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Group 5 Imido Complexes Supported by Diamido−pyridine Ligands: Aryloxide, Amide, Benzamidinate, Alkyl, and Cyclopentadienyl Derivatives

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A family of new organometallic and coordination group 5 compounds supported by an imido−diamido−pyridine ligand set are reported. Reaction of $[M(NR)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ ($M = Nb$, $R = {}^tBu$ **1**; $M = Ta$, $R = {}^tBu$ **2** or Ar **3**, where $N_2N_{py} = MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ and $Ar = 2,6\text{-}C_6H_3{}^iPr_2$) with LiOAr or $LiPhC(NSiMe_3)_2$ afforded the five-coordinate aryloxide and benzamidinate complexes $[M(NR)(OAr)(\kappa^3\text{-}N_2N_{py})]$ ($R = {}^tBu$, $M = Nb$ **4** or Ta **5**; $R = Ar$, $M = Ta$ **6**) and $[Nb(N^tBu)\{PhC(NSiMe_3)_2\}(\kappa^3\text{-}N_2N_{py})]$ (**7**), respectively. Reaction of **1** or **2** with $LiN(SiMe_3)_2$ or $LiCH(SiMe_3)_2$ gave the four-coordinate compounds $[M(N^tBu)(X)(\kappa^2\text{-}N_2N_{py})]$ ($M = Nb$, $X = N(SiMe_3)_2$ **8** or $CH(SiMe_3)_2$ **9**; $M = Ta$, $X = CH(SiMe_3)_2$ **10**). Reaction of **1** or **2** with the less sterically demanding alkyl reagent $LiCH_2SiMe_3$ gave, in the case of niobium, only the four-coordinate $[M(N^tBu)(CH_2SiMe_3)(\kappa^2\text{-}N_2N_{py})]$ (**11**), but for tantalum an equilibrium mixture of four- (κ^2-) and five- (κ^3-) coordinate isomers was identified by NMR spectroscopy. Reaction of **1** with $PhCH_2MgCl$ or LiC_5H_4Me gave the corresponding η^1- or η^5-hydrocarbyl complexes $[Nb(N^tBu)(CH_2Ph)(\kappa^3\text{-}N_2N_{py})(py)]$ (**13**) and $[Nb(N^tBu)(\eta^5\text{-}C_5H_4Me)(\kappa^2\text{-}N_2N_{py})]$ (**14**). The X-ray crystal structures of the compounds **4**, **6**, and **9** are reported.

Introduction

The chemistry of transition metal imido complexes (containing the NR ligand, where R is typically a hydrocarbyl group) has continued to attract considerable attention, particularly over the last 15 years.[1−8] Apart from theoretical aspects of such systems,[9−17] interest with regard to reactivity studies can broadly be divided into two areas: reactions at the M═NR linkage itself, and reactions in which the imido ligand acts as a supporting (spectator) ligand.[1−8] Our approach[8] to developing early transition metal imido chemistry has been to use the diamido−pyrdine ligand $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ (hereafter N_2N_{py})[18−20] and related systems[21−23] as a potential flexible, robust, dianionic supporting group. The new classes of groups 4−6 monoimido complexes of the N_2N_{py} ligand are summarized in Chart 1.[20,24−26]

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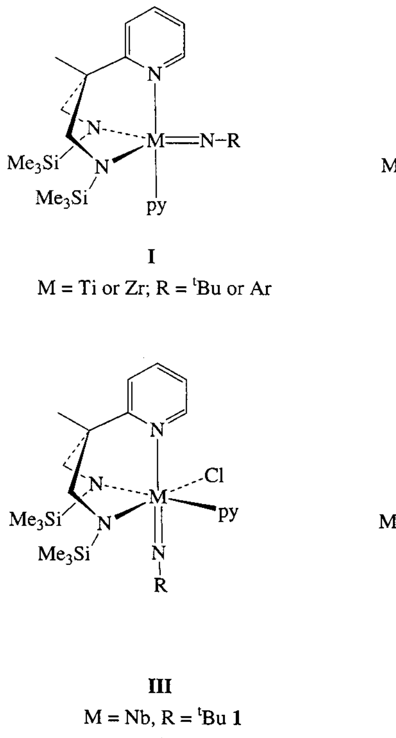
Chart 1



I

M = Ti or Zr; R = ^{t}Bu or Ar

II

R = ^{t}Bu or Ar

III

M = Nb, R = ^{t}Bu **1**

M = Ta, R = ^{t}Bu **2** or Ar **3**

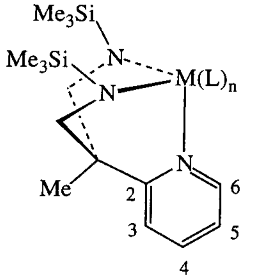
IV

R = H or Me

We have recently reported on the reactions of the group 4 imido systems **I** and **II** in which the M=NR bond itself is the main reactive site, undergoing reactions with a range of unsaturated substrates of the type RNC, RCN, RC≡CMe, $^tBuC\equiv P$, $RCH=C=CH_2$, and ArNCO (hereafter Ar = 2,6-$C_6H_3{}^iPr_2$).[20,27–31] Group 5 and 6 compounds of the type **III** and **IV** have not yet shown comparable reactivity of the M=NR bond. Nonetheless, the presence of M–Cl group(s) in these systems presents an opportunity for evaluating the supporting ligand characteristics of the combined tetraanionic-$\{(NR)(N_2N_{py})\}$ imido–diamido–pyridine ligand set.[32] Here we report a family of new group 5 organometallic and coordination derivatives of the complexes $[M(NR)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (M = Nb, R = ^{t}Bu **1**; M = Ta, R = ^{t}Bu **2** or Ar **3**).[25]

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H, $^{13}C\{^1H\}$, and ^{13}C NMR spectra were recorded on Bruker AM 300 and DPX 300 and Varian Unity Plus 500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of NOE, DEPT-135, DEPT-90, and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR experiments. All spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between CsBr or NaCl plates and were recorded on Perkin-Elmer 1600 and 1710 series, Nicolet Avatar 360, or Mattson Polaris FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). NMR assignments assume the following numbering scheme for the pyridyl group of N_2N_{py}:



Literature Preparations. $H_2N_2N_{py}$,[18] $Li_2[N_2N_{py}]$,[19] $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**1**),[25] $[Ta(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**2**),[25] and $[Ta(NAr)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**3**)[25] were prepared according to methods we have described previously.

$[Nb(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (4). To a mixture of solid $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (249 mg, 0.42 mmol) and solid LiOAr (78 mg, 0.42 mmol) was added cold (7 °C) benzene (10 mL). The yellow solution was allowed to stir at room temperature for 40 h, becoming very pale during this time. The solution was filtered, and the volatiles were removed under reduced pressure to provide $[Nb(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (**4**) as a cream-colored solid. Yield: 203 mg (74%). Colorless crystals suitable for X-ray diffraction were obtained from a saturated pentane solution at 5 °C over a period of 48 h. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): 8.95 (1 H, d, ^3J (H^6H^5) = 5.0 Hz, H^6), 7.26 (2 H, d, ^3J = 7.5 Hz, *m*-$C_6H_3{}^iPr_2$), 7.02 (1 H, t, ^3J = 7.5 Hz, *p*-$C_6H_3{}^iPr_2$), 6.99 (1 H, overlapping m, H^4), 6.84 (1 H, d, ^3J (H^3H^4) = 8.0 Hz, H^3), 6.48 (1 H, apparent t, apparent J = 5.5 Hz, H^5), 3.85 (2 H, d, ^2J = 13.5 Hz, CH_2), 3.60 (2 H, septet, ^3J = 7.0 Hz, $CHMe_2$), 3.49 (2 H, d, ^2J = 13.5 Hz, CH_2), 1.35 (12 H, d, ^3J = 6.5 Hz, $CHMe_2$), 1.35 (9 H, s, ^{t}Bu), 1.08 (3 H, s, Me of N_2N_{py}), 0.39 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): 164.6 (C^2), 160.5 (*ipso*-Ar), 148.4 (C^6), 138.0 (C^4), 135.9 (*o*-Ar), 123.4 (*m*-Ar), 121.3 (C^5), 119.5 (*p*-Ar), 119.0 (C^3), 61.6 (CH_2NSiMe_3), 49.9 ($C(CH_2NSiMe_3)_2$), 33.4 ($NCMe_3$), 27.3 ($CHMe_2$), 23.9 ($CHMe_2$), 22.2 (Me of N_2N_{py}), 2.4 ($SiMe_3$) (the signal for $NCMe_3$ was not observed). IR (NaCl plates, Nujol, cm^{-1}): 1601 (m), 1589 (m), 1574 (w), 1358 (s), 1337 (s), 1304 (w), 1267 (s), 1245 (s), 1211 (s), 1159 (m), 1138 (w), 1122 (m), 1091 (m), 1070 (m), 1057 (m), 1037 (m), 1014 (m), 986 (m), 962 (s), 915 (s), 890 (s), 854 (s), 788 (m), 753 (s), 723 (m), 693 (m), 640 (w), 604 (m), 583 (m), 562 (w), 525 (w), 496 (w), 473 (w). Anal. Found (calcd for $C_{31}H_{55}N_4NbOSi_2$): C 57.9 (57.4), H 8.7 (8.5), N 8.2 (8.6).

$[Ta(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (5). To a mixture of solid $[Ta(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (190 mg, 0.28 mmol) and solid LiOAr

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(52 mg, 0.28 mmol) was added cold (7 °C) benzene (10 mL). The yellow solution was allowed to stir at room temperature for 65 h, becoming very pale during this time. The solution was filtered, and the volatiles were removed under reduced pressure to provide [Ta(N^{t}Bu)(OAr)(κ^3-N$_2$N$_{py}$)] (**5**) as a cream-colored solid. Yield: 120 mg (58%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): 9.03 (1 H, d, ^3J (H^{6}H^5) = 4.5 Hz, H^6), 7.27 (2 H, d, ^3J = 7.5 Hz, *m*-C$_6$H$_3$^{i}Pr$_2$), 7.02 (1 H, t, ^3J = 7.5 Hz, *p*-C$_6$*H*$_3$-^{i}Pr$_2$), 6.99 (1 H, dd, ^3J (H^{4}H^5) = 8.0 Hz, ^3J (H^{4}H^3) = 8.0 Hz, H^4), 6.79 (1 H, d, ^3J (H^{3}H^4) = 8.0 Hz, H^3), 6.48 (1 H, apparent t, apparent *J* = 5.5 Hz, H^5), 3.85 (2 H, d, ^2J = 13.0 Hz, CH$_2$), 3.64 (2 H, septet, ^3J = 7.0 Hz, C*H*Me$_2$), 3.58 (2 H, d, ^2J = 13.0 Hz, CH$_2$), 1.36 (9 H, s, ^{t}Bu), 1.35 (12 H, d, ^3J = 7.0 Hz, CH*Me$_2$*), 1.03 (3 H, s, Me of N$_2$N$_{py}$), 0.40 (18 H, s, Si*Me*$_3$).^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 164.6 (C^2), 160.6 (*ipso*-Ar), 148.1 (C^6), 138.4 (C^4), 136.2 (*o*-Ar), 123.4 (*m*-Ar), 121.5 (C^5), 120.0 (*p*-Ar), 119.0 (C^3), 65.7 (N*C*Me$_3$), 61.4 (*C*H$_2$NSiMe$_3$), 49.2 (*C*(CH$_2$NSiMe$_3$)$_2$), 34.8 (NC*Me*$_3$), 27.1 (*C*HMe$_2$), 24.0 (CH*Me*$_2$), 22.3 (Me of N$_2$N$_{py}$), 2.5 (Si*Me*$_3$). IR (NaCl plates, Nujol, cm^{-1}): 1602 (s), 1452 (s), 1432 (m), 1358 (s), 1341 (m), 1335 (m), 1257 (s), 1210 (s), 1159 (m), 1137 (m), 1114 (m), 1092 (s), 1073 (m), 1060 (m), 1036 (s), 1013 (w), 968 (s), 933 (m), 925 (w), 891 (m), 862 (s), 834 (m), 807 (w), 787 (w), 755 (m), 740 (w), 604 (m), 593 (m), 583 (m). Anal. Found (calcd for C$_{31}$H$_{55}$N$_4$OSi$_2$-Ta): C 50.7 (50.5), H 7.2 (7.5), N 6.8 (7.6).

