

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

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Received April 17, 2001

A family of new organometallic and coordination group 5 compounds supported by an imido–diamido–pyridine ligand set are reported. Reaction of $[M(NR)Cl(\kappa^3-N_2N_{py})(py)]$ ($M = Nb$, $R = {}^tBu$ **1**; $M = Ta$, $R = {}^tBu$ **2** or Ar **3**, where $N_2N_{py} = MeC(2-C_5H_4N)(CH_2NSiMe_3)_2$ and $Ar = 2,6-C_6H_3Pr_2$) with $LiOAr$ or $LiPhC(NSiMe_3)_2$ afforded the five-coordinate aryloxo and benzamidinate complexes $[M(NR)(OAr)(\kappa^3-N_2N_{py})]$ ($R = {}^tBu$, $M = Nb$ **4** or Ta **5**; $R = Ar$, $M = Ta$ **6**) and $[Nb(N^tBu)\{PhC(NSiMe_3)_2\}(\kappa^3-N_2N_{py})]$ (**7**), respectively. Reaction of **1** or **2** with $LiN(SiMe_3)_2$ or $LiCH(SiMe_3)_2$ gave the four-coordinate compounds $[M(N^tBu)(X)(\kappa^2-N_2N_{py})]$ ($M = Nb$, $X = N(SiMe_3)_2$ **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 $[M(N^tBu)(CH_2SiMe_3)(\kappa^2-N_2N_{py})]$ (**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 $[Nb(N^tBu)(CH_2Ph)(\kappa^3-N_2N_{py})(py)]$ (**13**) and $[Nb(N^tBu)(\eta^5-C_5H_4Me)(\kappa^2-N_2N_{py})]$ (**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 approach⁸ to developing early transition metal imido chemistry has been to use the diamido–pyridine ligand $MeC(2-C_5H_4N)(CH_2NSiMe_3)_2$ (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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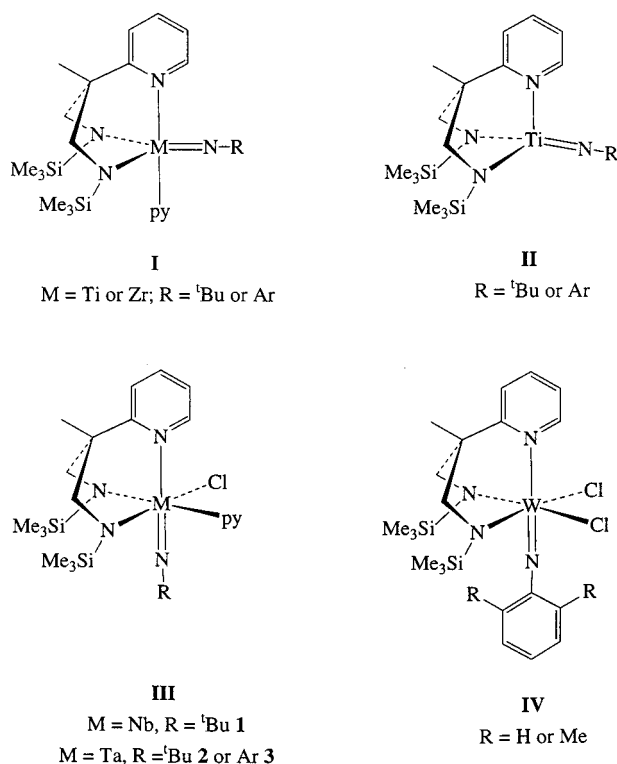
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Chart 1



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≡P, RCH=C=CH₂, and ArNCO (hereafter Ar = 2,6-C₆H₃iPr₂).^{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)(N₂Npy)} 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(κ³-N₂Npy)(py)] (M = Nb, R = ^tBu **1**; M = Ta, R = ^tBu **2** or Ar **3**).²⁵

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox

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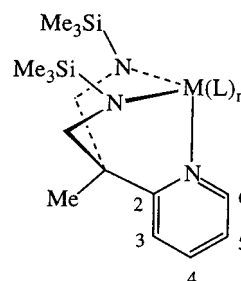
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techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H}, and ¹³C NMR spectra were recorded on Bruker AM 300 and DPX 300 and Varian Unity Plus 500 spectrometers. ¹H and ¹³C assignments were confirmed when necessary with the use of NOE, DEPT-135, DEPT-90, and two-dimensional ¹H–¹H and ¹³C–¹H NMR experiments. All spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane (δ = 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 N₂Npy:



Literature Preparations. H₂N₂Npy,¹⁸ Li₂[N₂Npy],¹⁹ [Nb(N^tBu)Cl(κ³-N₂Npy)(py)] (**1**),²⁵ [Ta(N^tBu)Cl(κ³-N₂Npy)(py)] (**2**),²⁵ and [Ta(NAr)Cl(κ³-N₂Npy)(py)] (**3**)²⁵ were prepared according to methods we have described previously.

[Nb(N^tBu)(OAr)(κ³-N₂Npy)] (4**).** To a mixture of solid [Nb(N^tBu)Cl(κ³-N₂Npy)(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)(κ³-N₂Npy)] (**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 (C₆D₆, 500.0 MHz, 298 K): 8.95 (1 H, d, ³J(H⁶H⁵) = 5.0 Hz, H⁶), 7.26 (2 H, d, ³J = 7.5 Hz, *m*-C₆H₃iPr₂), 7.02 (1 H, t, ³J = 7.5 Hz, *p*-C₆H₃iPr₂), 6.99 (1 H, overlapping m, H⁴), 6.84 (1 H, d, ³J(H³H⁴) = 8.0 Hz, H³), 6.48 (1 H, apparent t, apparent *J* = 5.5 Hz, H⁵), 3.85 (2 H, d, ²J = 13.5 Hz, CH₂), 3.60 (2 H, septet, ³J = 7.0 Hz, CHMe₂), 3.49 (2 H, d, ²J = 13.5 Hz, CH₂), 1.35 (12 H, d, ³J = 6.5 Hz, CHMe₂), 1.35 (9 H, s, ^tBu), 1.08 (3 H, s, Me of N₂Npy), 0.39 (18 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 298 K): 164.6 (C²), 160.5 (*ipso*-Ar), 148.4 (C⁶), 138.0 (C⁴), 135.9 (*o*-Ar), 123.4 (*m*-Ar), 121.3 (C³), 119.5 (*p*-Ar), 119.0 (C³), 61.6 (CH₂NSiMe₃), 49.9 (C(CH₂NSiMe₃)₂), 33.4 (NCMe₃), 27.3 (CHMe₂), 23.9 (CHMe₂), 22.2 (Me of N₂Npy), 2.4 (SiMe₃) (the signal for NCMe₃ 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 C₃₁H₅₅N₄NbOSi₂): C 57.9 (57.4), H 8.7 (8.5), N 8.2 (8.6).

