pentane (2 × 25 mL) and dried in vacuo to yield 11.47 g (21.7 mmol, 97%) of $Ta(NC_9H_{10})Cl_4(OEt_2)$ as an analytically pure, intense burgundy-colored solid. Samples of $Ta(NC_9H_{10})Cl_4(OEt_2)$ can be readily recrystallized as black rods from Et_2O at −35 °C. ^{1}H NMR (C_6D_6): δ 8.59 (d, 1 H, H8), 7.22 (t, 1 H, H6), 6.86 (d, 1 H, H5), 6.64 (t, 1 H, H7), 5.13 (m, 2 H, H2), 4.19 (q, 4 H, OCH_2CH_3), 2.48 (t, 2 H, H4), 1.88 (m, 2 H, H3), 0.96 (t, 6 H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 148.30 (C8a), 130.82 (C8), 128.80 (C4a), 128.18 (C5), 127.45 (C7), 125.27 (C6), 67.75 (OCH_2CH_3), 55.05 (C2), 25.75 (C4), 20.97 (C3), 12.70 (OCH_2CH_3). Anal. Calcd for $C_{13}H_{20}Cl_4NOTa$: C, 29.51; H, 3.81; N, 2.65. Found: C, 29.07; H, 3.66; N, 2.67.

$Ta(NC_9H_{10})_2Cl_3$ (2). A toluene solution of $Me_3SiNC_9H_{10}$ (1.17 g, 5.70 mmol in 7 mL of toluene) was added dropwise to a rapidly stirred solution of $Ta(NC_9H_{10})Cl_4(Et_2O)$ (3.00 g, 5.67 mmol) in 10 mL of toluene. During $Me_3SiNC_9H_{10}$ addition, the reaction solution underwent a rapid but subtle color change as it darkened slightly. After $Me_3SiNC_9H_{10}$ addition was complete, the mixture was set aside without stirring for 2 d, after which the solution was cooled to −35 °C for 24 h. The dark burgundy-colored crystals that formed were collected by filtration, washed with cold pentane (ca. 10 mL), and dried in vacuo to afford 2.20 g (3.99 mmol, 70%) of $Ta(NC_9H_{10})_2Cl_3$ as an analytically pure, deep burgundy-colored microcrystalline product. Solvent was removed from the dark red filtrate under reduced pressure to provide a red solid that was shown by ^{1}H NMR spectroscopy to consist of a mixture of $Ta(NC_9H_{10})Cl_4(OEt_2)$, $Ta(NC_9H_{10})_2Cl_3$, and $Ta(NC_9H_{10})_3Cl_2$. ^{1}H NMR (C_6D_6): δ 7.76 (d, 1 H, H8), 6.91 (t, 1 H, H6), 6.81 (d, 1 H, H5), 6.66 (t, 1 H, H7), 3.88 (m, 2 H, H2), 2.23 (t, 2 H, H4), 1.59 (m, 2 H, H3). ^{13}C NMR (C_6D_6): δ 144.33 (C8a), 129.66 (C5), 126.66 (overlapping C6, C8), 126.24 (C7), 125.60 (C4a), 44.26 (C2), 25.29 (C4), 20.12 (C3). Anal. Calcd for $C_{18}H_{20}Cl_3N_2Ta$: C, 39.19; H, 3.65; N, 5.08. Found: C, 39.02; H, 3.68; N, 4.92.