[Ta(NAr)(OAr)(κ^3-N$_2$N$_{py}$)] (6). To a mixture of solid [Ta(NAr)Cl(κ^3-N$_2$N$_{py}$)(py)] (190 mg, 0.24 mmol) and solid LiOAr (45 mg, 0.24 mmol) was added cold (7 °C) benzene (10 mL). The yellow-green solution was stirred at room temperature for 72 h. The solution was filtered, and the volatiles were removed under reduced pressure to provide [Ta(NAr)(OAr)-(κ^3-N$_2$N$_{py}$)] (**6**) as a yellow solid. Yield: 124 mg (60%). Yellow crystals suitable for X-ray diffraction were prepared by recrystallization of the product from a 1:1 hexane/toluene solution at 5 °C over 48 h. ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 298 K): 8.82 (1 H, d, ^3J (H^{6}H^5) = 5.0 Hz, H^6), 7.90 (1 H, dd, ^3J (H^{4}H^5) = 8.0 Hz, ^3J (H^{4}H^3) = 8.0 Hz, H^4), 7.54 (1 H, d, ^3J (H^{3}H^4) = 8.0 Hz, H^3), 7.22 (1 H, apparent t, apparent *J* = 6.0 Hz, H^5), 7.14 (2 H, d, ^3J = 7.5 Hz, *m*-O-C$_6$*H*$_3$^{i}Pr$_2$), 6.95 (2 H, d, ^3J = 7.5 Hz, *m*-N-C$_6$*H*$_3$^{i}Pr$_2$), 6.89 (1 H, t, ^3J = 7.5 Hz, *p*-O-C$_6$*H*$_3$^{i}Pr$_2$), 6.67 (1 H, t, ^3J = 7.5 Hz, *p*-N-C$_6$*H*$_3$^{i}Pr$_2$), 3.89 (2 H, d, ^2J = 12.5 Hz, CH$_2$), 3.85 (2 H, br overlapping s, C*H*Me$_2$ of N-C$_6$H$_3$^{i}Pr$_2$), 3.82 (2 H, d, ^2J = 12.5 Hz, CH$_2$), 3.36 (2 H, septet, ^3J = 7.0 Hz, C*H*Me$_2$ of O-C$_6$H$_3$^{i}Pr$_2$), 1.57 (3 H, s, Me of N$_2$N$_{py}$), 1.35 (12 H, d, ^3J = 6.0 Hz, CH*Me*$_2$ of O-C$_6$H$_3$^{i}Pr$_2$), 0.98 (12 H, br s, CH*Me*$_2$ of N-C$_6$H$_3$^{i}Pr$_2$), 0.03 (18 H, s, Si*Me*$_3$). ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 218 K): 8.80 (1 H, d, ^3J (H^{6}H^5) = 4.0 Hz, H^6), 7.91 (1 H, dd, ^3J (H^{4}H^5) = 8.0 Hz, ^3J (H^{4}H^3) = 8.0 Hz, H^4), 7.53 (1 H, d, ^3J (H^{3}H^4) = 8.0 Hz, H^3), 7.23 (1 H, apparent t, apparent *J* = 6.0 Hz, H^5), 7.11 (2 H, d, ^3J = 7.5 Hz, *m*-O-C$_6$*H*$_3$^{i}Pr$_2$), 6.98 (1 H, d, ^3J = 6.5 Hz, *m*-N-C$_6$*H*$_3$^{i}Pr$_2$), 6.85 (1 H, overlapping t, ^3J = 7.5 Hz, *p*-O-C$_6$*H*$_3$^{i}Pr$_2$), 6.84 (1 H, overlapping d, *m*-N-C$_6$*H*$_3$^{i}Pr$_2$), 6.63 (1 H, t, ^3J = 7.5 Hz, *p*-N-C$_6$*H*$_3$-^{i}Pr$_2$), 4.23 (1 H, br s, C*H*Me$_2$ of N-C$_6$H$_3$^{i}Pr$_2$), 3.83 (2 H, d, ^2J = 12.5 Hz, CH$_2$), 3.73 (2 H, d, ^2J = 12.5 Hz, CH$_2$), 3.38 (1 H, br s, C*H*Me$_2$ of N-C$_6$H$_3$^{i}Pr$_2$), 3.30 (2 H, septet, ^3J = 7.0 Hz, C*H*Me$_2$ of O-C$_6$H$_3$^{i}Pr$_2$), 1.54 (3 H, s, Me of N$_2$N$_{py}$), 1.26 (6 H, d, ^3J = 6.5 Hz, CHMe*Me* of N-C$_6$H$_3$^{i}Pr$_2$), 1.21 (6 H, d, ^3J = 6.5 Hz, CHMe*Me* of O-C$_6$*H*$_3$^{i}Pr$_2$), 0.97 (6 H, d, ^3J = 6.5 Hz, CH*Me*Me of O-C$_6$*H*$_3$^{i}Pr$_2$), 0.53 (6 H, d, ^3J = 6.5 Hz, CH*Me*Me of N-C$_6$H$_3$-^{i}Pr$_2$), −0.04 (18 H, s, Si*Me*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 218 K): 163.9 (C^2), 159.0 (*ipso*-OAr), 153.0 (*ipso*-NAr), 147.5 (C^6), 139.8 (C^4), 136.3 (*o*-NAr), 128.8 (*o*-OAr), 123.5 (*m*-OAr), 122.4 (C^5), 121.8 (*m*-NAr), 120.4 (*p*-NAr), 119.5, 119.4 (*p*-OAr & C^3), 62.6 (*C*H$_2$NSiMe$_3$), 49.6 (*C*(CH$_2$NSiMe$_3$)$_2$), 27.4 (*C*HMe$_2$ of NAr), 27.0 (*C*HMe$_2$ of OAr), 26.0 (CHMe*Me* of OAr), 24.8 (CH*Me*$_2$ of NAr), 24.4 (CH*Me*$_2$ of NAr), 23.4 (Me of N$_2$N$_{py}$), 22.3 (CH*Me*Me of OAr), 0.7 (Si*Me*$_3$). IR (NaCl plates, Nujol, cm^{-1}): 1602 (s), 1589 (m), 1577 (m), 1456 (s), 1353 (s), 1328 (s), 1296 (s), 1285 (s), 1262 (s), 1209 (s), 1163 (m), 1140 (m), 1110 (m), 1091 (m), 1062 (m), 1029 (s), 1013 (m), 993 (w), 981 (m), 952 (w), 914 (s), 894 (s), 873 (s), 834 (s), 782 (m), 752 (s), 741 (s), 702 (m), 677 (w), 641 (w), 626 (w), 603 (s), 587 (m), 559 (w), 551 (w), 495 (w), 464 (w), 441 (w), 428 (w). Anal. Found (calcd for C$_{39}$H$_{63}$N$_4$OSi$_2$Ta): C 55.3 (55.7), H 7.2 (7.6), N 6.5 (6.7).

[Nb(N^{t}Bu){PhC(NSiMe$_3$)$_2$}(κ^3-N$_2$N$_{py}$)] (7). To a mixture of solid [Nb(N^{t}Bu)Cl(κ^3-N$_2$N$_{py}$)(py)] (263 mg, 0.44 mmol) and solid LiPhC(NSiMe$_3$)$_2$ (121 mg, 0.44 mmol) was added cold (7 °C) benzene (20 mL). The yellow solution was stirred at room temperature for 40 h, turning paler during this time. The solution was filtered, and the volatiles were removed under reduced pressure to yield an orange powder. This powder was extracted into pentane (5 mL) and filtered, and the solvent was stripped under reduced pressure to give [Nb(N^{t}Bu){PhC-(NSiMe$_3$)$_2$}(κ^3-N$_2$N$_{py}$)] (**7**) as a pale orange powder. Yield: 204 mg (62%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): 8.70 (1 H, m, H^6), 7.42 (2 H, d, ^3J = 6.5 Hz, *o*-C$_6$*H*$_5$), 7.06 (1 H, overlapping m, *m*-C$_6$*H*$_5$), 7.06 (1 H, overlapping m, *p*-C$_6$*H*$_5$), 7.06 (1 H, overlapping m, H^4), 7.03 (1 H, overlapping d, H^3), 6.62 (1 H, apparent t, apparent *J* = 5.5 Hz, H^5), 4.13 (2 H, d, ^2J = 15.0 Hz, CH$_2$), 3.51 (2 H, d, ^2J = 15.0 Hz, CH$_2$), 1.64 (9 H, s, ^{t}Bu), 1.25 (3 H, s, Me of N$_2$N$_{py}$), 0.50 (18 H, s, CH$_2$NSi*Me*$_3$), −0.06 (18 H, s, C(NSi*Me*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 182.8 (*C*(NSiMe$_3$)$_2$), 168.2 (C^2), 148.8 (C^6), 142.6 (*ipso*-C$_6$H$_5$), 136.8 (C^4), 128.6, 128.1 (*m*-C$_6$H$_5$ and *p*-C$_6$H$_5$), 127.0 (*o*-C$_6$H$_5$), 120.4 (C^5), 120.0 (C^3), 67.7 (N*C*Me$_3$), 59.7 (*C*H$_2$NSiMe$_3$), 44.5 (*C*(CH$_2$NSiMe$_3$)$_2$), 33.3 (NC*Me*$_3$), 22.9 (Me of N$_2$N$_{py}$), 3.8, 3.1 (CH$_2$NSi*Me*$_3$ and C(NSi*Me*$_3$)$_2$). IR (NaCl plates, Nujol, cm^{-1}): 1663 (w), 1602 (m), 1590 (w), 1574 (w), 1435 (s), 1355 (m), 1289 (w), 1244 (s), 1225 (s), 1160 (w), 1138 (w), 1117 (m), 1090 (w), 1075 (w), 1063 (w), 1038 (m), 1020 (m), 1008 (m), 990 (m), 976 (m), 965 (m), 953 (w), 911 (s), 844 (s), 784 (m), 754 (s), 724 (m), 701 (m), 670 (w), 638 (w), 600 (m), 553 (w), 529 (w), 488 (m), 478 (w). Anal. Found (calcd for C$_{32}$H$_{61}$N$_6$-NbSi$_4$): C 52.1 (52.3), H 8.1 (8.4), N 11.3 (11.4).