[Ta(N^tBu)(OAr)(κ³-N₂Npy)] (5**).** To a mixture of solid [Ta(N^tBu)Cl(κ³-N₂Npy)(py)] (190 mg, 0.28 mmol) and solid LiOAr

(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^tBu)(OAr)(κ³-N₂N_{py})] (**5**) as a cream-colored solid. Yield: 120 mg (58%). ¹H NMR (C₆D₆, 500.0 MHz, 298 K): 9.03 (1 H, d, ³J (H⁶H⁵) = 4.5 Hz, H⁶), 7.27 (2 H, d, ³J = 7.5 Hz, *m*-C₆H₃ⁱPr₂), 7.02 (1 H, t, ³J = 7.5 Hz, *p*-C₆H₃ⁱPr₂), 6.99 (1 H, dd, ³J (H⁴H⁵) = 8.0 Hz, ³J (H⁴H³) = 8.0 Hz, H⁴), 6.79 (1 H, d, ³J (H³H⁴) = 8.0 Hz, H³), 6.48 (1 H, apparent t, apparent *J* = 5.5 Hz, H⁵), 3.85 (2 H, d, ²J = 13.0 Hz, CH₂), 3.64 (2 H, septet, ³J = 7.0 Hz, CHMe₂), 3.58 (2 H, d, ²J = 13.0 Hz, CH₂), 1.36 (9 H, s, ^tBu), 1.35 (12 H, d, ³J = 7.0 Hz, CHMe₂), 1.03 (3 H, s, Me of N₂N_{py}), 0.40 (18 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 298 K): 164.6 (C²), 160.6 (*ipso*-Ar), 148.1 (C⁶), 138.4 (C⁴), 136.2 (*o*-Ar), 123.4 (*m*-Ar), 121.5 (C⁵), 120.0 (*p*-Ar), 119.0 (C³), 65.7 (NCMe₃), 61.4 (CH₂NSiMe₃), 49.2 (C(CH₂NSiMe₃)₂), 34.8 (NCMe₃), 27.1 (CHMe₂), 24.0 (CHMe₂), 22.3 (Me of N₂N_{py}), 2.5 (SiMe₃). 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 C₃₁H₅₅N₄O_{Si}₂-Ta): C 50.7 (50.5), H 7.2 (7.5), N 6.8 (7.6).

[Ta(NAr)(OAr)(κ³-N₂N_{py})] (**6**). To a mixture of solid [Ta(NAr)Cl(κ³-N₂N_{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)(κ³-N₂N_{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. ¹H NMR (CD₂Cl₂, 500.0 MHz, 298 K): 8.82 (1 H, d, ³J (H⁶H⁵) = 5.0 Hz, H⁶), 7.90 (1 H, dd, ³J (H⁴H⁵) = 8.0 Hz, ³J (H⁴H³) = 8.0 Hz, H⁴), 7.54 (1 H, d, ³J (H³H⁴) = 8.0 Hz, H³), 7.22 (1 H, apparent t, apparent *J* = 6.0 Hz, H⁵), 7.14 (2 H, d, ³J = 7.5 Hz, *m*-O-C₆H₃ⁱPr₂), 6.95 (2 H, d, ³J = 7.5 Hz, *m*-N-C₆H₃ⁱPr₂), 6.89 (1 H, t, ³J = 7.5 Hz, *p*-O-C₆H₃ⁱPr₂), 6.67 (1 H, t, ³J = 7.5 Hz, *p*-N-C₆H₃ⁱPr₂), 3.89 (2 H, d, ²J = 12.5 Hz, CH₂), 3.85 (2 H, br overlapping s, CHMe₂ of N-C₆H₃ⁱPr₂), 3.82 (2 H, d, ²J = 12.5 Hz, CH₂), 3.36 (2 H, septet, ³J = 7.0 Hz, CHMe₂ of O-C₆H₃ⁱPr₂), 1.57 (3 H, s, Me of N₂N_{py}), 1.35 (12 H, d, ³J = 6.0 Hz, CHMe₂ of O-C₆H₃ⁱPr₂), 0.98 (12 H, br s, CHMe₂ of N-C₆H₃ⁱPr₂), 0.80 (18 H, s, SiMe₃). ¹H NMR (CD₂Cl₂, 500.0 MHz, 218 K): 8.03 (1 H, d, ³J (H⁶H⁵) = 4.0 Hz, H⁶), 7.91 (1 H, dd, ³J (H⁴H⁵) = 8.0 Hz, ³J (H⁴H³) = 8.0 Hz, H⁴), 7.53 (1 H, d, ³J (H³H⁴) = 8.0 Hz, H³), 7.23 (1 H, apparent t, apparent *J* = 6.0 Hz, H⁵), 7.11 (2 H, d, ³J = 7.5 Hz, *m*-O-C₆H₃ⁱPr₂), 6.98 (1 H, d, ³J = 6.5 Hz, *m*-N-C₆H₃ⁱPr₂), 6.85 (1 H, overlapping t, ³J = 7.5 Hz, *p*-O-C₆H₃ⁱPr₂), 6.84 (1 H, overlapping d, *m*-N-C₆H₃ⁱPr₂), 6.63 (1 H, t, ³J = 7.5 Hz, *p*-N-C₆H₃ⁱPr₂), 4.23 (1 H, br s, CHMe₂ of N-C₆H₃ⁱPr₂), 3.83 (2 H, d, ²J = 12.5 Hz, CH₂), 3.73 (2 H, d, ²J = 12.5 Hz, CH₂), 3.38 (1 H, br s, CHMe₂ of N-C₆H₃ⁱPr₂), 3.30 (2 H, septet, ³J = 7.0 Hz, CHMe₂ of O-C₆H₃ⁱPr₂), 1.54 (3 H, s, Me of N₂N_{py}), 1.26 (6 H, d, ³J = 6.5 Hz, CHMe₂ of N-C₆H₃ⁱPr₂), 1.21 (6 H, d, ³J = 6.5 Hz, CHMe₂ of O-C₆H₃ⁱPr₂), 0.97 (6 H, d, ³J = 6.5 Hz, CHMe₂ of O-C₆H₃ⁱPr₂), 0.53 (6 H, d, ³J = 6.5 Hz, CHMe₂ of N-C₆H₃ⁱPr₂), -0.04 (18 H, s, SiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz, 218 K): 163.9 (C²), 159.0 (*ipso*-OAr), 153.0 (*ipso*-NAr), 147.5 (C⁶), 139.8 (C⁴), 136.3 (*o*-NAr), 128.8 (*o*-OAr), 123.5 (*m*-OAr), 122.4 (C⁵), 121.8 (*m*-NAr), 120.4 (*p*-NAr), 119.5, 119.4 (*p*-OAr & C³), 62.6 (CH₂NSiMe₃), 49.6 (C(CH₂NSiMe₃)₂), 27.4 (CHMe₂ of NAr), 27.0 (CHMe₂ of OAr), 26.0 (CHMe₂ of OAr), 24.8 (CHMe₂ of NAr), 24.4 (CHMe₂ of NAr), 23.4 (Me of N₂N_{py}), 22.3 (CHMe₂ of OAr), 0.7 (SiMe₃). 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 C₃₉H₆₃N₄O_{Si}₂Ta): C 55.3 (55.7), H 7.2 (7.6), N 6.5 (6.7).