$Ta(NC_9H_{10})_3Cl_2$ (3). A solution of $TaCl_5$ (5.00 g, 14.0 mmol) in 75 mL of toluene and 15 mL of Et_2O was rapidly stirred while an excess of neat $Me_3SiNC_9H_{10}$ (17.2 g, 0.084 mol, 6 equiv) was slowly added, whereupon the solution rapidly changed from pale yellow to dark red. This mixture was heated in a 100 °C oil bath for 22 h, after which it was allowed to cool and the reaction volatiles were removed in vacuo to provide an oily, bright red solid. Trituration of this mixture with ca. 25 mL of cold (−35 °C) pentane afforded a bright red solid, which was quickly filtered off, washed with cold pentane (2 × 25 mL), and dried in vacuo. This procedure provided 8.60 g (13.3 mmol, 95%) of $Ta(NC_9H_{10})_3Cl_2$ as a bright orange-red powder. The red pentane filtrate was stripped of solvent to yield a red oil, shown by ^{1}H NMR to be relatively pure $Me_3SiNC_9H_{10}$ with a trace of $Ta(NC_9H_{10})_3Cl_2$ impurity. The excess $Me_3SiNC_9H_{10}$ reagent could be reclaimed and purified by vacuum distillation. Performing this synthesis with only 3 equiv of $Me_3SiNC_9H_{10}$ yields inseparable mixtures of $Ta(NC_9H_{10})_2Cl_3$ and $Ta(NC_9H_{10})_3Cl_2$, even under high temperatures (120 °C) and/or long reaction times (3 d). ^{1}H NMR (C_6D_6): δ 8.15 (d, 1 H, H8), 7.10 (t, 1 H, H6), 6.96 (d, 1 H, H5), 6.80 (t, 1 H, H7), 3.81 (m, 2 H, H2), 2.35 (t, 2 H, H4), 1.71 (m, 2 H, H3). ^{13}C NMR (C_6D_6): δ 146.87 (C8a), 130.10 (C5), 126.57 (C6), 124.65 (C4a), 124.48 (C8), 124.14

(C7), 46.19 (C2), 26.19 (C4), 19.22 (C3). Anal. Calcd for $C_{27}H_{30}Cl_2N_3Ta$: C, 50.01; H, 4.66; N, 6.48. Found: C, 49.54; H, 4.86; N, 6.10.

$Ta(NC_9H_{10})_4Cl$ (4). A solution of $LiNC_9H_{10}\cdot 2THF$ (0.88 g, 3.10 mmol) in 5 mL of THF was added dropwise to a stirred solution of $Ta(NC_9H_{10})_3Cl_2$ (2.00 g, 3.10 mmol) in 20 mL of THF. This mixture was stirred for 20 h, during which the solution developed an lighter, orange color. Removing the reaction volatiles in vacuo afforded an orange-red oil from which the product was extracted with Et_2O (100 mL). This extract was filtered through Celite, the Celite was washed with Et_2O (ca. 50 mL) until the washings were colorless, and the volatiles were removed from the orange filtrate under reduced pressure, yielding an orange crystalline solid. This solid was washed with cold pentane (2×25 mL) and dried in vacuo to provide 2.02 g (2.71 mmol, 87%) of $Ta(NC_9H_{10})_4Cl$ as a bright orange solid. Analytically pure samples were obtained by recrystallization from Et_2O at −35 °C. ^{1}H NMR (C_6D_6): δ 7.42 (d, 1 H, H8), 6.90, 6.86 (overlapping t and d, 2 H total, H6 and H5), 6.68 (t, 1 H, H7), 4.23 (m, 2 H, H2), 2.53 (t, 2 H, H4), 1.85 (m, 2 H, H3). ^{13}C NMR (C_6D_6): δ 149.73 (C8a), 129.15 (C5), 127.30 (C4a), 125.20 (C6), 124.12 (C8), 123.33 (C7), 51.64 (C2), 26.61 (C4), 23.26 (C3). Anal. Calcd for $C_{36}H_{40}ClN_4Ta$: C, 58.03; H, 5.41; N, 7.52. Found: C, 57.91; H, 5.51; N, 7.46.

$Ta(NC_9H_{10})_5$ (5). A solution of 0.31 g (1.09 mmol) of $LiNC_9H_{10}\cdot$ 2THF in 10 mL of benzene was added to a rapidly stirred solution of 0.20 g (0.36 mmol) of $Ta(NC_9H_{10})_2Cl_3$ in 10 mL of benzene, whereupon the solution changed from dark red to orange. After the addition was complete, the mixture was stirred for 20 h, after which it was filtered through Celite and the reaction volatiles were removed under reduced pressure to afford the product as an orange powder; yield 0.256 g (0.304 mmol, 84%). Samples of $Ta(NC_9H_{10})_5$ obtained in this fashion were analytically pure. ^{1}H NMR (C_6D_6): δ 7.38 (d, 1 H, H8), 6.87, 6.83 (overlapping t and d, 2 H total, H6 and H5), 6.65 (t, 1 H, H7), 4.26 (t, 2 H, H2), 2.51 (t, 2 H, H4), 1.72 (m, 2 H, H3). ^{13}C NMR (C_6D_6): δ 150.40 (C8a), 128.79 (C5), 126.90 (C4a), 125.37 (C6), 124.45 (C8), 121.58 (C7), 51.30 (C2), 27.48 (C4), 24.50 (C3). Anal. Calcd for $C_{45}H_{50}N_5Ta$: C, 64.20; H, 5.99; N, 8.32. Found: C, 64.18; H, 5.88; N, 8.10.