[Nb(N^{t}Bu){N(SiMe$_3$)$_2$}(κ^2-N$_2$N$_{py}$)] (8). To a mixture of solid [Nb(N^{t}Bu)Cl(κ^3-N$_2$N$_{py}$)(py)] (225 mg, 0.38 mmol) and solid LiN(SiMe$_3$)$_2$ (64 mg, 0.38 mmol) was added cold (7 °C) benzene (10 mL). The solution was allowed to warm to room temperature, then stirred at 50 °C for 65 h. The resulting pale yellow solution was filtered, and the volatiles were removed under reduced pressure to provide a waxy yellow solid. This solid was extracted with hexane (10 mL) and filtered, and the volatiles were again removed under reduced pressure. [Nb-(N^{t}Bu){N(SiMe$_3$)$_2$}(κ^2-N$_2$N$_{py}$)] (**8**) was obtained as an orange solid. Yield: 145 mg (61%). Compound **8** was spectroscopically >90% pure, but trace impurites could not be removed by washing with hexanes, and the compound could not be successfully recrystallized. ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): 8.47 (1 H, d, ^3J (H^{6}H^5) = 4.0 Hz, H^6), 7.08 (1 H, overlapping m, H^4), 7.08 (1 H, overlapping d, H^3), 6.57 (1 H, apparent t, apparent *J* = 5.5 Hz, H^5), 4.64 (2 H, d, ^2J = 15.5 Hz, CH$_2$), 3.62 (2 H, d, ^2J = 15.5 Hz, CH$_2$), 1.55 (9 H, s, ^{t}Bu), 1.14 (3 H, s, Me of N$_2$N$_{py}$), 0.41 (18 H, s, N(Si*Me*$_3$)$_2$), 0.36 (18 H, s, CH$_2$-NSi*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 166.1 (C^2), 149.4 (C^6), 136.0 (C^4), 121.1 (C^5), 120.3 (C^3), 56.7 (*C*H$_2$NSiMe$_3$), 45.7 (*C*(CH$_2$NSiMe$_3$)$_2$), 33.6 (NC*Me*$_3$), 19.6 (Me of N$_2$N$_{py}$), 6.2 (N(Si*Me*$_3$)$_2$), 3.5 (CH$_2$NSi*Me*$_3$ (signal for N*C*Me$_3$not observed). IR (NaCl plates, Nujol, cm^{-1}): 1588 (m), 1571 (m), 1434 (s), 1402 (m), 1356 (m), 1311 (w), 1247 (s), 1232 (s), 1214 (m), 1157 (w), 1133 (m), 1083 (m), 1029 (s), 987 (m), 960 (m), 938 (m), 895 (s), 839 (s), 786 (s), 711 (m), 667 (m), 636 (w), 620 (w), 586 (w), 552 (w), 501 (w). Anal. Found (calcd for C$_{25}$H$_{56}$N$_5$NbSi$_4$): C 45.9 (47.5), H 8.5 (8.9), N 10.3 (11.1).

[Nb(N^{t}Bu){CH(SiMe$_3$)$_2$}(κ^2-N$_2$N$_{py}$)] (9). To a mixture of solid [Nb(N^{t}Bu)Cl(κ^3-N$_2$N$_{py}$)(py)] (200 mg, 0.34 mmol) and solid LiCH(SiMe$_3$)$_2$ (57 mg, 0.34 mmol) was added cold (7 °C) benzene (10 mL). The resulting solution was stirred for 5 h at room temperature, becoming red during this time. The solution was then filtered, and the volatiles were removed under reduced pressure to leave [Nb(N^{t}Bu){CH(SiMe$_3$)$_2$}(κ^2-N$_2$N$_{py}$)] (**9**) as an orange-white solid. Yield: 126 mg (59%). Colorless crystals suitable for X-ray diffraction were obtained from a saturated solution of $[Nb(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ in hexane at 5 °C over 2 weeks. ^1H NMR (C_6D_6, 300.1 MHz, 298 K): 8.45 (1 H, dt, ^3J (H^6H^5) = 4.8 Hz, ^4J (H^6H^4) = 1.3 Hz, H^6), 7.07 (1 H, overlapping m, H^4), 7.07 (1 H, overlapping d, H^3), 6.55 (1 H, apparent t, apparent J = 6.0 Hz, H^5), 4.81 (2 H, d, ^2J = 15.1 Hz, CH_2), 3.67 (2 H, d, ^2J = 15.6 Hz, CH_2), 1.63 (9 H, s, ^tBu), 1.10 (3 H, s, Me of N_2N_{py}), 0.61 (1 H, s, $C\mathit{H}(SiMe_3)_2$), 0.36 (18 H, s, $CH(Si\mathit{Me}_3)_2$), 0.33 (18 H, s, $NSi\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): 166.0 (C^2), 149.5 (C^6), 136.2 (C^4), 121.3 (C^5), 120.3 (C^3), 69.9 ($N\mathit{C}Me_3$), 58.1 ($\mathit{C}H(SiMe_3)_2$), 56.7 ($\mathit{C}H_2NSiMe_3$), 47.3 ($\mathit{C}(CH_2NSiMe_3)_2$), 34.2 ($NC\mathit{Me}_3$), 19.5 (Me of N_2N_{py}), 5.1 ($CH(Si\mathit{Me}_3)_2$), 3.5 ($NSi\mathit{Me}_3$). IR (CsBr plates, Nujol, cm^{-1}): 1735 (w), 1590 (m), 1508 (w), 1248 (s), 1154 (w), 1051 (m), 965 (w), 904 (s), 843 (s), 787 (m), 689 (m), 660 (w). Anal. Found (calcd for $C_{26}H_{57}N_4NbSi_4$): C 48.9 (49.5), H 9.2 (9.1), N 8.9 (8.9).

$[Ta(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ (10). To a mixture of solid $[Ta(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (218 mg, 0.32 mmol) and solid $LiCH(SiMe_3)_2$ (54 mg, 0.32 mmol) was added cold (7 °C) benzene (10 mL). The solution was stirred for 17 h at room temperature, becoming orange during this time. The solution was then filtered, and the volatiles were removed under reduced pressure to leave the compound $[Ta(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ (**10**) as an orange-white solid. Yield: 111 mg (48%). ^1H NMR (C_6D_6, 500.0 MHz, 298 K): 8.43 (1 H, dt, ^3J (H^6H^5) = 4.5 Hz, ^4J (H^6H^4) = 1.5 Hz, H^6), 7.06 (1 H, overlapping m, H^4), 7.06 (1 H, overlapping m, H^3), 6.54 (1 H, apparent t, apparent J = 6.0 Hz, H^5), 4.64 (2 H, d, ^2J = 15.0 Hz, CH_2), 3.60 (2 H, d, ^2J = 15.0 Hz, CH_2), 1.76 (1 H, s, $C\mathit{H}(SiMe_3)_2$), 1.63 (9 H, s, ^tBu), 1.16 (3 H, s, Me of N_2N_{py}), 0.37 (18 H, s, $CH(Si\mathit{Me}_3)_2$), 0.35 (18 H, s, $NSi\mathit{Me}_3$). ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K): 165.7 (C^2), 149.5 (C^6), 136.3 (C^4), 121.4 (C^5), 120.4 (C^3), 67.9 ($N\mathit{C}Me_3$), 63.2 ($\mathit{C}H(SiMe_3)_2$), 56.3 ($\mathit{C}H_2NSiMe_3$), 47.1 ($\mathit{C}(CH_2NSiMe_3)_2$), 35.4 ($NC\mathit{Me}_3$), 19.7 (Me of N_2N_{py}), 5.3 (d, $^1J_{(CH)}$ = 94 HzCH$(Si\mathit{Me}_3)_2$), 3.7 ($NSi\mathit{Me}_3$). IR (NaCl plates, Nujol, cm^{-1}): 1651 (w), 1604 (m), 1588 (m), 1572 (m), 1401 (w), 1356 (m), 1250 (s), 1214 (m), 1157 (m), 1092 (w), 1048 (m), 1015 (s), 990 (s), 945 (m), 920 (s), 901 (s), 839 (s), 793 (s), 755 (s), 703 (w), 663 (s), 632 (w), 618 (m), 600 (w), 555 (w), 532 (w). Anal. Found (calcd for $C_{26}H_{57}N_4Si_4Ta$): C 42.3 (43.4), H 7.1 (7.8), N 7.7 (8.0).

$[Nb(N^tBu)(CH_2SiMe_3)(\kappa^2\text{-}N_2N_{py})]$ (11). To a mixture of solid $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (270 mg, 0.46 mmol) and solid $LiCH_2SiMe_3$ (43 mg, 0.46 mmol) was added cold (7 °C) benzene (10 mL). The resulting yellow solution was stirred at room temperature for 17 h, turning red during this time. The solution was filtered, and the volatiles were removed under reduced pressure to leave a red oil. The oil was extracted with hexane (3 mL) and filtered, and the volatiles were again removed under reduced pressure to provide $[Nb(N^tBu)(CH_2SiMe_3)(\kappa^2\text{-}N_2N_{py})]$ (**11**) as a red viscous oil, which could not be crystallized. Yield: 180 mg (70%). ^1H NMR (C_6D_6, 500.0 MHz, 298 K): 8.52 (1 H, d, ^3J (H^6H^5) = 4.5 Hz, ^4J (H^6H^4) = 1.0 Hz, H^6), 7.06 (1 H, dd, ^3J (H^4H^5) = 7.5 Hz, ^3J (H^4H^3) = 7.5 Hz, H^4), 7.01 (1 H, d, ^3J (H^3H^4) = 7.5 Hz, H^3), 6.58 (1 H, apparent t, apparent J = 6.0 Hz, H^5), 4.62 (2 H, d, ^2J = 14.5 Hz, CH_2), 3.59 (2 H, d, ^2J = 14.0 Hz, CH_2), 1.59 (9 H, s, ^tBu), 1.09 (3 H, s, Me of N_2N_{py}), 0.79 (2 H, s, $C\mathit{H}_2SiMe_3$), 0.29 (9 H, s, $CH_2Si\mathit{Me}_3$), 0.26 (18 H, s, $NSi\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): 165.8 (C^2), 149.1 (C^6), 136.4 (C^4), 121.3 (C^5), 120.1 (C^3), 62.8 ($\mathit{C}H_2SiMe_3$), 58.1 ($\mathit{C}H_2NSiMe_3$), 50.2 ($\mathit{C}(CH_2NSiMe_3)_2$), 33.9 ($NC\mathit{Me}_3$), 19.3 (Me of N_2N_{py}), 3.1 ($CH_2Si\mathit{Me}_3$), 2.7 ($NSi\mathit{Me}_3$) (the signal for $N\mathit{C}Me_3$ was not observed. IR (NaCl plates, thin film, cm^{-1}): 1600 (w), 1588 (m), 1572 (w), 1456 (w), 1432 (m), 1402 (w), 1355 (m), 1311 (w), 1244 (s), 1213 (m), 1157 (w), 1138 (m), 1089 (w), 1051 (m), 1030 (s), 1000 (m), 990 (m), 942 (m), 916 (s), 892 (s), 839 (s), 792 (s), 711 (m), 683 (w), 666 (m), 633 (w), 619 (w), 596 (w), 576 (w), 554 (w), 498 (w), 453 (w), 403 (w). Anal. Found (calcd for $C_{23}H_{49}N_4NbSi_3$): C 49.4 (48.6), H 8.8 (8.2), N 10.0 (10.0).