[Nb(N^tBu){PhC(NSiMe₃)₂}(κ³-N₂N_{py})] (**7**). To a mixture of solid [Nb(N^tBu)Cl(κ³-N₂N_{py})(py)] (263 mg, 0.44 mmol) and solid LiPhC(NSiMe₃)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^tBu){PhC(NSiMe₃)₂}(κ³-N₂N_{py})] (**7**) as a pale orange powder. Yield: 204 mg (62%). ¹H NMR (C₆D₆, 500.0 MHz, 298 K): 8.70 (1 H, m, H⁶), 7.42 (2 H, d, ³J = 6.5 Hz, *o*-C₆H₅), 7.06 (1 H, overlapping m, *m*-C₆H₅), 7.06 (1 H, overlapping m, *p*-C₆H₅), 7.06 (1 H, overlapping m, H⁴), 7.03 (1 H, overlapping d, H³), 6.62 (1 H, apparent t, apparent *J* = 5.5 Hz, H⁵), 4.13 (2 H, d, ²J = 15.0 Hz, CH₂), 3.51 (2 H, d, ²J = 15.0 Hz, CH₂), 1.64 (9 H, s, ^tBu), 1.25 (3 H, s, Me of N₂N_{py}), 0.50 (18 H, s, CH₂NSiMe₃), -0.06 (18 H, s, C(NSiMe₃)₂). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 298 K): 182.8 (C(NSiMe₃)₂), 168.2 (C²), 148.8 (C⁶), 142.6 (*ipso*-C₆H₅), 136.8 (C⁴), 128.6, 128.1 (*m*-C₆H₅ and *p*-C₆H₅), 127.0 (*o*-C₆H₅), 120.4 (C⁵), 120.0 (C³), 67.7 (NCMe₃), 59.7 (CH₂NSiMe₃), 44.5 (C(CH₂NSiMe₃)₂), 33.3 (NCMe₃), 22.9 (Me of N₂N_{py}), 3.8, 3.1 (CH₂NSiMe₃ and C(NSiMe₃)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 C₃₂H₆₁N₆-NbSi₄): C 52.1 (52.3), H 8.1 (8.4), N 11.3 (11.4).

[Nb(N^tBu){N(SiMe₃)₂}(κ²-N₂N_{py})] (**8**). To a mixture of solid [Nb(N^tBu)Cl(κ³-N₂N_{py})(py)] (225 mg, 0.38 mmol) and solid LiN(SiMe₃)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^tBu){N(SiMe₃)₂}(κ²-N₂N_{py})] (**8**) was obtained as an orange solid. Yield: 145 mg (61%). Compound **8** was spectroscopically >90% pure, but trace impurities could not be removed by washing with hexanes, and the compound could not be successfully recrystallized. ¹H NMR (C₆D₆, 500.0 MHz, 298 K): 8.47 (1 H, d, ³J (H⁶H⁵) = 4.0 Hz, H⁶), 7.08 (1 H, overlapping m, H⁴), 7.08 (1 H, overlapping d, H³), 6.57 (1 H, apparent t, apparent *J* = 5.5 Hz, H⁵), 4.64 (2 H, d, ²J = 15.5 Hz, CH₂), 3.62 (2 H, d, ²J = 15.5 Hz, CH₂), 1.55 (9 H, s, ^tBu), 1.14 (3 H, s, Me of N₂N_{py}), 0.41 (18 H, s, N(SiMe₃)₂), 0.36 (18 H, s, CH₂-NSiMe₃). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 298 K): 166.1 (C²), 149.4 (C⁶), 136.0 (C⁴), 121.1 (C⁵), 120.3 (C³), 56.7 (CH₂NSiMe₃), 45.7 (C(CH₂NSiMe₃)₂), 33.6 (NCMe₃), 19.6 (Me of N₂N_{py}), 6.2 (N(SiMe₃)₂), 3.5 (CH₂NSiMe₃ (signal for NCMe₃ 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 C₂₅H₅₆N₅NbSi₄): C 45.9 (47.5), H 8.5 (8.9), N 10.3 (11.1).

[Nb(N^tBu){CH(SiMe₃)₂}(κ²-N₂N_{py})] (**9**). To a mixture of solid [Nb(N^tBu)Cl(κ³-N₂N_{py})(py)] (200 mg, 0.34 mmol) and solid LiCH(SiMe₃)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^tBu){CH(SiMe₃)₂}(κ²-N₂N_{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 $[\text{Nb}(\text{N}^i\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\kappa^2\text{-N}_2\text{Npy})]$ in hexane at 5 °C over 2 weeks. ^1H NMR (C_6D_6 , 300.1 MHz, 298 K): 8.45 (1 H, dt, $^3J(\text{H}^6\text{H}^5) = 4.8$ Hz, $^4J(\text{H}^6\text{H}^4) = 1.3$ 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, Bu), 1.10 (3 H, s, Me of N_2Npy), 0.61 (1 H, s, $\text{CH}(\text{SiMe}_3)_2$), 0.36 (18 H, s, $\text{CH}(\text{SiMe}_3)_2$), 0.33 (18 H, s, NSiMe_3). $^{13}\text{C}\{^1\text{H}\}$ 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 (NCMe_3), 58.1 ($\text{CH}(\text{SiMe}_3)_2$), 56.7 ($\text{CH}_2\text{NSiMe}_3$), 47.3 ($\text{C}(\text{CH}_2\text{NSiMe}_3)_2$), 34.2 (NCMe_3), 19.5 (Me of N_2Npy), 5.1 ($\text{CH}(\text{SiMe}_3)_2$), 3.5 (NSiMe_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 $\text{C}_{26}\text{H}_{57}\text{N}_4\text{NbSi}_4$): C 48.9 (49.5), H 9.2 (9.1), N 8.9 (8.9).

$[\text{Ta}(\text{N}^i\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\kappa^2\text{-N}_2\text{Npy})]$ (10). To a mixture of solid $[\text{Ta}(\text{N}^i\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (218 mg, 0.32 mmol) and solid $\text{LiCH}(\text{SiMe}_3)_2$ (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 $[\text{Ta}(\text{N}^i\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\kappa^2\text{-N}_2\text{Npy})]$ (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, $^3J(\text{H}^6\text{H}^5) = 4.5$ Hz, $^4J(\text{H}^6\text{H}^4) = 1.5$ 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, $\text{CH}(\text{SiMe}_3)_2$), 1.63 (9 H, s, Bu), 1.16 (3 H, s, Me of N_2Npy), 0.37 (18 H, s, $\text{CH}(\text{SiMe}_3)_2$), 0.35 (18 H, s, NSiMe_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 (NCMe_3), 63.2 ($\text{CH}(\text{SiMe}_3)_2$), 56.3 ($\text{CH}_2\text{NSiMe}_3$), 47.1 ($\text{C}(\text{CH}_2\text{NSiMe}_3)_2$), 35.4 (NCMe_3), 19.7 (Me of N_2Npy), 5.3 (d, $^1J_{\text{CH}} = 94$ Hz $\text{CH}(\text{SiMe}_3)_2$), 3.7 (NSiMe_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 $\text{C}_{26}\text{H}_{57}\text{N}_4\text{Si}_4\text{Ta}$): C 42.3 (43.4), H 7.1 (7.8), N 7.7 (8.0).