$Ta(NC_8H_8)Cl_4(THF)$ (6). A solution of 1.49 g (7.79 mmol) of $Me_3SiNC_8H_8$ in 10 mL of benzene was added dropwise to a rapidly stirred solution of 2.78 g (7.76 mmol) of $TaCl_5$ in 10 mL of benzene and 1 mL of Et_2O. Upon $Me_3SiNC_8H_8$ addition, the tantalum solution rapidly changed from pale yellow to dark purple. After 24 h, the volatiles were removed from the solution under reduced pressure, the dark residue was dissolved in 5 mL of THF, and this solvent was removed in vacuo to afford 3.85 g (7.50 mmol, 96%) of dark purple, solid $Ta(NC_8H_8)Cl_4(THF)$. Analytically pure samples were obtained by recrystallization from 3:1 (v/v) Et_2O/THF solutions. ^{1}H NMR (C_6D_6): δ 8.10 (d, 1 H, H7), 7.27 (t, 1 H, H6), 6.88 (d, 1 H, H4), 6.65 (m, 2 H, H2), 6.51 (t, 1 H, H5), 4.31 (m, 4 H, Hα THF), 2.98 (m, 2 H, H3), 1.07 (m, 4 H, Hβ THF). ^{13}C NMR (C_6D_6): δ 149.79 (C7a), 133.01 (C3a), 127.39, 126.97, 122.72 (C4, C5, C6, C7), 77.25 (C2), 63.69 (Cα THF), 31.45 (C3), 25.41 (Cβ THF). One resonance from the C4, C5, C6, C7 set is not observed and is presumed to be coincident with another resonance. Anal. Calcd for $C_{12}H_{16}Cl_4NOTa$: C, 28.09; H, 3.14; N, 2.73. Found: C, 27.59; H, 3.11; H, 2.58.

$Ta(NC_8H_8)_2Cl_3(THF)$ (7). A solution of 0.36 g (1.88 mmol) of $Me_3SiNC_8H_8$ in 10 mL of benzene was added slowly to a solution of 1.00 g (1.95 mmol) of $Ta(NC_8H_8)Cl_4(THF)$ in 10 mL of benzene. Upon $Me_3SiNC_8H_8$ addition, the $Ta(NC_8H_8)Cl_4(THF)$ solution rapidly changed from dark purple to orange-brown. After 46 h, the volatiles were removed in vacuo to afford a brown powder, which was washed with pentane (10 mL) to yield 1.12 g (1.88 mmol; 96% based upon tantalum, quantitative based on $Me_3SiNC_8H_8$) of $Ta(NC_8H_8)_2Cl_3(THF)$ as a brown powder. Analytically pure samples were obtained by recrystallization from THF at −35 °C. ^{1}H NMR (C_6D_6): δ 7.27−7.19 (overlapping d, 2 H total, H7, H7′), 7.11−7.03 (m, 2 H, H4, H6′), 6.92−6.83 (overlapping m, 2 H total, H4′, H6), 6.66, 6.53 (t, 1 H each, H5′, H5), 5.88, 4.99 (m, 2 H each, H2, H2′), 4.06 (m, 4 H, Hα THF), 2.90, 2.82 (t, 2 H each, H3′, H3), 1.11 (m, 4 H, Hβ THF). ^{13}C NMR (C_6D_6): δ 151.10, 150.83 (C7a, C7a′), 133.11, 132.30 (C3a, C3a′), 127.11 (C6), 126.97 (C6′), 125.69 (C5), 124.84 (C5′), 123.67 (C4), 123.29 (C4′), 123.06 (C7), 122.14 (C7′), 75.93 (Cα THF), 60.92 (C2), 58.81 (C2′), 32.86 (C3), 31.72 (C3′), 25.61 (Cβ THF). Anal. Calcd for $C_{20}H_{24}Cl_3N_2OTa$: C, 40.32; H, 4.06; N, 4.70. Found C, 40.06; H, 4.07; N, 4.60.

$Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ (8). A solution of 10.00 mmol of $Ta(OAr)Cl_4(OEt_2)$ was prepared by dissolving 5.00 g (5.00 mmol) of $[Ta(OAr)Cl_4]_2$ in 60 mL of Et_2O. This mixture was stirred rapidly while a solution of 2.00 g (9.74 mmol) of $Me_3SiNC_9H_{10}$ in 40 mL of Et_2O was added dropwise. Over the course of the addition, the yellow-orange solution became dark red-orange and after 1 h had developed a dark cherry red color. After 24 h, the reaction solution was filtered through Celite, and the reaction volatiles were removed in vacuo to provide an orange, iridescent foam. This product was dissolved in ca. 75 mL of Et_2O, and the mixture was stored at −35 °C to afford the desired compound as analytically pure, dark red crystals; these were collected by filtration and dried in vacuo; yield 5.85 g (8.72 mmol, 87%). ^{1}H NMR (C_6D_6): δ 8.11 (d, 1 H, H8), 6.90 (d, 2 H, Hm OAr), 6.85−6.74 (overlapping m, 3 H total, Hp OAr, H5, and H6), 6.48 (t, 1 H, H7), 5.09 (m, 2 H, H2), 3.89 (q, 4 H, OC*H*$_2$CH$_3$), 3.80 (spt, 2 H, C*H*Me$_2$), 2.49 (t, 2 H, H4), 1.94 (m, 2 H, H3), 1.11 (d, 12 H, CH*Me*$_2$), 0.95 (t, 6 H, OCH$_2$C*H*$_3$). ^{1}H NMR ($CDCl_3$): δ 7.68 (d, 1 H, H8), 7.11 (d, 1 H, H5), 7.01−6.83 (overlapping m, 4 H total, H$_{aryl}$ OAr, H6), 6.73 (t, 1 H, H7), 5.19 (m, 2 H, H2), 4.01 (q, 4 H, OC*H*$_2$CH$_3$), 3.54 (spt, 2 H, C*H*Me$_2$), 3.00 (t, 2 H, H4), 2.31 (m, 2 H, H3), 1.28 (t, 6 H, OCH$_2$C*H*$_3$), 1.02 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.10 (C$_{ipso}$), 147.12 (C8a), 141.44 (Co), 129.06 (C$_5$), 128.27 (C4a), 126.26 (C7), 125.83 (C6), 125.75 (Cp), 124.11 (Cm), 66.68 (O*C*H$_2$CH$_3$), 56.14 (C2), 26.35 (*C*HMe$_2$), 26.12 (C4), 25.04 (CH*Me*$_2$), 21.18 (C3), 12.63 (OCH$_2$*C*H$_3$). Anal. Calcd for $C_{25}H_{37}Cl_3NO_2Ta$: C, 44.75; H, 5.56; N, 2.09. Found: C, 44.44; H, 5.69; N, 2.17.

$Ta(NC_8H_8)(OAr)Cl_3(OEt_2)$ (9). A solution of 4.28 mmol of $Ta(OAr)Cl_4(OEt_2)$ was prepared by dissolving 2.14 g (2.14 mmol) of $[Ta(OAr)Cl_4]_2$ in 10 mL of Et_2O. This mixture was stirred rapidly while a solution of 0.82 g (4.29 mmol) of $Me_3SiNC_8H_8$ in 10 mL of Et_2O was added dropwise. Over the course of the addition, the pale yellow solution became dark red, and after 24 h of stirring, the reaction volatiles were removed in vacuo to afford a dark red solid. This solid was washed with pentane, filtered off, and dried in vacuo to afford 1.90 g (2.89 mmol, 68% yield) of product as a microcrystalline burgundy-colored solid. Samples of $Ta(NC_8H_8)(OAr)Cl_3(OEt_2)$ prepared in this fashion were sufficiently pure for futher reactions; analytically pure samples were obtained by recrystallization from Et_2O at −35 °C. ^{1}H NMR (C_6D_6): δ 7.53 (d, 1 H, H7), 6.99 (d, 2 H, Hm), 6.87−6.76 (overlapping m, 3 H total, Hp OAr, H4, H6), 6.44 (t, 1 H, H5), 6.02 (m, 2 H, H2), 4.06 (q, 4 H, OC*H*$_2$CH$_3$), 3.81 (spt, 2 H, C*H*Me$_2$), 2.83 (m, 2 H, H3), 1.11 (d, 12 H, CH*Me*$_2$), 0.93 (t, 6 H, OCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 155.40 (C$_{ipso}$), 147.20 (C7a), 141.20 (Co), 132.70 (C3a), 127.20, 126.32, 125.72, 124.32, 123.52, 122.49 (Cm, Cp, C4, C5, C6, C7), 67.19 (C2), 63.05 (O*C*H$_2$CH$_3$), 31.77 (C3), 26.17 (*C*HMe$_2$), 24.99 (CH*Me*$_2$), 12.43 (OCH$_2$*C*H$_3$). Anal. Calcd for $C_{24}H_{35}Cl_3NO_2Ta$: C, 43.89; H, 5.37; N, 2.13. Found: C, 44.29; H, 5.54; N, 2.15.