$[Ta(N^tBu)(CH_2SiMe_3)(\kappa^{2,3}\text{-}N_2N_{py})]$ (12a,b). To a mixture of solid $[Ta(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (195 mg, 0.29 mmol) and solid $LiCH_2SiMe_3$ (27 mg, 0.29 mmol) was added cold (7 °C) benzene (10 mL). The resulting solution was stirred at 50 °C for 20 h, turning orange during this time. The solution was filtered, and the volatiles were removed under reduced pressure to leave an orange oil. The oil was extracted with hexane (10 mL) and filtered, and the volatiles were again removed under reduced pressure to provide $[Ta(N^tBu)(CH_2SiMe_3)(\kappa^{2,3}\text{-}N_2N_{py})]$ (**12**) as an orange viscous oil, which could not be crystallized. Yield: 159 mg (85%). ^1H NMR (C_6D_6, 500.0 MHz, 298 K) (signals associated with the five-coordinate isomer (**12b**) are denoted with a prime (′); H′ and H are in an approximate ratio 1 H′:2 H): 9.02 (1 H′, d, ^3J (H^4H^5) = 4.5 Hz, $H^{6'}$), 8.50 (1 H, d, ^3J (H^4H^5) = 4.5 Hz, H^6), 7.07 (1 H, dd, ^3J (H^4H^5) = 8.0 Hz, ^3J (H^4H^3) = 8.0 Hz, H^4), 7.01 (1 H, overlapping d, H^3), 7.01 (1 H′, overlapping m, $H^{4'}$), 6.69 (1 H′, d, ^3J ($H^{3'}H^{4'}$) = 8.0 Hz, $H^{3'}$), 6.59 (1 H, apparent t, apparent J = 6.0 Hz, H^5), 6.57 (1 H′, apparent t, apparent J = 6.0 Hz, $H^{5'}$), 4.57 (2 H, d, ^2J = 14.5 Hz, CH_2), 4.05 (2 H′, d, ^2J = 13.0 Hz, CH_2'), 3.63 (2 H, d, ^2J = 15.0 Hz, CH_2'), 3.38 (2 H′, d, ^2J = 13.5 Hz, CH_2), 1.65 (9 H′, s, $^tBu'$), 1.62 (9 H, s, ^tBu), 1.17 (3 H, s, Me of N_2N_{py}), 0.95 (3 H′, s, Me′ of N_2N_{py}), 0.47 (2 H, s, $C\mathit{H}_2SiMe_3$), 0.45 (2 H′, s, $C\mathit{H}'_2SiMe_3$), 0.44 (9 H′, s, $CH_2Si\mathit{Me}'_3$), 0.30 (18 H, s,$NSi\mathit{Me}_3$), 0.30 (9 H, s, $CH_2Si\mathit{Me}_3$), −0.01 (18 H′, s, $NSi\mathit{Me}'_3$). ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K) (signals associated with the five-coordinate complex (**12b**) are denoted with a prime [′]): 165.5 (C^2), 160.3 ($C^{2'}$), 149.1 (C^6), 147.9 ($C^{6'}$), 137.2 ($C^{4'}$), 136.3 (C^4), 121.4 (C^5), 121.0 ($C^{5'}$), 120.7 ($C^{3'}$), 120.1 (C^3), 67.0 ($N\mathit{C}Me_3$), 66.3 ($N\mathit{C}'Me_3$), 62.1 ($\mathit{C}'H_2NSiMe_3$), 57.4 ($\mathit{C}H_2NSiMe_3$), 49.8 ($\mathit{C}'H_2SiMe_3$), 49.7 ($\mathit{C}(CH_2NSiMe_3)_2$), 45.9 ($\mathit{C}'(CH_2NSiMe_3)_2$), 42.3 ($\mathit{C}H_2SiMe_3$), 35.2 ($NC\mathit{Me}_3$), 34.9 ($NC\mathit{Me}'_3$), 23.5 (Me′ of N_2N_{py}), 19.2 (Me of N_2N_{py}), 3.6 (t, $^1J_{(CH)}$ = 117 Hz, $CH_2Si\mathit{Me}'_3$), 3.2 (t, $^1J_{(CH)}$ = 104 Hz, $CH_2Si\mathit{Me}_3$), 2.9 ($NSi\mathit{Me}_3$), 0.9 ($NSi\mathit{Me}'_3$). IR (NaCl plates, thin film, cm^{-1}): 1602 (s), 1588 (s), 1572 (s), 1469 (s), 1432 (s), 1402 (w), 1378 (w), 1354 (s), 1311 (w), 1245 (s), 1212 (s), 1157 (w), 1139 (m), 1089 (m), 1039 (s), 1000 (s), 945 (s), 683 (m), 668 (m), 631 (w), 620 (w), 594 (m), 554 (m), 520 (w), 496 (m), 450 (m). Anal. Found (calcd for $C_{23}H_{49}N_4Si_3Ta$): C 42.1 (42.7), H 7.4 (7.6), N 8.5 (8.6).

$[Nb(N^tBu)(CH_2Ph)(\kappa^3\text{-}N_2N_{py})(py)]$ (13). To a cooled (10 °C) solution of $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (204 mg, 0.35 mmol) in benzene (15 mL) was added $PhCH_2MgCl$ (1.0 M solution in diethyl ether, 0.37 mL, 0.35 mmol). The resulting solution was stirred at room temperature for 17 h, during which time an orange color developed. 1,4-Dioxane (1 mL) was added to the solution in order to precipitate $MgCl_2$ as $MgCl_2$·dioxane, and the solution was filtered. The volatiles were removed under reduced pressure, and the orange residues were washed with hexane (3 × 10 mL). $[Nb(N^tBu)(CH_2Ph)(\kappa^3\text{-}N_2N_{py})(py)]$ (**13**) was obtained as an orange powder, but attempted recrystallization led to decomposition. Yield: 85 mg (38%). ^1H NMR (C_6D_6, 300.1 MHz, 298 K): 8.81 (1 H, d, ^3J (H^6H^5) = 5.0 Hz, H^6), 7.87 (2 H, d, ^3J ($o\text{-}C_6H_5m\text{-}C_6H_5$) = 7.5 Hz, $o\text{-}C_6H_5$), 7.58 (2 H, br s, $o\text{-}NC_5H_5$), 7.25 (2 H, t, ^3J = 7.7 Hz, $m\text{-}C_6H_5$), 7.04 (1 H, overlapping m, H^4), 6.99 (1 H, overlapping m, H^3), 6.99 (1 H, overlapping m, $p\text{-}C_6H_5$), 6.70 (1 H, br s, $p\text{-}NC_5H_5$), 6.51 (1 H, apparent t, apparent J = 6.5 Hz, H^5), 6.44 (2 H, br s, $m\text{-}NC_5H_5$), 3.67 (1 H, d, ^2J = 11.8 Hz, Me_3SiNCH_2), 3.18 (1 H, d, ^2J = 11.4 Hz, Me_3SiNCH_2), 3.00 (1 H, d, ^2J = 12.5 Hz, Me_3SiNCH_2), 2.83 (1 H, d, ^2J = 12.5 Hz, Me_3SiNCH_2), 1.43 (3 H, s, Me of N_2N_{py}), 1.16 (9 H, s, ^tBu), 0.08 (9 H, s, $Si\mathit{Me}_3$), −0.14 (9 H, s,$Si\mathit{Me}_3$) (the signals for $PhC\mathit{H}_2$ were not observed). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): 170.5 (C^2), 153.4 (*ipso*-C_6H_5), 148.4 (C^6), 147.9 ($o\text{-}NC_5H_5$), 139.0 (C^4), 137.7 ($p\text{-}NC_5H_5$), 130.5 ($o\text{-}C_6H_5$), ca. 128 (obscured by solvent signal, $m\text{-}C_6H_5$, $p\text{-}C_6H_5$), 124.0 ($m\text{-}NC_5H_5$), 121.4 (C^5), 119.5 (C^3), 65.0 ($N\mathit{C}Me_3$), 60.9 ($\mathit{C}H_2NSiMe_3$), 46.9 ($\mathit{C}H_2NSiMe_3$), 32.2 ($NC\mathit{Me}_3$), 26.7 (Me of N_2N_{py}), 1.9 ($Si\mathit{Me}_3$), 0.1 ($Si\mathit{Me}_3$) (signals for $\mathit{C}(CH_2NSiMe_3)_2$ and $Ph\mathit{C}H_2$ were not observed). IR (CsBr plates, Nujol, cm^{-1}): 1735 (w), 1630 (w), 1602 (m), 1572 (m), 1523 (w), 1508 (w),

Table 1. X-ray Data Collection and Processing Parameters for [Nb(N^{t}Bu)(O-2,6-$C_6H_3{}^iPr_2$)(N_2N_{py})] (4), [Ta(N-2,6-$C_6H_3{}^iPr_2$)(O-2,6-$C_6H_3{}^iPr_2$)(N_2N_{py})] (6), and [Nb(N^{t}Bu){CH($SiMe_3)_2$}(N_2N_{py})] (9)

	4	**6**	**9**
molecular formula	$C_{31}H_{55}N_4NbOSi_2$	$C_{39}H_{63}N_4OSi_2Ta$	$C_{26}H_{57}N_4NbSi_4$
fw	648.89	841.08	631.03
temperature/°C	−98	−123	−103
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
unit cell dimens: a/Å	15.1000(6)	11.5100(3)	11.296(6)
b/Å	13.0490(5)	11.9300(2)	17.556(7)
c/Å	18.6330(4)	14.9600(4)	18.07(1)
α/deg	96.504(2)	92.37(5)	
β/deg	97.705(2)	98.040(1)	93.16(5)
γ/deg	92.121(2)	92.05(4)	
volume/Å^3	3638.3	2018.0	3572.9
Z	4	2	2
density(calcd)/Mg m^{-3}	1.18	1.38	1.17
radiation (λ/Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Cu Kα (1.54180)
abs coeff/mm^{-1}	0.41	2.78	4.26
F(000)	1384	868	1352
cryst description	colorless block	yellow block	colorless block
cryst size/mm	0.40 × 0.30 × 0.30	0.35 × 0.25 × 0.25	0.80 × 0.65 × 0.50
θ range for data collection/deg	1.4 to 26.5	0.5 to 27	2.45 to 74.90
scan type	ω scans	ω scans	$\omega-2\theta$ scans
decay correction/%	not measured	not measured	9.69
index ranges	$0 \le h \le 18$, $0 \le k \le 16$, $-21 \le l \le 20$	$0 \le h \le 14$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-14 \le h \le 14$, $-21 \le k \le 21$, $-22 \le l \le 0$
no. of reflns collected	20 879	12 281	14 970
no. of ind reflns	7344	7866	14 493
no. of obsd reflns [$I > 3\sigma(I)$]	4637	7025	11 933
R(merge)	0.030	0.035	0.030
abs corr	multiscan	multiscan	Ψ-scans
max. and min. transmn	$T_{min} = 0.848$, $T_{max} = 0.884$	$T_{min} = 0.378$, $T_{max} = 0.488$	$T_{min} = 0.71$, $T_{max} = 1.00$
no. of data used in refinement	4637	7025	11 933
no. of restraints applied	0	0	0
no. of params refined	352	425	633
weighting scheme	Chebychev polynomial	Chebchev polynomial	Chebychev polynomial
extinction coeff	none required	43(6)	83(8)
final R indices^a [$I > 3\sigma(I)$]	$R_1 = 0.041$ $R_w = 0.038$	$R_1 = 0.0264$ $R_w = 0.0295$	$R_1 = 0.0531$ $Rw = 0.0615$
goodness-of-fit (on F)	1.126	1.0539	0.9920
final $(\Delta/\sigma)_{max}$	0.001	0.0038	0.064
largest residual peaks/e Å^{-3}	0.52 and −0.98	0.95 and −1.27	0.97 and −2.20

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w\,(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}}$.

1247 (s), 1211 (m), 1156 (w), 1070 (w), 945 (m), 838 (s), 770 (m), 752 (s), 701 (m), 634 (w). A satisfactory elemental analysis could not be obtained for this compound.