$[\text{Nb}(\text{N}^i\text{Bu})(\text{CH}_2\text{SiMe}_3)(\kappa^2\text{-N}_2\text{Npy})]$ (11). To a mixture of solid $[\text{Nb}(\text{N}^i\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (270 mg, 0.46 mmol) and solid $\text{LiCH}_2\text{SiMe}_3$ (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 $[\text{Nb}(\text{N}^i\text{Bu})(\text{CH}_2\text{SiMe}_3)(\kappa^2\text{-N}_2\text{Npy})]$ (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, $^3J(\text{H}^6\text{H}^5) = 4.5$ Hz, $^4J(\text{H}^6\text{H}^4) = 1.0$ Hz, H^6), 7.06 (1 H, dd, $^3J(\text{H}^4\text{H}^5) = 7.5$ Hz, $^3J(\text{H}^4\text{H}^3) = 7.5$ Hz, H^4), 7.01 (1 H, d, $^3J(\text{H}^3\text{H}^4) = 7.5$ 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, Bu), 1.09 (3 H, s, Me of N_2Npy), 0.79 (2 H, s, CH_2SiMe_3), 0.29 (9 H, s, CH_2SiMe_3), 0.26 (18 H, s, NSiMe_3). $^{13}\text{C}\{^1\text{H}\}$ 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 (CH_2SiMe_3), 58.1 ($\text{CH}_2\text{NSiMe}_3$), 50.2 ($\text{C}(\text{CH}_2\text{NSiMe}_3)_2$), 33.9 (NCMe_3), 19.3 (Me of N_2Npy), 3.1 (CH_2SiMe_3), 2.7 (NSiMe_3) (the signal for NCMe_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 $\text{C}_{23}\text{H}_{49}\text{N}_4\text{NbSi}_3$): C 49.4 (48.6), H 8.8 (8.2), N 10.0 (10.0).

$[\text{Ta}(\text{N}^i\text{Bu})(\text{CH}_2\text{SiMe}_3)(\kappa^{2,3}\text{-N}_2\text{Npy})]$ (12a,b). To a mixture of solid $[\text{Ta}(\text{N}^i\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (195 mg, 0.29 mmol) and solid $\text{LiCH}_2\text{SiMe}_3$ (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 $[\text{Ta}(\text{N}^i\text{Bu})(\text{CH}_2\text{SiMe}_3)(\kappa^{2,3}\text{-N}_2\text{Npy})]$ (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, $^3J(\text{H}^4\text{H}^5) = 4.5$ Hz, H^6), 8.50 (1 H , d, $^3J(\text{H}^4\text{H}^5) = 4.5$ Hz, H^6), 7.07 (1 H , dd, $^3J(\text{H}^4\text{H}^5) = 8.0$ Hz, $^3J(\text{H}^4\text{H}^3) = 8.0$ Hz, H^4), 7.01 (1 H , overlapping d, H^3), 7.01 (1 H' , overlapping m, H^4), 6.69 (1 H' , d, $^3J(\text{H}^3\text{H}^4) = 8.0$ 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, Bu), 1.62 (9 H , s, Bu), 1.17 (3 H , s, Me of N_2Npy), 0.95 (3 H' , s, Me' of N_2Npy), 0.47 (2 H , s, CH_2SiMe_3), 0.45 (2 H' , s, CH_2SiMe_3), 0.44 (9 H' , s, CH_2SiMe_3), 0.30 (18 H , s, NSiMe_3), 0.30 (9 H , s, CH_2SiMe_3), -0.01 (18 H' , s, NSiMe_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 (NCMe_3), 66.3 (NCMe_3), 62.1 ($\text{CH}_2\text{NSiMe}_3$), 57.4 ($\text{CH}_2\text{NSiMe}_3$), 49.8 (CH_2SiMe_3), 49.7 ($\text{C}(\text{CH}_2\text{NSiMe}_3)_2$), 45.9 ($\text{C}(\text{CH}_2\text{NSiMe}_3)_2$), 42.3 (CH_2SiMe_3), 35.2 (NCMe_3), 34.9 (NCMe_3), 23.5 (Me' of N_2Npy), 19.2 (Me of N_2Npy), 3.6 (t, $^1J_{\text{CH}} = 117$ Hz, CH_2SiMe_3), 3.2 (t, $^1J_{\text{CH}} = 104$ Hz, CH_2SiMe_3), 2.9 (NSiMe_3), 0.9 (NSiMe_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 $\text{C}_{23}\text{H}_{49}\text{N}_4\text{Si}_3\text{Ta}$): C 42.1 (42.7), H 7.4 (7.6), N 8.5 (8.6).

$[\text{Nb}(\text{N}^i\text{Bu})(\text{CH}_2\text{Ph})(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (13). To a cooled (10 °C) solution of $[\text{Nb}(\text{N}^i\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (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 $\text{MgCl}_2 \cdot \text{dioxane}$, and the solution was filtered. The volatiles were removed under reduced pressure, and the orange residues were washed with hexane (3×10 mL). $[\text{Nb}(\text{N}^i\text{Bu})(\text{CH}_2\text{Ph})(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (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, $^3J(\text{H}^6\text{H}^5) = 5.0$ Hz, H^6), 7.87 (2 H, d, $^3J(o\text{-C}_6\text{H}_5\text{m-C}_6\text{H}_5) = 7.5$ Hz, $o\text{-C}_6\text{H}_5$), 7.58 (2 H, br s, $o\text{-NC}_5\text{H}_5$), 7.25 (2 H, t, $^3J = 7.7$ Hz, $m\text{-C}_6\text{H}_5$), 7.04 (1 H, overlapping m, H^4), 6.99 (1 H, overlapping m, H^3), 6.99 (1 H, overlapping m, $p\text{-C}_6\text{H}_5$), 6.70 (1 H, br s, $p\text{-NC}_5\text{H}_5$), 6.51 (1 H, apparent t, apparent $J = 6.5$ Hz, H^5), 6.44 (2 H, br s, $m\text{-NC}_5\text{H}_5$), 3.67 (1 H, d, $^2J = 11.8$ Hz, $\text{Me}_3\text{SiNCH}_2$), 3.18 (1 H, d, $^2J = 11.4$ Hz, $\text{Me}_3\text{SiNCH}_2$), 3.00 (1 H, d, $^2J = 12.5$ Hz, $\text{Me}_3\text{SiNCH}_2$), 2.83 (1 H, d, $^2J = 12.5$ Hz, $\text{Me}_3\text{SiNCH}_2$), 1.43 (3 H, s, Me of N_2Npy), 1.16 (9 H, s, Bu), 0.08 (9 H, s, SiMe_3), -0.14 (9 H, s, SiMe_3) (the signals for PhCH_2 were not observed). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 298 K): 170.5 (C^2), 153.4 ($ipso\text{-C}_6\text{H}_5$), 148.4 (C^6), 147.9 ($o\text{-NC}_5\text{H}_5$), 139.0 (C^4), 137.7 ($p\text{-NC}_5\text{H}_5$), 130.5 ($o\text{-C}_6\text{H}_5$), ca. 128 (obscured by solvent signal, $m\text{-C}_6\text{H}_5$, $p\text{-C}_6\text{H}_5$), 124.0 ($m\text{-NC}_5\text{H}_5$), 121.4 (C^5), 119.5 (C^3), 65.0 (NCMe_3), 60.9 ($\text{CH}_2\text{NSiMe}_3$), 46.9 ($\text{CH}_2\text{NSiMe}_3$), 32.2 (NCMe_3), 26.7 (Me of N_2Npy), 1.9 (SiMe_3), 0.1 (SiMe_3) (signals for $\text{C}(\text{CH}_2\text{NSiMe}_3)_2$ and PhCH_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^tBu)(O-2,6-C₆H₃iPr₂)(N₂N_{py})] (4), [Ta(N-2,6-C₆H₃iPr₂)(O-2,6-C₆H₃iPr₂)(N₂N_{py})] (6), and [Nb(N^tBu){CH(SiMe₃)₂}(N₂N_{py})] (9)