$Ta(NC_9H_{10})_2(OAr)_2Cl$ (10). A solution of $Ta(NC_9H_{10})_2Cl_3$ (1.87 g, 3.39 mmol) in 10 mL of benzene was rapidly stirred while a solution of 1.75 g (6.78 mmol) of $LiOAr\cdot OEt_2$ in 10 mL of Et_2O was added dropwise. Over the course of the addition, the reaction solution underwent a subtle color change from dark red to yellow-orange, with the concomitant formation of a precipitate. The mixture was stirred at room temperature for 24 h and filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford the product as a yellow-orange solid (2.77 g, 3.32 mmol, 98%) sufficiently pure for further reactions. Analytically pure, yellow-orange needles were obtained by recrystallization from pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 7.59 (d, 2 H, H8), 7.08−6.81 (overlapping m, 10 H total, H$_{aryl}$ OAr, H6, H5) 6.62 (t, 2 H, H7), 4.54 (m, 4 H, H2), 3.46 (spt, 4 H, C*H*Me$_2$), 2.59 (t, 4 H, H4), 1.89 (m, 4 H, H3), 1.20 (d, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 156.34 (C$_{ipso}$), 148.50 (C8a), 138.93 (Co), 129.56 (C5), 126.82 (C4a), 126.30 (C6), 124.77 (C8), 124.00 (C7), 123.78 (overlapping Cm and Cp), 53.44 (C2), 27.58 (*C*HMe$_2$), 26.79 (C4), 25.05 (C3), 24.95 (CH*Me*$_2$). Anal. Calcd for $C_{42}H_{54}ClN_2O_2Ta$: C, 60.39; H, 6.52; N, 3.35. Found: C, 60.00; H, 6.68; N, 3.22.

$Ta(NC_9H_{10})(OAr)Me_2Cl$ (11). A 2.88 mL aliquot of $ZnMe_2$ (1.0 M in heptane, 2.88 mmol) was added to a rapidly stirred solution of

1.00 g (1.49 mmol) of $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ in 18 mL of benzene, whereupon the mixture changed from dark red to yellow. After the solution was stirred for 1 h, the solvent was removed in vacuo to provide a pale yellow, oily solid. The product was extracted with ca. 20 mL of pentane, the extract was filtered through Celite, and the filtrate was stripped of solvent to afford the yellow microcrystalline product. The crystals were collected on a frit, washed with cold (−35 °C) pentane, and dried in vacuo to afford 0.53 g (0.95 mmol, 64%) of analytically pure, golden yellow crystals. ^{1}H NMR (C_6D_6): δ 7.26 (d, 1 H, H8), 7.06−6.86 (overlapping m, 5 H total, H_{aryl} OAr, H5, H6), 6.66 (t, 1 H, H7), 3.51 (m, 2 H, H2), 3.36 (spt, 2 H, C*H*Me$_2$), 2.37 (t, 2 H, H4), 1.66 (m, 2 H, H3), 1.53 (s, 6 H, TaMe), 1.02 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.85 (C_{ipso}), 139.58 (Co), 130.35 (C5), 126.88 (C6), 124.35 (Cm), 124.17 (C4a), 123.89 (Cp), 122.75 (C7), 120.29 (C8), 66.10 (TaMe), 38.84 (C2), 27.14 (*C*HMe$_2$), 23.95 (C4), 23.73 (CH*Me*$_2$), 20.81 (C3). The resonance for C8a was not observed. Anal. Calcd for $C_{23}H_{33}ClNOTa$: C, 49.69; H, 5.98; N, 2.52. Found: C, 49.89; H, 6.17; N, 2.58.