[Nb(N^{t}Bu)(η^5-C_5H_4Me)(κ^2-N_2N_{py})] (14). To a mixture of solid [Nb(N^{t}Bu)Cl(κ^3-N_2N_{py})(py)] (187 mg, 0.32 mmol) and solid LiC_5H_4Me (28 mg, 0.32 mmol) was added cold (7 °C) benzene (10 mL). The solution was heated to 60 °C and stirred for 72 h, becoming orange during this time. It was then filtered, and the volatiles were removed under reduced pressure, to leave [Nb(N^{t}Bu)(η^5-C_5H_4Me)(κ^2-N_2N_{py})] (**14**) as an orange solid. Yield: 115 mg (65%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): 8.57 (1 H, d, ^3J (H^6H^5) = 4.0 Hz, H^6), 7.10 (1 H, overlapping m, H^4), 7.09 (1 H, overlapping d, H^3), 6.58 (1 H, apparent t, apparent J = 6.0 Hz, H^5), 6.22 (2 H, apparent s, $C_5\mathit{H}_4Me$), 5.86 (2 H, apparent s, $C_5\mathit{H}_4Me$), 4.16 (2 H, d, ^2J = 15.0 Hz, CH_2), 3.48 (2 H, d, ^2J = 15.0 Hz, CH_2), 1.89 (3 H, s, $C_5H_4\mathit{Me}$), 1.37 (9 H, s, ^{t}Bu), 1.01 (3 H, s, Me of N_2N_{py}), 0.27 (18 H, s, $Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): 167.6 (C^2), 149.4 (C^6), 135.9 (C^4), 124.0 (1-C_5H_4Me), 120.8, 120.7 (C^5 and C^3), 105.6, 104.2 (2 × ring $\mathit{C}H$ of C_5H_4Me), 61.4 ($\mathit{C}H_2NSiMe_3$), 44.5 ($\mathit{C}(CH_2NSiMe_3)_2$), 33.3 ($NC\mathit{Me}_3$), 20.3 (Me of N_2N_{py}), 14.2 ($C_5H_4\mathit{Me}$), 3.6 ($Si\mathit{Me}_3$) (the signal for $NCMe_3$ was not observed). IR (NaCl plates, Nujol, cm^{-1}): 1587 (s), 1569 (m), 1496 (w), 1435 (m), 1356 (m), 1342 (w), 1314 (w), 1262 (m), 1242 (s), 1222 (s), 1153 (m), 1119 (s), 1091 (w), 1055 (m), 1036 (s), 994 (w), 981 (m), 938 (m), 918 (s), 839 (s), 800 (m), 787 (s), 681 (w), 666 (s), 630 (w), 620 (m), 590 (w), 557 (s), 531 (w), 496 (w), 481 (w), 453 (m), 429 (w). Anal. Found (calculated for $C_{25}H_{45}N_4NbSi_2$): C 54.6 (54.5), H 7.8 (8.2), N 9.8 (10.2).

Crystal Structure Determinations of [Nb(N^{t}Bu)(OAr)(κ^3-N_2N_{py})] (4), [Ta(NAr)(OAr)(κ^3-N_2N_{py})] (6), and [Nb(N^{t}Bu){CH($SiMe_3)_2$}(κ^2-N_2N_{py})] (9). Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to an Enraf-Nonius DIP2000 image plate diffractometer or CAD4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[33] Data were collected at low temperature using Mo Kα (**4** and **6**) or Cu Kα (for **9**) radiation; equivalent reflections were merged and for **4** and **6** the images were processed with the DENZO and SCALEPACK programs.[34] Corrections for Lorentz-polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[35] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined in a riding model. Extinction corrections were applied as required.[36] Crystallographic calculations were performed using SIR92[35] and CRYSTALS.[36] A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **4**, **6**, and **9** have been deposited at the

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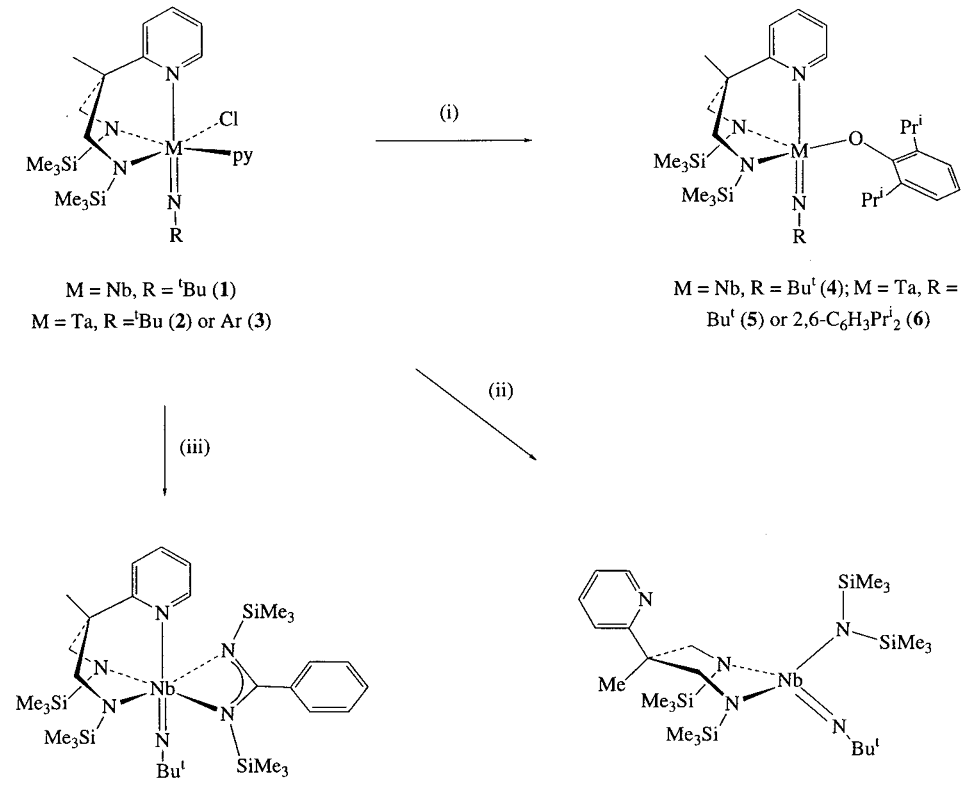
Scheme 1. Aryloxide, Amide, and Benzamidinate Complexes with Imido−Diamido−Pyridine Ligand Sets[a]



M = Nb, R = ^{t}Bu (**1**)
M = Ta, R = ^{t}Bu (**2**) or Ar (**3**)

M = Nb, R = Bu^t (**4**); M = Ta, R = Bu^t (**5**) or 2,6-$C_6H_3Pr^i_2$ (**6**)

7

8

[a] (i) Li−OAr, benzene, 7 °C then rt, 40−72 h, 58−74%; (ii) $LiN(SiMe_3)_2$, benzene, 7 °C then 50 °C, 65 h, 61%; (iii) $LiPhNC(NSiMe_3)_2$, benzene, 7 °C then rt, 40 h, 62%.

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Results and Discussion

The compounds $[M(NR)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (M = Nb, R = ^{t}Bu **1**; M = Ta, R = ^{t}Bu **2** or Ar **3**, where N_2N_{py} = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ and Ar = $2,6\text{-}C_6H_3{}^iPr_2$) were prepared according to methods we have reported previously.[25] The syntheses and proposed structures of the new complexes with O- or N-donor ligands are summarized in Scheme 1.

Aryloxide Derivatives. Cooled benzene was added to a mixture of solid $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**1**) and solid LiOAr. The yellow solution was stirred at ambient temperature for 40 h to give analytically pure $[Nb(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ as a cream-colored solid in 74% yield. Analogous methods were used to obtain the tantalum *tert*-butylimido and arylimido analogues $[Ta(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (**5**) and $[Ta(NAr)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (**6**) as cream and yellow solids, respectively. The reactions for tantalum required longer reaction times than for niobium and gave slightly lower yields (**5**, 58%; **6**, 60%). The new compounds **4**−**6** were characterized by IR and NMR spectroscopy and also by elemental analysis. Compounds **4** and **6** were, in addition, characterized by X-ray structural analysis.

Colorless single crystals of $[Nb(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (**4**) were grown from a saturated pentane solution, and crystals of **6** were grown from a 1:1 (v/v) hexane/toluene solution, at 5 °C over 48 h. The molecular structures are shown in Figures 1 and 2, respectively; selected bond distances and angles are compared in Table 2. The structures of **4** and **6** are distorted trigonal bipyramidal about a pentavalent metal center. They contain a facially coordinated N_2N_{py} ligand with the pyridyl group occupying one of the axial positions of the trigonal bipyramid. The other axial site is occupied by the imido group, with the aryloxide ligand in the remaining equatorial position. The low-temperature ^1H and ^{13}C NMR spectra of **4**−**6** are consistent with the solid-state structures shown, with evidence of restricted rotation

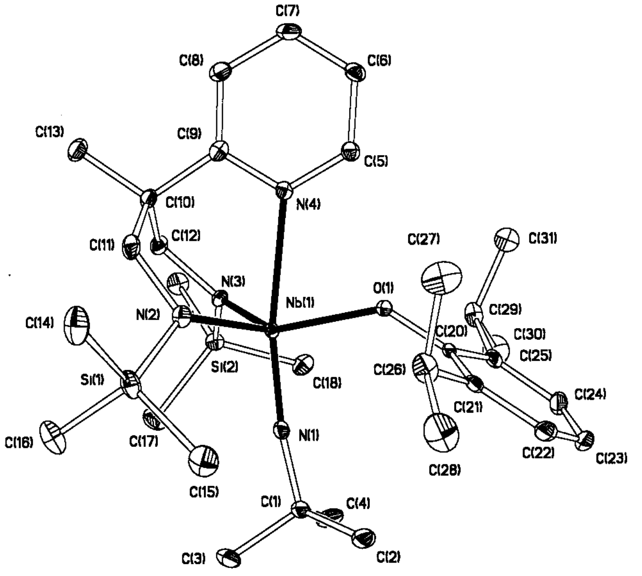

Figure 1. Displacement ellipsoid plot (20% probablility) of $[Nb(N^tBu)(OAr)(\kappa^3\text{-}N_2N_{py})]$ (**4**) with hydrogen atoms omitted.

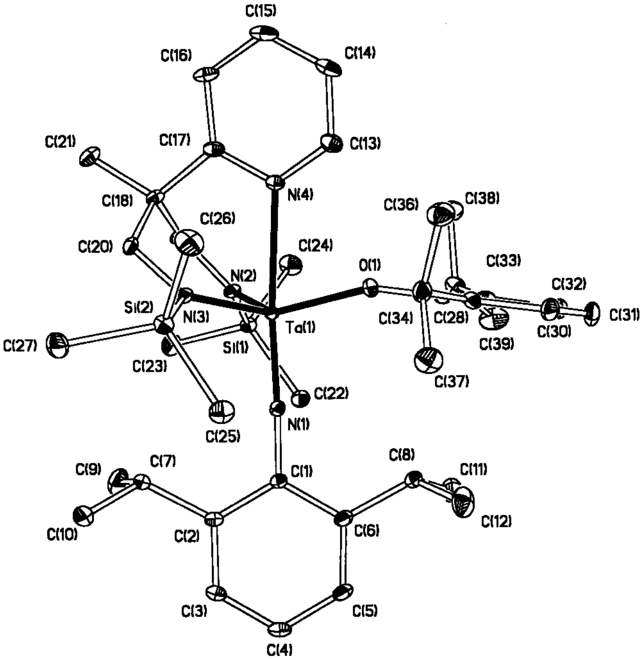

Figure 2. Displacement ellipsoid plot (20% probablility) of [Ta(NAr)(OAr)(κ^3-N_2N_{py})] (**6**) with hydrogen atoms omitted.

Table 2. Comparison of Bond Lengths (Å) and Angles (deg) for [Nb(N^{t}Bu)(OAr)(κ^3-N_2N_{py})] (4) and [Ta(NAr)(OAr)(κ^3-N_2N_{py})] (6)

4		**6**	
distance		distance	
Nb(1)−N(1)	1.782(3)	Ta(1)−N(1)	1.808(2)
Nb(1)−N(2)	2.010(3)	Ta(1)−N(2)	1.990(3)
Nb(1)−N(3)	2.022(3)	Ta(1)−N(3)	2.000(2)
Nb(1)−N(4)	2.475(3)	Ta(1)−N(4)	2.473(2)
Nb(1)−O(1)	2.022(2)	Ta(1)−O(1)	1.954(2)
N(1)−C(1)	1.464(4)	N(1)−C(1)	1.384(4)
angle		angle	
Nb(1)−N(1)−C(1)	172.1(2)	Ta(1)−N(1)−C(1)	176.1(2)
Nb(1)−O(1)−C(20)	135.8(2)	Ta(1)−O(1)−C(20)	158.5(2)
N(1)−Nb(1)−N(2)	104.8(1)	N(1)−Ta(1)−N(2)	103.5(1)
N(1) − Nb(1)−N(3)	104.2(1)	N(1)−Ta(1)−N(3)	102.3(1)
N(1)−Nb(1)−N(4)	169.7(1)	N(1)−Ta(1)−N(4)	173.0(1)
N(1)−Nb(1)−O(1)	96.9(1)	N(1)−Ta(1)−O(1)	100.9(1)
N(2)−Nb(1)−N(3)	99.1(1)	N(2)−Ta(1)−N(3)	100.8(1)

about the N−Ar and O−Ar bonds in the more sterically crowded **6**. Complete NMR assignments (suported by NOE and correlation experiments) are given in the Experimental Section for these and all the new complexes described herein.