	4	6	9
molecular formula	C ₃₁ H ₅₅ N ₄ NbOSi ₂	C ₃₉ H ₆₃ N ₄ OSi ₂ Ta	C ₂₆ H ₅₇ N ₄ NbSi ₄
fw	648.89	841.08	631.03
temperature/°C	−98	−123	−103
cryst syst	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 1
unit cell dims: <i>a</i> /Å	15.1000(6)	11.5100(3)	11.296(6)
<i>b</i> /Å	13.0490(5)	11.9300(2)	17.556(7)
<i>c</i> /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
<i>Z</i>	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
<i>F</i> (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	ω−2θ scans
decay correction/%	not measured	not measured	9.69
index ranges	0 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 16, −21 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 14, −14 ≤ <i>k</i> ≤ 14, −18 ≤ <i>l</i> ≤ 18	−14 ≤ <i>h</i> ≤ 14, −21 ≤ <i>k</i> ≤ 21, −22 ≤ <i>l</i> ≤ 0
no. of reflns collected	20 879	12 281	14 970
no. of ind reflns	7344	7866	14 493
no. of obsd reflns [<i>I</i> > 3σ(<i>I</i>)]	4637	7025	11 933
<i>R</i> (merge)	0.030	0.035	0.030
abs corr	multiscan	multiscan	ψ-scans
max. and min. transmn	<i>T</i> _{min} = 0.848, <i>T</i> _{max} = 0.884	<i>T</i> _{min} = 0.378, <i>T</i> _{max} = 0.488	<i>T</i> _{min} = 0.71, <i>T</i> _{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	Chebyshev polynomial	Chebyshev polynomial	Chebyshev polynomial
extinction coeff	none required	43(6)	83(8)
final <i>R</i> indices ^a [<i>I</i> > 3σ(<i>I</i>)]	<i>R</i> ₁ = 0.041 <i>R</i> _w = 0.038	<i>R</i> ₁ = 0.0264 <i>R</i> _w = 0.0295	<i>R</i> ₁ = 0.0531 <i>R</i> _w = 0.0615
goodness-of-fit (on <i>F</i>)	1.126	1.0539	0.9920
final (Δ/ <i>o</i>) _{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^tBu)(η⁵-C₅H₄Me)(κ²-N₂N_{py})] (14). To a mixture of solid [Nb(N^tBu)Cl(κ³-N₂N_{py})(py)] (187 mg, 0.32 mmol) and solid LiC₅H₄Me (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^tBu)(η⁵-C₅H₄Me)(κ²-N₂N_{py})] (14) as an orange solid. Yield: 115 mg (65%). ¹H NMR (C₆D₆, 500.0 MHz, 298 K): 8.57 (1 H, d, ³*J* (H⁶H⁵) = 4.0 Hz, H⁶), 7.10 (1 H, overlapping m, H⁴), 7.09 (1 H, overlapping d, H³), 6.58 (1 H, apparent t, apparent *J* = 6.0 Hz, H⁵), 6.22 (2 H, apparent s, C₅H₄Me), 5.86 (2 H, apparent s, C₅H₄Me), 4.16 (2 H, d, ²*J* = 15.0 Hz, CH₂), 3.48 (2 H, d, ²*J* = 15.0 Hz, CH₂), 1.89 (3 H, s, C₅H₄Me), 1.37 (9 H, s, ^tBu), 1.01 (3 H, s, Me of N₂N_{py}), 0.27 (18 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 298 K): 167.6 (C²), 149.4 (C⁶), 135.9 (C⁴), 124.0 (1-C₅H₄Me), 120.8, 120.7 (C⁵ and C³), 105.6, 104.2 (2 × ring CH of C₅H₄Me), 61.4 (CH₂NSiMe₃), 44.5 (C(CH₂NSiMe₃)₂), 33.3 (NCMe₃), 20.3 (Me of N₂N_{py}), 14.2 (C₅H₄Me), 3.6 (SiMe₃) (the signal for NCMe₃ 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 C₂₅H₄₅N₄NbSi₂): C 54.6 (54.5), H 7.8 (8.2), N 9.8 (10.2).

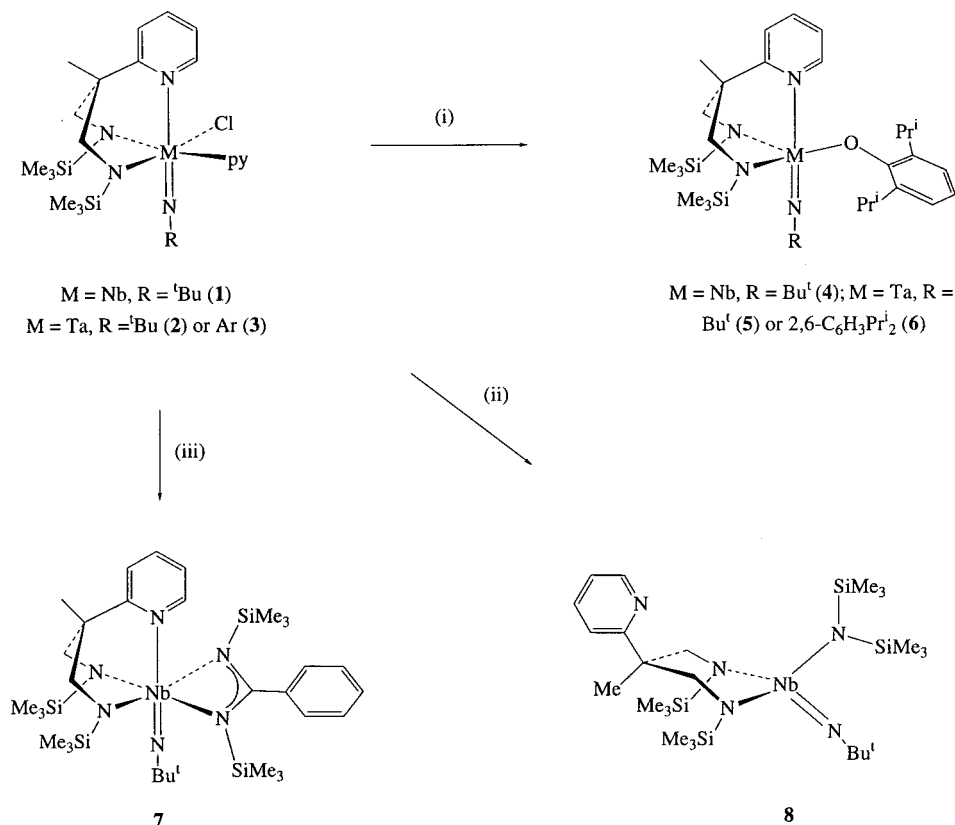
Crystal Structure Determinations of [Nb(N^tBu)(OAr)(κ³-N₂N_{py})] (4), [Ta(NAr)(OAr)(κ³-N₂N_{py})] (6), and [Nb(N^tBu){CH(SiMe₃)₂}(κ²-N₂N_{py})] (9). Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and 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 SIR92³⁵ 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. Aryloxyde, Amide, and Benzamidinate Complexes with Imido–Diamido–Pyridine Ligand Sets^a

^a (i) Li–OAr, benzene, 7 °C then rt, 40–72 h, 58–74%; (ii) LiN(SiMe₃)₂, benzene, 7 °C then 50 °C, 65 h, 61%; (iii) LiPhNC(NSiMe₃)₂, benzene, 7 °C then rt, 40 h, 62%.