$Ta(NC_9H_{10})(OAr)Et_2Cl$ (12). A 2.00 mL aliquot of $ZnEt_2$ (1.0 M in heptane, 2.00 mmol) was added dropwise to a rapidly stirred solution of 1.00 g (1.49 mmol) of $Ta(NC_9H_{10})(OAr)Cl_3(OEt_2)$ in 20 mL of benzene. Over the course of the addition, the solution changed from deep red to pale yellow with the concomitant formation of a precipitate. After 5 min, the mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford a yellow, oily solid. The product was extracted from this solid with 25 mL of pentane, the pentane extract was filtered, and the filtrate was concentrated in vacuo, whereupon a bright yellow microcrystalline solid formed. This product was collected by filtration and dried in vacuo to afford 0.55 g (0.94 mmol, 63%) of product. Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 7.23 (d, J = 7.9 Hz, 1 H, H8), 6.89−7.07 (overlapping m, 5 H total, H_{aryl} OAr, H5, H6), 6.68 (t, J = 7.5 Hz, 1 H, H7), 3.51 (t, J = 5.9 Hz, 2 H, H2), 3.44 (spt, 2 H, C*H*Me$_2$), 2.43 (t, J = 6.5 Hz, 2 H, H4), 2.11 (br s, 10 H, TaEt), 1.77 (m, 2 H, H3), 1.06 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 154.5 (C_{ipso}), 139.45 (Co), 130.45 (C5), 126.82 (C6), 124.88 (C4a), 124.00 (Cm), 123.89 (Cp), 122.55 (C7), 120.02 (C8), 78.08 (Ta*C*H$_2$CH$_3$), 40.66 (C2), 26.95 (*C*HMe$_2$), 26.42 (C4), 24.13 (CH*Me*$_2$), 20.49 (C3), 15.68 (TaCH$_2$*C*H$_3$). Anal. Calcd for $C_{25}H_{37}ClNOTa$: C, 51.42; H, 6.39; N, 2.40. Found: C, 51.39; H, 6.14; N, 2.36.

$Ta(NC_9H_{10})_2(OAr)_2Me$ (13). A 1.20 mL aliquot of $AlMe_3$ (1.0 M in heptane, 1.20 mmol) was added dropwise to a rapidly stirred solution of 1.00 g (1.20 mmol) of $Ta(NC_9H_{10})_2(OAr)_2Cl$ in 20 mL of toluene. This yellow-orange solution was stirred for 24 h, during which it gradually darkened. The reaction volatiles were removed in vacuo to afford an orange oil. The product was extracted with pentane, the extract was filtered through Celite, and the solvent was removed from the filtrate (in vacuo) to yield an oily orange solid. This solid was dissolved in minimal pentane and the solution cooled to −35 °C to provide the product as yellow crystals, which were filtered off and dried in vacuo; yield 0.75 g (0.92 mmol, 77%). ^{1}H NMR (C_6D_6): δ 7.37 (d, 2 H, H8), 7.06−6.83 (overlapping m, 10 H total, H_{aryl} OAr, H6, H5), 6.61 (t, 2 H, H7), 3.92 (m, 4 H, H2), 3.71 (spt, 4 H, C*H*Me$_2$), 2.51 (t, 4 H, H4), 1.68 (m, 4 H, H3), 1.63 (s, 3 H, TaMe), 1.09 (d, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 156.25 (C_{ipso}), 148.78 (C8a), 139.31 (Co), 129.77 (C8), 124.66 (C4a), 123.84 (Cm), 126.25, 122.89, 121.77, 121.37 (C5, C6, C7, Cp), 55.11 (TaMe), 47.21 (C2), 27.04 (C4), 26.79 (*C*HMe$_2$), 24.59 (CH*Me*$_2$), 24.04 (C3). Anal. Calcd for $C_{43}H_{57}N_2O_2Ta$: C, 63.38; H, 7.05; N, 3.44. Found: C, 62.70; H, 7.12; N, 3.32.