Compound **4** is only the second structurally characterized example of an aryloxide-supported niobium imido complex, the first being [Nb(NMe)(O-2,6-C_6H_3-Ph_2)$_3$($NHMe_2$)] (**4.2**).[38] At 1.782(3) Å, the Nb═$N_{(imide)}$ bond length is effectively identical to that in the octahedral starting complex [Nb(N^{t}Bu)Cl(κ^3-N_2N_{py})(py)] (**1**). The Nb−$N_{(amide)}$ bonds are both marginally shorter [by 0.030(7) and 0.022(7) Å] relative to those in **1**,[25] while the Nb−$N_{(pyridyl)}$ bond is longer by 0.047(6) Å. The most significant features of this structure, however, are

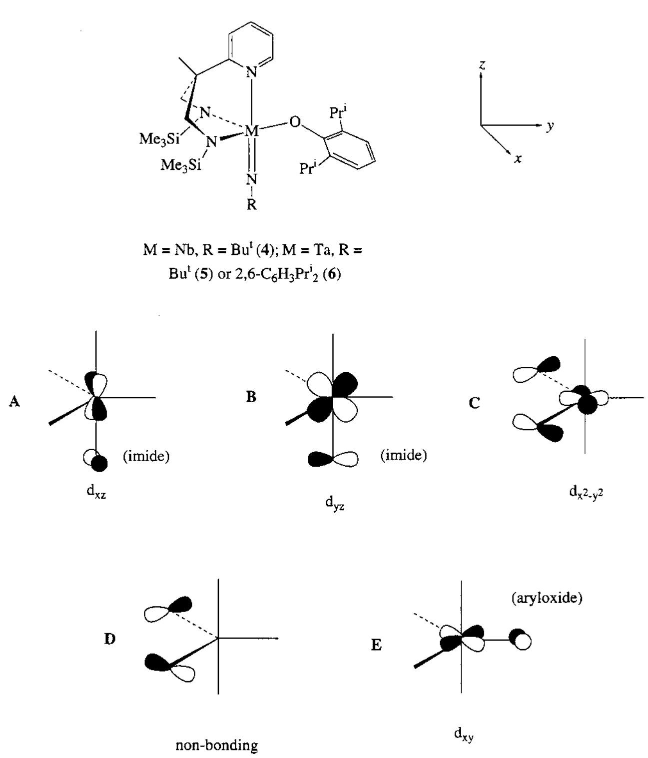

Figure 3. Qualitative analysis of Nb 4d$_\pi$−(N,O) 2$\pi\pi$ bonding interactions and N_2N_{py} ligand π-nonbonding orbitals for [M(NR)(OAr)(N_2N_{py})] (**4**−**6**), showing the Cartesian coordinate system chosen.

the unusually long Nb−O linkage [2.022(2) Å]; such linkages more typically lie in the range 1.82−1.92 Å (average 1.882 Å for six examples),[39,40] and the highly bent Nb−O−C linkage (Nb−O−C(20) = 135.8(2)°, cf. the previously known range: 139.3(4)−176.7(3)°, average 172.4°, for the above examples). The Nb−O−C linkage bends such that the aryl group is oriented “downward” toward the imido ligand, with the atoms Nb(1), O(1), and C(20) lying in the approximate molecular mirror plane that also contains N(1), N(4), and C(10). It seems likely that the origin of this bend is electronic, serving to remove any competition between the aryloxide and the imido π-donor ligands for the same metal π-acceptor orbital, as discussed below with reference to Figure 3. The reason that the aryloxide is oriented toward the imide, rather than toward the pyridyl group, probably lies in the *trans* influence of the imido ligand,[17] which will tend to increase the $N_{(imide)}$−Nb−O bond angle to greater than 90° [N(1)−Nb−O = 96.9(1)°]. An “upward” (toward pyridyl) bend of the Nb−O−Ar linkage would then place the aryl group close to the N_2N_{py} pyridyl group and particularly close to the pyridyl H^6 atom. To relieve steric pressure, a bend away from the pyridyl group is therefore expected. Despite the relatively long Nb−O bond length, the angle of the Nb−O−C(20) bend suggests that the oxygen atom may still be capable of π-donation to the metal by way of a 2p π-donor orbital lying in the equatorial plane (see below).

The sum of the angles about the amide nitrogen atoms N(2) and N(3) (357.7(4)° and 356.4(4)°, respectively)

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shows both to be effectively planar, so that the atoms are sp^2-hybridized and capable of π-donation to the metal. Comparison of the angles between the amide planes containing {C(11), N(2), Si(1)} and {C(12), N(3), Si(2)} with that of the best fit equatorial plane {N(2)−N(3)−Nb−O(1)} shows that they are oriented at 57.0° and 49.1° with respect to the latter and hence that the π-donor 2p orbitals on N(2) and N(3) should achieve some overlap with the niobium 4d π-acceptor orbitals in the equatorial plane as discussed below. The orientation of the amido $SiMe_3$ groups "down" toward the imido ligand and displacement of the aryloxide substituent in the same direction help to orient the OAr isopropyl groups further away from the $SiMe_3$ groups.

The most obvious difference between the structure of $[Ta(NAr)(OAr)(N_2N_{py})]$ (**6**, Figure 2) and that of its niobium *tert*-butylimido analogue **4** is the much more sterically crowded environment of the tantalum complex. The aryloxide M−O−C linkage is much more linear in **6** [158.5(2)°] than in **4** [135.8(2)°], due presumably to the steric pressure exerted by the arylimide isopropyl groups (note that the bending of the aryloxide Ta−O−C(28) linkage remains "upward" toward the imido group). Bond lengths and angles in this compound are, on the whole, unremarkable, with little change from the starting complex $[Ta(NAr)Cl(N_2N_{py})(py)]$ (**3**) in metal imide and amide bond lengths. Only the Ta−O bond length [1.990(3) Å] lies outside typical ranges (range 1.875(3)−1.945(5) Å, average 1.909 Å, for 10 examples),[38,41−45] just as for the niobium complex **4**. It is notable, however, that with two amide donors in addition to the imide and aryloxide ligands, complexes **4** and **6** are both considerably more heavily "π-loaded"[46] than most other structurally characterized niobium or tantalum aryloxides, which may well reduce the π-donor ability and thus the effective bond order of the aryloxide ligand in these two cases. Note that despite the more linear Ta−O−Ar angle in **6**, the oxygen is still unlikely to be able sigificantly to donate π-electron density to the appropriate metal π-acceptor orbital (d_{yz} in Figure 3, see discussion of π-bonding framework below) from its developing second 2p π-donor orbital because of competition with the dominant imido $2p_y$ π-donor orbital.

The bond angles about the amide groups in **6** show that both are, as in **4**, effectively planar and thus in principle capable of π-donation to the metal (sums of angles about N(2) and N(3), 360.0(3)° and 359.7(3)°, respectively). The planes defined by {C(18), N(2), Si(1)} and by {C(20), N(3), Si(2)} make angles of 49.9° and 39.5°, respectively, with the best fit equatorial plane {N(2), N(3), Ta, O(1)}, suggesting that the amide 2p π-donor orbitals are twisted slightly further out of the equatorial plane than in complex **4**. This effect would appear to be another result of the increased steric pressure from the arylimide isopropyl groups forcing the trimethylsilyl amide substituents away from the arylimido group.

Figure 3 presents a qualitative analysis of the metal−ligand π-bonding framework in the complexes **4**−**6**. Taking the coordination as trigonal bipyramidal and the Cartesian axes as shown, there are four *n*d π-acceptor orbitals available after forming the metal−ligand σ-bond framework.[47] The near-linear imido linkages ($M-N_{(imide)}-R$ = 172.1(2)° and 176.1(2)°) reveal that these nitrogen atoms are sp-hybridized and offer two $2p_\pi$-donor orbitals ($2p_x$ and $2p_y$ in the chosen coordinate system). These will interact strongly with the metal nd_{xz} and nd_{yz} atomic orbitals as shown in A and B, respectively in Figure 3. Taking the amido nitrogen 2p π-donor orbitals to lie mainly in the equatorial (*xy*) plane gives two symmetry-adapted linear combinations in the effective C_s point group of **4**−**6**. One of these will find a match with the $d_{x^2-y^2}$ orbital of the metal (C) while the other (D) is metal−ligand nonbonding since its nodal plane passes through the metal. Therefore there is one remaining metal π-acceptor orbital available, namely the nd_{xy} level. This matches with the $2p_x$ π-donor lone pair of OAr (E). The other lone pair of oxygen is nonbonding either because of the oxygen's hybridization (for **4**, Nb−O−Ar = 135.8(2)° so sp^2) or (for **6**) because the only suitable metal acceptor orbital (d_{yz}) is used in the comparatively stronger $M-N_{(imide)}$ π-bonding. This analysis accounts for the bending of the M−O−Ar linkages in **4** and **6** which removes the oxygen $2p_x$ lone pair from the bonding picture. It is also clear that (formally) the imido ligands in **4**−**6** acts as four-electron donors, the OAr as a three-electron donor, and each of the amido nitogens as two-electron donors, with a ligand-based lone pair localized on the amido nitrogens.

Benzamidinato and Bis(trimethylsilyl)amido Derivatives Given the similarities of the reactions of the niobium and tantalum starting complexes **1**−**3** with LiOAr as described above, subsequent studies focused mainly on the *tert*-butylimido niobium homologue **1**, as it can be most readily prepared in synthetically useful quantities.[25]

Reactions of **1** with $LiPhC(NSiMe_3)_2$ and $LiN(SiMe_3)_2$ are summarized in Scheme 1. In both cases cold benzene was added to a mixture of solid $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**1**) and the lithiated benzamidinate or amide reagent. Subsequent workup after stirring at room temperature or heating (for $LiN(SiMe_3)_2$) for 40−65 h gave $[Nb(N^tBu)\{PhC(NSiMe_3)_2\}(\kappa^3\text{-}N_2N_{py})]$ (**7**) and $[Nb(N^tBu)\{N(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ (**8**) as pale orange solids in 61−62% isolated yield. The compound **8** was spectroscopically >90% pure, but trace impurites could not be removed by washing with hexanes, and the compound could not be successfully recrystallized. We now discuss the characterization of **7** and **8** in turn.

The ^1H and ^{13}C NMR spectra of **7** are consistent with the presence of a molecular mirror plane in solution. For example, the ^1H NMR spectrum features two $SiMe_3$ environments (each integrating as 18H) and one pair of mutually coupled doublets (total integral 4H) for the CH_2 groups of N_2N_{py}. Resonances for the apical Me of

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(42) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341.