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Results and Discussion

The compounds [M(NR)Cl(κ³-N₂N_{py})(py)] (M = Nb, R = ^tBu **1**; M = Ta, R = ^tBu **2** or Ar **3**, where N₂N_{py} = MeC(2-C₅H₄N)(CH₂NSiMe₃)₂ and Ar = 2,6-C₆H₃^tPr₂) 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.

Aryloxyde Derivatives. Cooled benzene was added to a mixture of solid [Nb(N^tBu)Cl(κ³-N₂N_{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)(κ³-N₂N_{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)(κ³-N₂N_{py})] (**5**) and [Ta(NAr)(OAr)(κ³-N₂N_{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)(κ³-N₂N_{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

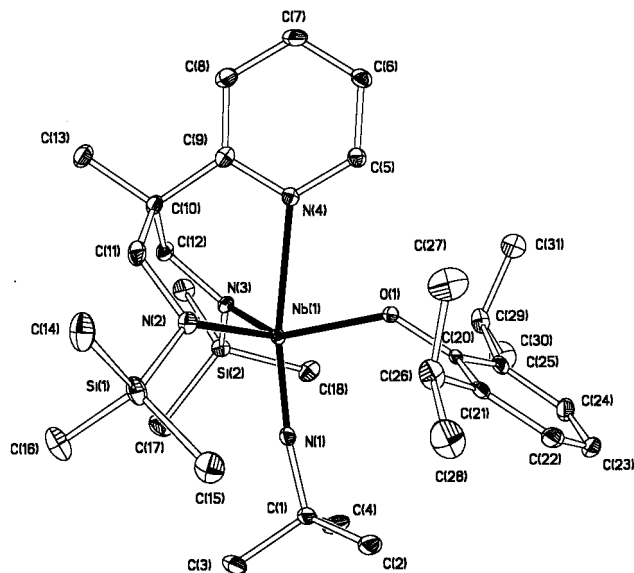


Figure 1. Displacement ellipsoid plot (20% probability) of [Nb(N^tBu)(OAr)(κ³-N₂N_{py})] (**4**) with hydrogen atoms omitted.

structures of **4** and **6** are distorted trigonal bipyramidal about a pentavalent metal center. They contain a facially coordinated N₂N_{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 aryloxyde ligand in the remaining equatorial position. The low-temperature ¹H and ¹³C NMR spectra of **4–6** are consistent with the solid-state structures shown, with evidence of restricted rotation

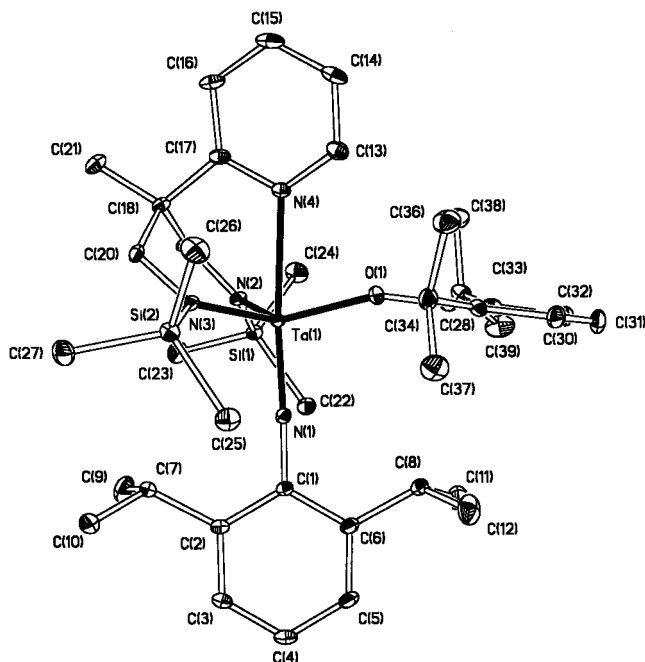


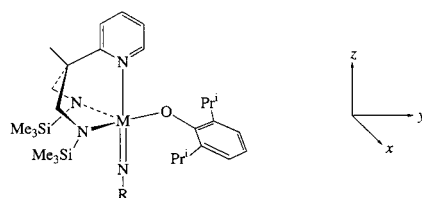
Figure 2. Displacement ellipsoid plot (20% probability) of $[\text{Ta}(\text{NAr})(\text{OAr})(\kappa^3\text{-N}_2\text{Npy})]$ (**6**) with hydrogen atoms omitted.

Table 2. Comparison of Bond Lengths (Å) and Angles (deg) for $[\text{Nb}(\text{N}^t\text{Bu})(\text{OAr})(\kappa^3\text{-N}_2\text{Npy})]$ (4**) and $[\text{Ta}(\text{NAr})(\text{OAr})(\kappa^3\text{-N}_2\text{Npy})]$ (**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 (supported 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 $[\text{Nb}(\text{NMe})(\text{O}-2,6\text{-C}_6\text{H}_3\text{-Ph}_2)_3(\text{NHMe}_2)]$ (**4.2**).³⁸ At 1.782(3) Å, the Nb=N(imide) bond length is effectively identical to that in the octahedral starting complex $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{Npy})(\text{py})]$ (**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



M = Nb, R = Bu^t (**4**); M = Ta, R = Bu^t (**5**) or 2,6-C₆H₃Pr₂ (**6**)

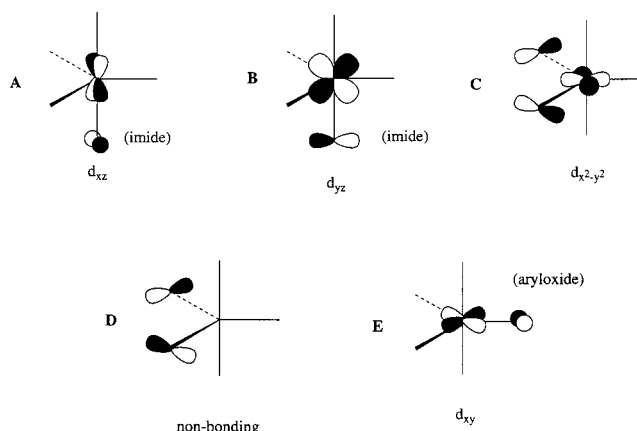


Figure 3. Qualitative analysis of Nb 4d_π–(N,O) 2ππ bonding interactions and N₂Npy ligand π-nonbonding orbitals for $[\text{M}(\text{NR})(\text{OAr})(\text{N}_2\text{Npy})]$ (**4**–**6**), showing the Cartesian coordinate system chosen.

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 N₂Npy pyridyl group and particularly close to the pyridyl H⁶ 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 SiMe₃ groups “down” toward the imido ligand and displacement of the aryloxy substituent in the same direction help to orient the OAr isopropyl groups further away from the SiMe₃ groups.