$Ta(NC_9H_{10})Me_2Cl_2$ (14). A solution of 0.500 g (0.945 mmol) of $Ta(NC_9H_{10})Cl_4(OEt_2)$ in 20 mL of benzene was prepared and stirred rapidly while a 0.945 mL aliquot of $ZnMe_2$ solution (2.0 M in heptane, 1.89 mmol) was added dropwise. Upon $ZnMe_2$ addition, the dark purple solution smoothly developed a light orange color with the simultaneous formation of a sticky precipitate. After 24 h, the orange solution was decanted from the precipitate, the reaction volatiles were removed in vacuo, and the product was extracted from the residue with minimal pentane. This extract was filtered through Celite, and the filtrate was stripped of solvent in vacuo to provide 0.34 g (0.82 mmol, 87%) of product as an orange solid. Analytically pure $Ta(NC_9H_{10})Me_2Cl_2$ was obtained by recrystallization from pentane solution at −35 °C. ^{1}H NMR (C_6D_6): δ 7.331 (d, 1 H, H8), 6.70−6.94 (unresolved, 2 H, H5, H7), 6.667 (t, 1 H, H5), 3.507 (m, 2 H, H2), 2.285 (t, 2 H, H4), 1.822 (s, 6 H, TaMe), 1.579 (m, 2 H, H3) ^{13}C NMR (C_6D_6): δ 141.51 (C8a), 130.24 (C5), 126.89 (C6), 125.63 (C7), 125.25 (C4a), 121.70 (C8), 37.34 (C2), 25.55 (C4), 19.56 (C3). The Ta*C*H$_3$ carbon resonances were not observed. Anal. Calcd for $C_{11}H_{16}Cl_2NTa$: C, 31.95; H, 3.87; N, 3.34. Found: C, 32.14; H, 3.86; N, 3.27.

Equilibration Experiments of $Ta(NC_9H_{10})_nCl_{5-n}$ + (5 − *n*)$Me_3SiNC_9H_{10}$ + *n*Me_3SiCl (*n* = 0, 5) Mixtures. (i) A 5 mm NMR tube was charged with 0.024 g (0.028 mmol) of $Ta(NC_9H_{10})_5$ in 400 μL of toluene-d_8. A 17.5 μL (0.149 mmol) aliquot of Me_3SiCl was added, the solution was frozen in liquid nitrogen, and the tube was flame-sealed. The dark, red-orange solution was heated in a 100 °C oil bath for 36 h. Examining the solution by ^{1}H NMR indicated the presence of $Ta(NC_9H_{10})_3Cl_2$, $Me_3SiNC_9H_{10}$, and Me_3SiCl in an approximate 1:2:3 ratio.

(ii) A 5 mm NMR tube was charged with 0.010 g (0.028 mmol) of $TaCl_5$ in 400 μL of toluene-d_8. A 30.2 μL (0.140 mmol) aliquot of $Me_3SiNC_9H_{10}$ was added, the solution was frozen in liquid nitrogen, and the tube was flame-sealed. The dark red solution was heated in a 100 °C oil bath for 24 h. Examining the solution by ^{1}H NMR indicated the the presence of $Ta(NC_9H_{10})_3Cl_2$, $Me_3SiNC_9H_{10}$, and Me_3SiCl in approximately a 1:2:3 molar ratio.

Thermolysis Experiments of $Ta(NC_9H_{10})_4Cl$ (4) and $Ta(NC_9H_{10})_5$ (5). (i) A 5 mm NMR tube was charged with 0.020 g (0.027 mmol) of $Ta(NC_9H_{10})_4Cl$ (**4**) and 0.60 mL of C_6D_6 and was sealed in vacuo. The sample was heated in an 80 °C oil bath for 30 h and examined by ^{1}H NMR; the formation of HNC_9H_{10} was observed, along with a small amount of $Ta(NC_9H_{10})_3Cl_2$. The tube was then opened, the mixture was hydrolyzed with 10 mL of 0.5 M aqueous NaOH, and the organic products were extracted with 10 mL of Et_2O. Examining this organic phase by GC/mass spectroscopy confirmed the presence of HNC_9H_{10}, along with quinoline as a minor component (HNC_9H_{10}:quinoline ≈ 100:8).

(ii) The thermolysis of 0.020 g (0.024 mmol) of $Ta(NC_9H_{10})_5$ (**5**) was carried out in a 5 mm NMR tube in a manner identical with that described above for $Ta(NC_9H_{10})_4Cl$ (**4**), except that the sample was examined by ^{1}H NMR after 14 h (80 °C oil bath). The presence of HNC_9H_{10} and unreacted $Ta(NC_9H_{10})_5$ was noted. After hydrolysis (as described above for $Ta(NC_9H_{10})_4Cl$), an examination of the organic phase by GC/mass spectroscopy confirmed the presence of HNC_9H_{10}, along with quinoline as a minor component (HNC_9H_{10}:quinoline ≈ 100:3).