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N_2N_{py} and for the pyridyl and phenyl groups can also be assigned. The κ^3-coordination mode (i.e., with the pyridyl nitrogen bound to Nb) is established by the shift of the pyridyl H^6 (*ortho* to N) resonance which appears at 8.70 ppm. In the "free" (protonated) ligand $H_2N_2N_{py}$ in the same solvent, this resonance appears at 8.47 ppm.[18] To verify these assignments, NOE difference spectra were recorded. Irradiation at the benamidinate phenyl *ortho*-protons showed an NOE enhancement of both the *tert*-butyl signal and the higher field $SiMe_3$ resonance (confirming this as corresponding to the benzamidinate group) and also of the N_2N_{py} pyridyl H^6 proton. This final observation could only be made in the case of a coordinated pyridyl group. The orientation of the benamidinate ligand as being mutually *cis* to N^tBu and the pyridyl moiety (i.e., in the equatorial plane as shown in Scheme 1) is confirmed by the NOE experiments and rules out an alternative isomer with $PhC(NSiMe_3)_2$ *trans* to pyridyl and N^tBu in the equatorial plane of a pseudo-trigonal bipyramidal structure. Examples of amidinate-supported imido complexes of the heavier group 5 metals have been reported previously.[48-51]

In contrast to the situation found for **7**, the NMR spectra for $[Nb(N^tBu)\{N(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$, **8**, are consistent with the presence of a κ^2-bound N_2N_{py} ligand. The ^1H and ^{13}C NMR spectra of **8** in C_6D_6 show the expected resonances for all of the groups present and are consistent with C_s symmetry in solution. Interestingly the H^6 signal appears at 8.47 ppm and clearly implies that the N_2N_{py} pyridyl group is now pendant. This shift can be compared with the corresponding values (in C_6D_6) for the κ^2-coordinated N_2N_{py} ligand in the complexes $[Ti\{N(^tBu)PC(^tBu)\}(\kappa^2\text{-}N_2N_{py})]$ ($\delta = 8.50$) and $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)N^tBu\}_2(\kappa^2\text{-}N_2N_{py})_2]$ ($\delta = 8.50$).[29] No NOE enhancement of any other resonance (other than those of N_2N_{py} itself) was found on irradiation at the H^6 proton, consistent with a noncoordinated pyridyl group. The proposed κ^2-bound structure is related to those of some of the organometallic derivatives of **1**, which are presented in the next section. Compound **8** can be viewed as a tris(amido)−imido−niobium complex; compounds of the type $[M(NR)(NR'_2)_3]$ have been reported and structurally characterized previously.[3,52]

Bis(trimethylsilyl)methyl, Trimethylsilylmethyl, Benzyl, and Cyclopenadienyl Derivatives. Group 5 metal alkyl complexes incorporating imido coligands are well established.[3,53-57] Several nonimido group 5 alkyl complexes incorporating diamido ligands have also been prepared,[20] but none have yet been described incorporating both an imido ligand and a diamido ligand. The syntheses and proposed structures of the new organometallic compounds derived from **1** and **2** are summarized in Scheme 2.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Nb(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2Npy)]$ (9)[a]

	distances	
Nb(1)−N(1)	1.772(3)	[1.768(3)]
Nb(1)−N(2)	2.003(3)	[2.006(3)]
Nb(1)−N(3)	1.986(3)	[1.978(3)]
Nb(1)−C(20)	2.210(3)	[2.219(3)]
N(1)−C(1)	1.458(4)	[1.467(4)]
	angles	
Nb(1)−N(1)−C(1)	176.4(3)	[177.9(2)]
N(1)−Nb(1)−N(2)	111.6(1)	[112.9(1)]
N(1)−Nb(1)−N(3)	110.3(1)	[110.7(1)]
N(1)−Nb(1)−C(20)	112.6(1)	[111.2(1)]
N(2)−Nb(1)−N(3)	99.6(1)	[100.6(1)]
N(2)−Nb(1)−C(20)	112.9(1)	[112.5(1)]
N(3)−Nb(1)−C(20)	109.0(1)	[108.3(1)]

[a] The corresponding values for the other crystallographically independent molecule in the asymmetric unit are given in brackets.

The compounds $[M(N^tBu)\{CH(R)SiMe_3\}(\kappa^n\text{-}N_2N_{py})]$ ($R = SiMe_3$, M = Nb **9** or Ta **10**; R = H, M = Nb **11** or Ta **12a**,**b**; n = 2 or 3) were prepared from solid **1** or **2** and $LiCH(R)SiMe_3$ followed by addition of cold benzene and stirring for 5−20 h at room temperature or 50 °C (for **12a**,**b**). Subsequent workups gave $[M(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ in 59% (M = Nb, **9**) or 48% (M = Ta, **10**) yields as white solids. The less sterically demanding alkyl group CH_2SiMe_3 gave the corresponding products **11** and **12a**,**b** as viscous red oils in 70 and 85% yield, respectively. These could not be crystallized. Colorless crystals of $[Nb(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ (**9**) suitable for X-ray diffraction were obtained from a saturated hexane solution after 2 weeks at 5 °C. The crystals of **9** contain two independent molecules in the asymmetric unit. Selected bond lengths and angles are listed in Table 3, and a view of one of the molecules is given in Figure 4. Since the bond distances and angles for the two molecules are effectively identical, discussion will focus on only that shown in Figure 4.

Compound **9** contains a monomeric niobium(V) center coordinated by one carbon and three nitrogen atoms in a pseudo-tetrahedral manner. The N_2N_{py} ligand is coordinated in a bidentate fashion, with the pyridyl group acting as a pendant arm. The structure is analogous to that proposed on the basis of NMR data for $[Nb(N^tBu)\{N(SiMe_3)_2\}(\kappa^2\text{-}N_2N_{py})]$ (**8**) above. The κ^2 coordination mode is presumably the result of steric crowding at the metal center and the good donor abilities of the alkyl, amido, and imido ligands. The six-membered chelate ring {(Nb(1),N(2),C(11),C(10),C(12),N(3)} adopts a stable chair-type conformation, which places the pyridyl group as far as possible away from the metal. Even with full lone pair donation from all of the remaining nitrogen donor atoms, compound **9** can achieve a valence electron count of only 16 at niobium.

The $Nb-N_{(imide)}-C$ angle of 176.4(3)° in **9** shows that the imido group is effectively linear, and the $Nb{=}N_{(imide)}$ bond length of 1.772(3) Å is well within known ranges.[1,3,60] The Nb−C distance of 2.210(3) Å is also typical for such linkages.[60] Bond distances and

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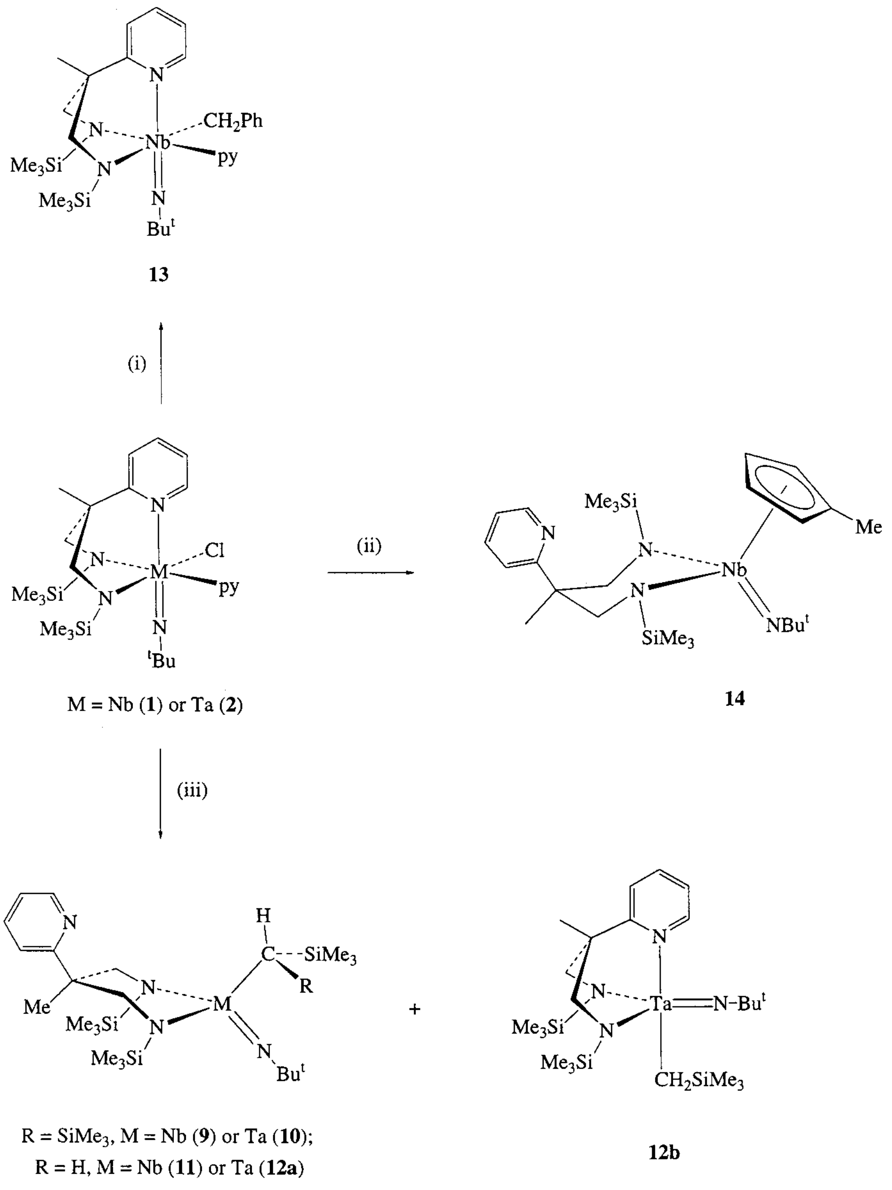
Scheme 2. Alkyl, Benzyl, and Cyclopentadienyl Complexes with Imido–Diamido–Pyridine Ligand Sets[a]



[a] (i) $PhCH_2MgCl$ (1.0 M solution in diethyl ether), benzene, rt, 17 h, 38%; (ii) LiC_5H_4Me, benzene, 7 °C then 60 °C, 72 h, 65%; (iii) $LiCHR(SiMe_3)$ (R = H or $SiMe_3$), benzene, 7 °C then rt, 5–20 h, 48–85%.

angles about the niobium center and the attached carbon atom C(20) give no direct indication of any α-agostic interactions, the Nb–C(20)–Si(3), Nb–C(20)–Si(4), and Si(3)–C(20)–Si(4) bond angles (115.7(2)°, 117.5(2)°, and 114.0(2)°, respectively) all being slightly greater than the ideal tetrahedral angle of ca. 109.5° presumably due to the bulk of the trimethylsilyl substituents, and showing no unexpected distortions. The hydrogen atom attached to C(20) could not be located and was placed in a calculated position based on the geometry at C(20). The placed H atom lies ca. 2.75 Å (2.79 Å in the second molecule) from Nb(1), a distance significantly greater than that observed in authentic α-agostic imido niobium systems (e.g., Nb···H = 2.321(29) and 2.405(33) Å in $[Nb(NAr)(\eta^5\text{-}C_5H_5)(CH_2{}^tBu)_2]$).[61] The possibility of α-agostic interactions has been further examined for the tantalum analogue $[Ta(N^tBu)\{CH(SiMe_3)_2\}(N_2N_{py})]$ (**10**) by spectroscopic means (see below).