The most obvious difference between the structure of [Ta(NAr)(OAr)(N₂N_{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 aryloxy M–O–C linkage is much more linear in **6** [$158.5(2)^\circ$] than in **4** [$135.8(2)^\circ$], due presumably to the steric pressure exerted by the arylimide isopropyl groups (note that the bending of the aryloxy 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(N₂N_{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 aryloxy 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 aryloxy 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 significantly 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), $360.0(3)^\circ$ and $359.7(3)^\circ$, 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 *nd* π -acceptor orbitals available after forming the metal–ligand σ -bond framework.⁴⁷ The near-linear imido linkages (M–N(imide)–R = $172.1(2)^\circ$ and $176.1(2)^\circ$) reveal that these nitrogen atoms are sp -hybridized and offer two 2p _{π} -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 = $135.8(2)^\circ$ 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 nitrogens 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(NSiMe₃)₂ and LiN(SiMe₃)₂ are summarized in Scheme 1. In both cases cold benzene was added to a mixture of solid [Nb(N^tBu)Cl(κ^3 -N₂N_{py})(py)] (**1**) and the lithiated benzamidinate or amide reagent. Subsequent workup after stirring at room temperature or heating (for LiN(SiMe₃)₂) for 40–65 h gave [Nb(N^tBu){PhC(NSiMe₃)₂}(κ^3 -N₂N_{py})] (**7**) and [Nb(N^tBu){N(SiMe₃)₂}(κ^2 -N₂N_{py})] (**8**) as pale orange solids in 61–62% isolated yield. The compound **8** was spectroscopically >90% pure, but trace impurities 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 ¹³C NMR spectra of **7** are consistent with the presence of a molecular mirror plane in solution. For example, the ¹H NMR spectrum features two SiMe₃ environments (each integrating as 18H) and one pair of mutually coupled doublets (total integral 4H) for the CH₂ groups of N₂N_{py}. Resonances for the apical Me of

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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 $[Nb(N^tBu)\{N(SiMe_3)_2\}(\kappa^2-N_2N_{py})]$, **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 $[Ti\{N^tBu\}PC(N^tBu)\{(\kappa^2-N_2N_{py})\}]$ ($\delta = 8.50$) and $[Ti_2\{\mu-\eta^2-NC(Me)N^tBu\}_2(\kappa^2-N_2N_{py})_2]$ ($\delta = 8.50$).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 $[M(NR)(NR')_3]$ have been reported and structurally characterized previously.^{3,52}

Bis(trimethylsilyl)methyl, Trimethylsilylmethyl, Benzyl, and Cyclophenadienyl Derivatives. Group 5 metal alkyl complexes incorporating imido coligands are well established.^{3,53–57} Several nonimido group 5

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Nb(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2-N_2N_{py})]$ (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.

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.

The compounds $[M(N^tBu)\{CH(R)SiMe_3\}(\kappa^2-N_2N_{py})]$ ($R = SiMe_3$, $M = Nb$ **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 $[M(N^tBu)\{CH-(SiMe_3)_2\}(\kappa^2-N_2N_{py})]$ 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 $[Nb(N^tBu)\{CH(SiMe_3)_2\}(\kappa^2-N_2N_{py})]$ (**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 $[Nb(N^tBu)\{N(SiMe_3)_2\}(\kappa^2-N_2N_{py})]$ (**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 $176.4(3)^\circ$ 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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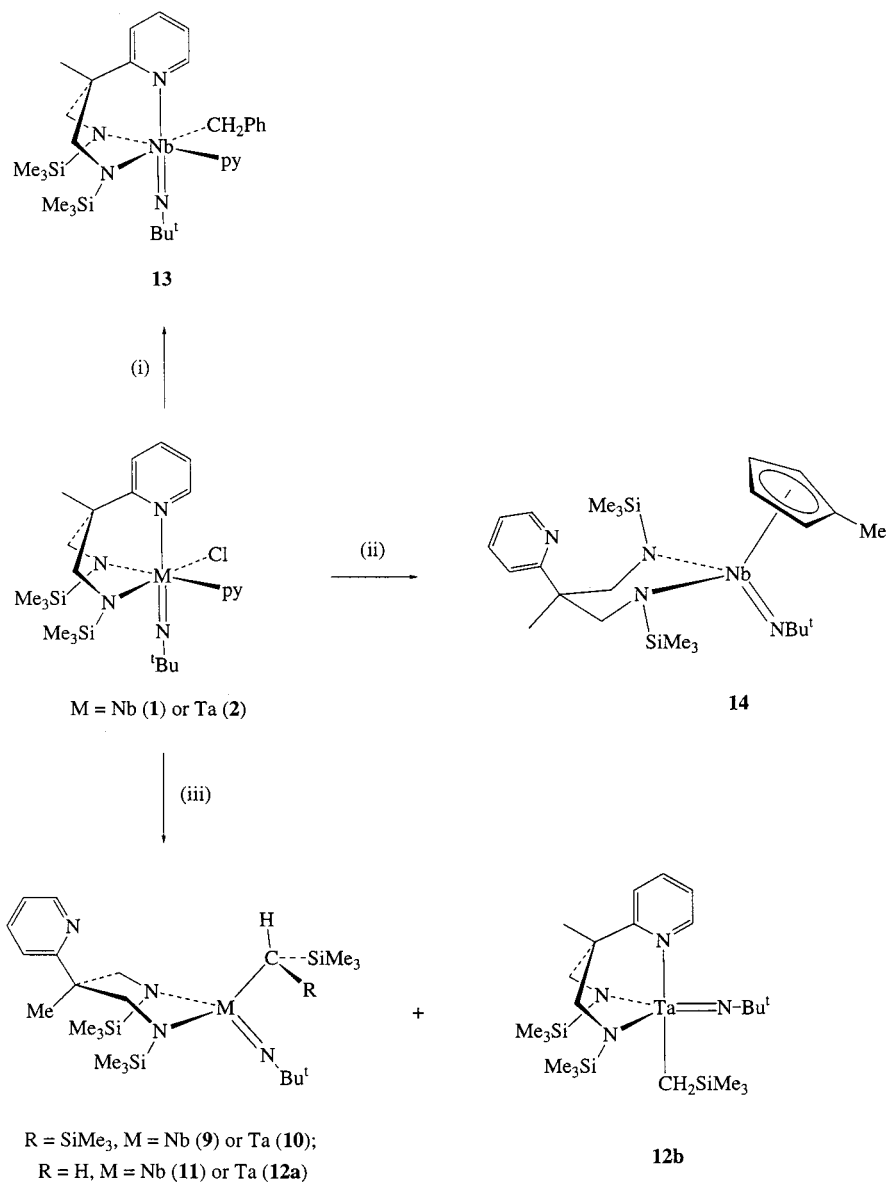
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Scheme 2. Alkyl, Benzyl, and Cyclopentadienyl Complexes with Imido–Diamido–Pyridine Ligand Sets^a

^a (i) PhCH_2MgCl (1.0 M solution in diethyl ether), benzene, rt, 17 h, 38%; (ii) $\text{LiC}_5\text{H}_4\text{Me}$, benzene, 7 °C then 60 °C, 72 h, 65%; (iii) $\text{LiCHR}(\text{SiMe}_3)$ (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., $\text{Nb}\cdots\text{H} = 2.321$ –(29) and 2.405(33) Å in $[\text{Nb}(\text{NAr})(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2^t\text{Bu})_2]$).⁶¹ The possibility of α -agostic interactions has been further examined for the tantalum analogue $[\text{Ta}(\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\text{N}_2\text{N}_{\text{py}})]$ (10) by spectroscopic means (see below).