(iii) A sample of DNC_9H_{10} was prepared by quenching 0.046 mL (0.214 mmol) of $Me_3SiNC_9H_{10}$ with 0.040 mL (2.00 mmol) of D_2O in THF/benzene solution (1:1 by volume). The resulting DNC_9H_{10} was isolated as an oil by removing the reaction volatiles in vacuo. The DNC_9H_{10} was added to a solution of 0.036 g (0.042 mmol) of $Ta(NC_9H_{10})_5$ (**5**) and ca. 0.50 mL of C_6D_6 in a 5 mm NMR tube, and the tube was sealed under partial vacuum. The sample was heated in an 80 °C oil bath for 18 h and examined by ^{1}H and ^{13}C NMR; the formation of HNC_9H_{10} was observed, along with a corresponding decrease in the concentration of $Ta(NC_9H_{10})_5$, but no incorporation of deuterium into the H2 or H8 positions of the coordinated tetrahydroquinolinyl NC_9H_{10} amide ligand was observed. The NMR tube was then opened, the mixture was hydrolyzed with 10 mL of 0.5 M aqueous NaOH (thereby exchanging the N-bound deuterium only), and the organic products were extracted with 10 mL of Et_2O. Examining this organic phase by GC/mass spectroscopy confirmed that no significant deuterium incorporation into HNC_9H_{10} had occurred.

X-ray Structural Determination of $Ta(NC_9H_{10})_2Cl_3$ (2). A red hexagonal block-shaped crystal of $C_{18}H_{20}Cl_3N_2Ta$ (grown directly from the toluene reaction solution at −35 °C) having approximate dimensions of 0.21 × 0.21 × 0.16 mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator and a Crystal Logics computer control system. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 53 reflections in the range $20 < 2\theta < 30°$. The monoclinic cell parameters and calculated volume are a = 15.409(1) Å, b = 9.946(1) Å, c = 12.310(1) Å, β = 96.62(8)°, V = 1874.0 Å^3. For Z = 4 and fw = 551.68, the calculated density is 1.96 g/cm^3.

As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was 0.25°, indicating good crystal quality. From the systematic absences of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at 20 ± 1 °C using the $\omega-2\theta$ scan technique (octants $+h,+k,\pm l$). The scan rate was fixed at 3.0°/min. Data were collected to a maximum 2θ of 50.0°. The scan range was determined as a function of θ to correct for the separation of the Kα doublet; the scan width was calculated from $(2\theta(K\alpha_1) - 1.30)$ to $(2\theta(K\alpha_2) + 1.60)$. The diameter of the incident beam collimator was 0.75 mm. A total of 3693 reflections were collected, of which 3308 were unique and not systematically absent. As a check on crystal and electronic stability, 3 representative reflections were measured after every 97 reflections. The intensities of these standards remained constant within experimental error throughout data collection; therefore, no decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 62.3 cm^{-1} for Mo Kα radiation. An absorption correction based on ψ-scan data was applied (minimum 1.00, maximum 1.35, average 1.20). Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 276 observed and accepted reflections was 1.5% based on intensity and 1.1% based on F_o.

The structure was solved using the Patterson heavy-atom method, which revealed the position of the Ta atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atom positions were visible in a difference map after anisotropic refinement of the non-hydrogen atoms. Hydrogen atoms were added at idealized positions. Hydrogen atoms were included in the refinement but constrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares procedures, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$.

Scattering factors were taken from Cromer and Waber.[60] Anomalous dispersion effects were included in F_c;[61] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[62] Only the 2427 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 217 variable parameters and converged (largest parameter shift was 0.00 times its esd) with agreement factors of $R = 0.025$, $R_w = 0.034$, and $S = 0.98$. There were three correlation coefficients greater than 0.50. The highest correlations were between the scale factor and the Ta (U_{11}, U_{22}, U_{33}) parameters. The highest peak in the final difference Fourier map had a height of 0.84(12) e/Å^3;[63] the minimum negative peak had a height of −0.26(12) e/Å^3. The maximum peaks were in the vicinity of the Ta and Cl positions. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using MolEN.[64]

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Supporting Information Available: Text giving details of the structure solution and refinement, tables of crystal data and data collection parameters, atomic positional and thermal parameters, bond distances, bond angles, least-squares planes, and torsional angles, and ORTEP figures for $Ta(NC_9H_{10})_2Cl_3$ (17 pages). Ordering information is given on any current masthead page.

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