Compounds **9**–**12** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by IR spectroscopy and elemental analysis. The spectra support the C_s-symmetric structures shown in Scheme 2. The NMR data for **9** in solution are consistent with the solid-state structure; in particular the H^6 proton resonance appears at 8.45 ppm, consistent with a noncoordinated pyridyl group. A singlet at 0.61 ppm of relative intensity 1H corresponds to the $C\mathit{H}(SiMe_3)_2$ methine proton. The Nb-bound carbon atom of $\mathit{C}H(SiMe_3)_2$ was not directly observed, presumably due to strong coupling to the

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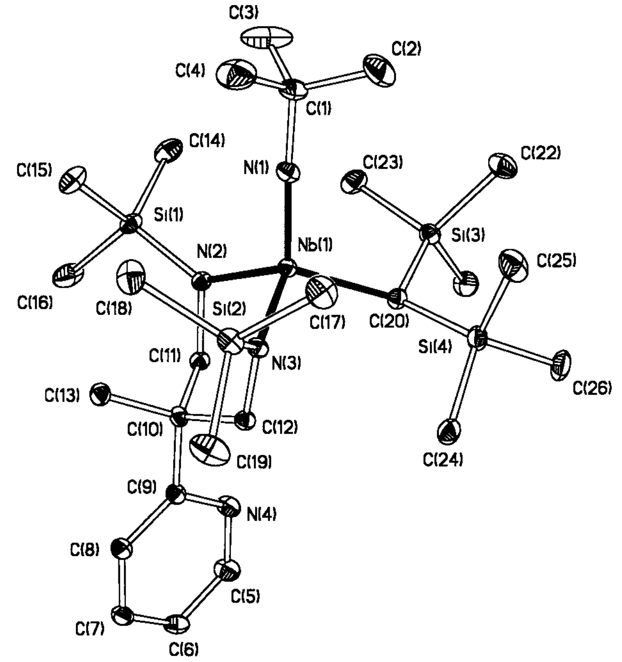

Figure 4. Displacement ellipsoid plot (20% probablility) of one of the two crystallographically independent molecules of [Nb(N^{t}Bu){CH(SiMe$_3$)$_2$}(κ^2-N$_2$N$_{py}$)] (**9**) with hydrogen atoms omitted.

quadrupolar metal nucleus (^{93}Nb, 100% abundance, $I = 9/2$), but was indirectly located at 56.7 ppm from an HMQC ^{13}C$-$^{1}H correlation spectrum. The spectra of the tanalum analogue **10** are very similar to those of **9**, the main difference being that the carbon atom of *C*H-(SiMe$_3$)$_2$ was now directly observable in the ^{13}C NMR spectra at 63.2 ppm (the corresponding C*H*(SiMe$_3$)$_2$ methine proton appears at 1.76 ppm).

To exclude the possibility of an α-agostic interaction in **9** and **10** (and to support conclusions based on the X-ray structure of **9**), we wished to measure $^1J_{(CH)}$ for the metal-bound *C*H(SiMe$_3$)$_2$ carbon.[62] This was not possible for **9** even at low temperature (where “thermal decoupling” due to shorter T_1 nuclear relaxation times might assist), and so measurements focused on the tantalum system **10**. Measurement of the gated-decoupled ^{13}C NMR spectrum of **10** yielded a $^1J_{(CH)}$ value of 94 Hz for the *C*H(SiMe$_3$)$_2$ methine carbon. This value is lower than might be expected for a typical sp^3-hybridized carbon atom ($^1J_{(CH)} \approx 120-130$ Hz), although is higher than the values normally expected for carbons bearing α-agostic hydrogens ($^1J_{(CH)} \approx 60-90$ Hz).[62] Thus although the $^1J_{(CH)}$ value for **10** may indicate an α-agostic interaction, it is equally possible that it is caused by the presence of the two large, electropositive trimethylsilyl substituents on the carbon atom. The titanium imido complexes [Ti(NR){CH(SiMe$_3$)$_2$}{PhC-(NSiMe$_3$)$_2$}(py)] (R = ^{t}Bu, 2,6-C$_6$H$_3$Me$_2$) feature $^1J_{(CH)}$ values of 93 and 91 Hz for the bis(trimethylsilyl)methyl methine carbon atoms.[63] These 14 valence electron complexes were shown by X-ray crystallography not to possess α-agostic interactions, and the low $^1J_{(CH)}$ values were therefore deemed to be a characteristic of the bis(trimethylsilyl)methyl ligand rather than of agostic interactions. Furthermore, in a study of tantalum alkylidene complexes supported by facially coordinating tridentate N-donor ligands, Boncella and co-workers noted that α-agostic interactions tend to compete with π-donation.[64] With three π-donor ligands present in **9** and **10**, it seems unlikely that an α-agostic interaction will be observed. If such an interaction were to take place, then the crystal structure of **9** suggests that the α-agostic hydrogen would bond *trans* to the imido group and would thus find itself competing for metal d orbitals with the strongly *trans*-labilizing imido ligand, again making an α-agostic interaction seem unlikely. The IR spectra of both **9** and **10** also give no indications of agostic interactions, with no absorptions visible in the range 2250$-$2800 cm^{-1}, which could be attributable to ν(C$-$H$\cdots$M) bands.[62]

The NMR spectra of [Nb(N^{t}Bu){CH$_2$SiMe$_3$}(κ^2-N$_2$N$_{py}$)] (**11**) are analogous to those of **9**. The ^{1}H spectrum suggests molecular C_s symmetry. The pyridyl H^6 resonance at 8.52 ppm is indicative of a noncoordinated pyridyl group. The C*H*$_2$SiMe$_3$ methylene H atoms appear as a singlet at 0.79 ppm, and the corresponding ^{13}C resonance was at 62.8 ppm. However, the ^{1}H NMR spectrum of [Ta(N^{t}Bu)(CH$_2$SiMe$_3$)($\kappa^{2,3}$-N$_2$N$_{py}$)] (**12a**,**b**) is more complicated than those of **9**$-$**11**. Thus, in addition to resonances corresponding to the four-coordinate tantalum species **12a** (with H^6 appearing at 8.50 ppm) a second product (**12b**) is also present in an approximately 1(**12b**):2(**12a**) ratio by integration. The κ^3-coordinated N$_2$N$_{py}$ ligand in **12b** is characterized by an H^6 resonance at 9.02 ppm, indicative of a coordinated pyridyl group. Other resonances in the ^{1}H NMR spectrum are broadly similar to those discussed above; the ^{13}C{^{1}H} NMR spectrum shows two distinct sets of resonances attributed to the κ^2- and κ^3-isomers **12a** and **12b**, respectively. Since the atomic radii of Nb and Ta are effectively identical,[65a] the apparent tendency to increase coordination number from M = Nb (for **11**) to Ta (for **12b**) is consistent with the well-known increase in metal$-$ligand bond strengths down a transition metal triad.[65b]

We were interested to probe for α-agostic interactions in the four- and five-coordinate complexes, and again it was necessary to focus on the tantalum systems **12a**,**b**. Measurement of the gated decoupled ^{13}C NMR spectrum of [Ta(N^{t}Bu)(CH$_2$SiMe$_3$)(N$_2$N$_{py}$)] (**12**) produced averaged $^1J_{(CH)}$ coupling constants for the metal-bound methylene group of 117 Hz for **12b** and 104 Hz for **12a**. The value of $^1J_{(CH)} = 104$ Hz for **12a** is somewhat less than the typical $^1J_{(CH)}$ value for an sp^3-hybridized carbon atom (120$-$130 Hz). As before, this may simply reflect the steric bulk of the trimethylsilyl group (note that the alkyl ligand in **12a**,**b** is less bulky than that in [Ta-(N^{t}Bu){CH(SiMe$_3$)$_2$}(N$_2$N$_{py}$)] (**10**), for which $^1J_{(CH)} = 94$ Hz). The value of $^1J_{(CH)} = 117$ Hz for five-coordinate **12b** is nearer to the commonly encountered $^1J_{(CH)}$ range for nonagostic sp^3 carbon atoms of 120$-$130 Hz, so is less likely to suggest any α-agostic interactions. Similar values and trends for $^1J_{(CH)}$ were reported recently for

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(62) For a review see: Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(63) Stewart, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271.

(64) Boncella, J. M.; Cajigal, M. L.; Abboud, K. A. *Organometallics* **1996**, *15*, 1905.

(65) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1994; p 1141. (b) Mingos, D. M. P. *Essential Trends in Inorganic Chemistry*; Oxford University Press: Oxford, 1998.

two crystallographically characterized titanium imido derivatives with CH_2SiMe_3 ligands.[63,66] It was demonstrated in these cases that a $^1J_{(CH)}$ value of 104 Hz for the methylene carbon atom of a CH_2SiMe_3 ligand did *not* necessarily indicate the presence of α-agostic interactions. The IR spectra of $[Nb(N^tBu)(CH_2SiMe_3)(N_2N_{py})]$ (**11**) and $[Ta(N^tBu)(CH_2SiMe_3)(N_2N_{py})]$ (**12**) do not provide any evidence of agostic interactions, since no ν(C−H···M) absorption bands were visible in the 2250−2800 cm^{-1} range.

Attempts to prepare methyl analogues of **9**−**13** from **1** or **2** and methyllithium or methyl Grignard reagents were unsuccessful. The benzyl derivative $[Nb(N^tBu)(CH_2Ph)(\kappa^3\text{-}N_2N_{py})(py)]$ (**13**, Scheme 2) was prepared from a cooled solution of $[Nb(N^tBu)Cl(N_2N_{py})(py)]$ (**1**) in benzene and 1 equiv of $PhCH_2MgCl$ as solution in diethyl ether. Standard workup gave **13** as an orange powder in 38% yield. The compound **13** was fairly unstable in solution, and attempts to obtain analytically pure samples by recrystallization were unsuccessful. It was therefore characterized by IR and NMR spectroscopy only. The compound is notable in being the first example of a derivative of $[Nb(N^tBu)Cl(N_2N_{py})(py)]$ (**1**) to retain the pyridine ligand after chloride substitution.

In the ^1H NMR spectrum of **13** the N_2N_{py} trimethylsilyl resonances appear as two separate singlets at −0.14 and 0.08 ppm, consistent with a six-coordinate complex in which there is no plane of symmetry and no fast exchange of pyridine and benzyl ligand coordination sites on the NMR time scale. The H^6 atom appears at 8.81 ppm, consistent with a coordinated pyridyl group. Resonances corresponding to a coordinated pyridine ligand are also visible, but all of these signals are broad. This broadening may possibly be related to fluxionality involving dissociation/association of the ligand similar to that observed in the parent complex $[Nb(N^tBu)Cl(N_2N_{py})(py)]$ (**1**).[25] Unusually, the benzyl group CH_2 resonances were observed in neither the ^1H nor ^{13}C spectra.

Treatment of an equimolar mixture of solid $[Nb(N^tBu)Cl(\kappa^3\text{-}N_2N_{py})(py)]$ (**1**) and solid LiC_5H_4Me with cooled benzene provided a yellow solution, which was heated to 60 °C and stirred for 72 h, yielding $[Nb(N^tBu)(\eta^5\text{-}C_5H_4Me)(\kappa^2\text{-}N_2N_{py})]$ (**14**) as an orange solid in 65% yield. An analogous reaction between $[Nb(N^tBu)Cl(N_2N_{py})(py)]$ (**1**) and LiC_5Me_5 yielded only complex mixtures presumably because of the bulkier nature of C_5Me_5.

The ^1H NMR spectrum of $[Nb(N^tBu)(\eta^5\text{-}C_5H_4Me)(N_2N_{py})]$ (**14**) features characteristic N_2N_{py} ligand signals, with the pyridyl H^6 resonance appearing at 8.57 ppm, indicative of an uncoordinated pyridyl group. Signals for the cyclopentadienyl ring protons are at 5.86 and 6.22 ppm, and the ring methyl group is a singlet at 1.89 ppm. The C_6D_6 $^{13}C\{^1H\}$ NMR spectrum of **14** is entirely as expected for the proposed structure.

The proposed structure of $[Nb(N^tBu)(\eta^5\text{-}C_5H_4Me)(N_2N_{py})]$ (**14**) is analogous to those of $[Nb(NAr)(\eta^5\text{-}C_5H_4Me)(NMe_2)_2]$[67] and the complexes $[Nb(NR)(\eta^5\text{-}C_5H_5)(NHR)_2]$ ($R = {}^tBu$, 2,6-$C_6H_3Me_2$).[68] All of these compounds possess an imido−cyclopentadienyl−bis(amido) coordination sphere similar to that of **14**, which has an 18 valence electron count.

Conclusions

We have reported a range of new organometallic and coordination complexes supported by an imido−diamido−pyridine ligand set. The flexible nature of the diamido−pyridine ligand is revealed by the crystal structure of the κ^2-bound compound **9** and the formation of the compounds **8**, **10**, **11**, **12a**,**b**, and **14**.

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Supporting Information Available: X-ray crystallographic files in CIF and PDF format for the structure determinations of **4**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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