Compounds 9–12 were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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^b 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 $\text{CH}(\text{SiMe}_3)_2$ methine proton. The Nb-bound carbon atom of $\text{CH}(\text{SiMe}_3)_2$ was not directly observed, presumably due to strong coupling to the

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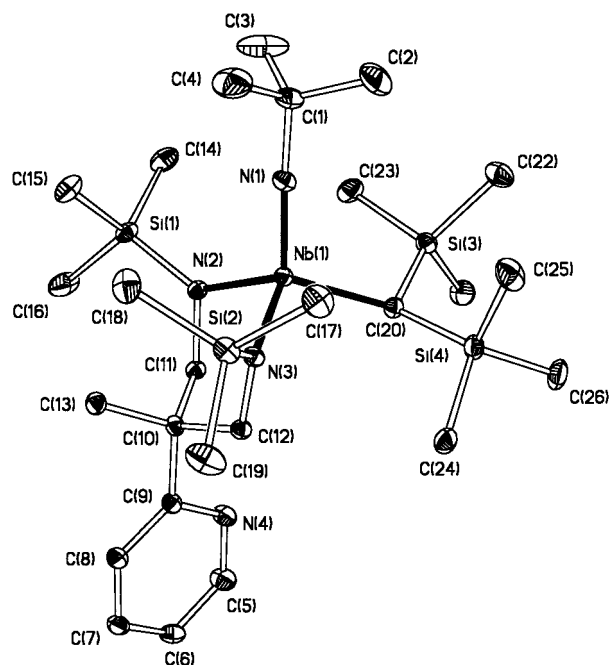


Figure 4. Displacement ellipsoid plot (20% probability) of one of the two crystallographically independent molecules of $[\text{Nb}(\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\kappa^2\text{-N}_2\text{Npy})]$ (**9**) with hydrogen atoms omitted.

quadrupolar metal nucleus (^{93}Nb , 100% abundance, $I = 9/2$), but was indirectly located at 56.7 ppm from an HMQC ^{13}C – ^1H correlation spectrum. The spectra of the tantalum analogue **10** are very similar to those of **9**, the main difference being that the carbon atom of $\text{CH}(\text{SiMe}_3)_2$ was now directly observable in the ^{13}C NMR spectra at 63.2 ppm (the corresponding $\text{CH}(\text{SiMe}_3)_2$ 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 $^1J_{\text{CH}}$ for the metal-bound $\text{CH}(\text{SiMe}_3)_2$ 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 $^1J_{\text{CH}}$ value of 94 Hz for the $\text{CH}(\text{SiMe}_3)_2$ methine carbon. This value is lower than might be expected for a typical sp^3 -hybridized carbon atom ($^1J_{\text{CH}} \approx 120$ – 130 Hz), although is higher than the values normally expected for carbons bearing α -agostic hydrogens ($^1J_{\text{CH}} \approx 60$ – 90 Hz).⁶² Thus although the $^1J_{\text{CH}}$ 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 $[\text{Ti}(\text{NR})\{\text{CH}(\text{SiMe}_3)_2\}\{\text{PhC}(\text{NSiMe}_3)_2(\text{py})\}]$ ($\text{R} = t\text{Bu}$, 2,6- $\text{C}_6\text{H}_3\text{Me}_2$) feature $^1J_{\text{CH}}$ 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 $^1J_{\text{CH}}$ 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 $\nu(\text{C}=\text{H}\cdots\text{M})$ bands.⁶²

The NMR spectra of $[\text{Nb}(\text{N}^t\text{Bu})\{\text{CH}_2\text{SiMe}_3\}(\kappa^2\text{-N}_2\text{Npy})]$ (**11**) are analogous to those of **9**. The ^1H spectrum suggests molecular C_s symmetry. The pyridyl H^6 resonance at 8.52 ppm is indicative of a noncoordinated pyridyl group. The CH_2SiMe_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 ^1H NMR spectrum of $[\text{Ta}(\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\kappa^{2,3}\text{-N}_2\text{Npy})]$ (**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_2Npy ligand in **12b** is characterized by an H^6 resonance at 9.02 ppm, indicative of a coordinated pyridyl group. Other resonances in the ^1H NMR spectrum are broadly similar to those discussed above; the $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{M} = \text{Nb}$ (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 $[\text{Ta}(\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{N}_2\text{Npy})]$ (**12**) produced averaged $^1J_{\text{CH}}$ coupling constants for the metal-bound methylene group of 117 Hz for **12b** and 104 Hz for **12a**. The value of $^1J_{\text{CH}} = 104$ Hz for **12a** is somewhat less than the typical $^1J_{\text{CH}}$ 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 $[\text{Ta}(\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}(\text{N}_2\text{Npy})]$ (**10**), for which $^1J_{\text{CH}} = 94$ Hz). The value of $^1J_{\text{CH}} = 117$ Hz for five-coordinate **12b** is nearer to the commonly encountered $^1J_{\text{CH}}$ 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 $^1J_{\text{CH}}$ were reported recently for

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two crystallographically characterized titanium imido derivatives with CH_2SiMe_3 ligands.^{63,66} It was demonstrated in these cases that a $^1J_{\text{CH}}$ 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 $[\text{Nb}(\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{N}_2\text{N}_{\text{py}})]$ (**11**) and $[\text{Ta}(\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{N}_2\text{N}_{\text{py}})]$ (**12**) do not provide any evidence of agostic interactions, since no $\nu(\text{C}-\text{H}\cdots\text{M})$ 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 $[\text{Nb}(\text{N}^t\text{Bu})(\text{CH}_2\text{Ph})(\kappa^3\text{-N}_2\text{N}_{\text{py}})(\text{py})]$ (**13**, Scheme 2) was prepared from a cooled solution of $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\text{N}_2\text{N}_{\text{py}})(\text{py})]$ (**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 $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\text{N}_2\text{N}_{\text{py}})(\text{py})]$ (**1**) to retain the pyridine ligand after chloride substitution.

In the ^1H NMR spectrum of **13** the $\text{N}_2\text{N}_{\text{py}}$ 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 $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\text{N}_2\text{N}_{\text{py}})(\text{py})]$ (**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 $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\kappa^3\text{-N}_2\text{N}_{\text{py}})(\text{py})]$ (**1**) and solid $\text{LiC}_5\text{H}_4\text{Me}$ with cooled benzene provided a yellow solution, which was

heated to 60 °C and stirred for 72 h, yielding $[\text{Nb}(\text{N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{Me})(\kappa^2\text{-N}_2\text{N}_{\text{py}})]$ (**14**) as an orange solid in 65% yield. An analogous reaction between $[\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\text{N}_2\text{N}_{\text{py}})(\text{py})]$ (**1**) and LiC_5Me_5 yielded only complex mixtures presumably because of the bulkier nature of C_5Me_5 .

The ^1H NMR spectrum of $[\text{Nb}(\text{N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{N}_2\text{N}_{\text{py}})]$ (**14**) features characteristic $\text{N}_2\text{N}_{\text{py}}$ 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **14** is entirely as expected for the proposed structure.

The proposed structure of $[\text{Nb}(\text{N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{N}_2\text{N}_{\text{py}})]$ (**14**) is analogous to those of $[\text{Nb}(\text{NAr})(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{NMe}_2)_2]$ ⁶⁷ and the complexes $[\text{Nb}(\text{NR})(\eta^5\text{-C}_5\text{H}_5)(\text{NHR})_2]$ ($\text{R} = ^t\text{Bu}, 2,6\text{-C}_6\text{H}_3\text{Me}_2$).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**.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Engineering and Physical Sciences Research Council, the Leverhulme Trust, the Fonds der Chemischen Industrie, the Royal Society, the DAAD, and the British Council for financial support.

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>.

OM0103153

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