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Synthesis and Reactivity of Cyclometalated Triamidophosphine Complexes of Niobium and Tantalum

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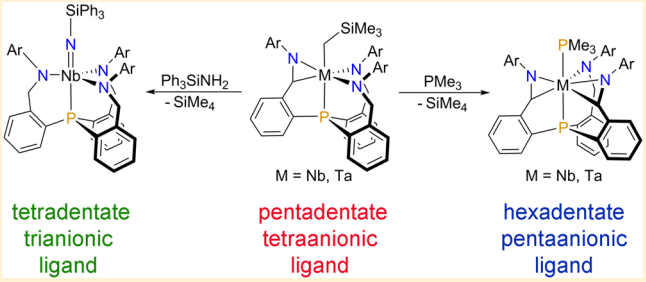
Supporting Information

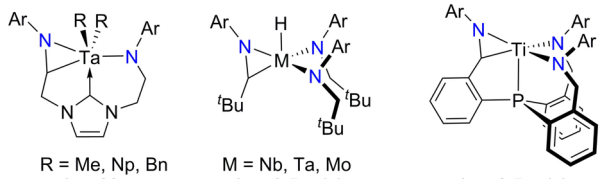
ABSTRACT: The triamidophosphine protioligand **1** reacts with the homoleptic pentakis(dimethylamido) precursors of niobium and tantalum [$M(NMe_2)_5$, where M = Nb, Ta] to form cyclometalated complexes of the type [N_2PCN-κ^5-*N,N,P,C,N*]$M(NMe_2)$ (**2-M**). Apart from the three amido donors, one benzylic position of the ligand backbone is deprotonated over the course of this reaction, resulting in the formation of a new M−C bond. As a consequence, a metallaziridine substructure is formed, and the triamidophosphine moiety thus serves as a tetraanionic pentadentate ligand. The dimethylamido complexes **2-M** can be converted into the corresponding triflates [N_2PCN-κ^5-*N,N,P,C,N*]M(OTf) (**3-M**) and alkyl complexes [N_2PCN-κ^5-*N,N,P,C,N*]$M(CH_2SiMe_3)$ (**4-M**) by treatment with triethylsilyl triflate ($Et_3SiO_3SCF_3$) followed by (trimethylsilyl)methyllithium ($LiCH_2SiMe_3$). The alkyl complexes exhibit interesting reactivities, including a second cyclometalative backbone activation affording the trimethylphosphine-stabilized complexes [$NP(CN)_2$-κ^6-*N,P,C,N,C,N*]$M(PMe_3)$ (**5-M**). In the case of tantalum, the formation of a dinuclear hydrido complex (**6**) is observed upon hydrogenation of **4-Ta**. In the case of niobium, the metallaziridine substructure in **4-Nb** is prone to ring opening via protonation with triphenylsilylamine (Ph_3SiNH_2), resulting in formation of the corresponding imido complex [PN_3-κ^4-*P,N,N,N*]Nb═$NSiPh_3$ (**7**).



INTRODUCTION

Low-coordinate or low-valent alkyl and hydrido complexes of early transition metals are typically highly reactive species that are not easily isolated unless a certain degree of spatial protection is provided by the employed ligand set.[1] Even in cases where such a protective ligand environment impedes decomposition and dimerization pathways efficiently, the desired reactive monomers are often prone to oxidative C−H addition or intramolecular cyclometalation processes.[2] While the former oxidative C−H addition is only accessible for low-valent species, the latter cyclometalative stabilization is also feasible for d^0 species via σ-bond metathesis.[3] For substituted cyclopentadienyl complexes, "tuck-in" or "tuck-over" compounds are formed frequently,[4] while low-valent trimethylphosphine complexes are known to undergo reversible phosphametallacyclopropane formation.[5] In the case of amido ligands, which offer β-hydrogens, metallaziridines seem to represent the preferred products of intramolecular cyclometalation processes.[6] Such metallaziridine motifs are found in a number of early-transition-metal complexes,[7] and only a few cyclopentadienyl-free compounds are provided as examples in Chart 1. The first example, the mixed carbene/amido tantalum complex **A** reported by Fryzuk and co-workers,[8] is formed via backbone deprotonation during the reaction of R_3TaCl_2 (R = Me, $CH_2{}^tBu$, Bn) with the ligand's dilithium salt. The originally envisioned product, the trialkyl species, was not observed but instead reacted via an alkylidene intermediate to form the stable dialkyltantalaziridine **A**. However, the formation of metallaziridines should not be considered as an undesirable deactivation pathway, as indisputably demonstrated by Cummins and co-workers. They have found that the trianilide complexes of the general formula $M^{III}({}^tBuCH_2NAr)_3$ (M = Nb, Ta, Mo; Ar = 3,5-xylyl) are in equilibrium with the metal(V) metallaziridine hydrides **B** and that this equilibrium lies on the side of the oxidized species (see Chart 1).[9] Conveniently, these complexes can still serve as a source for the low-valent, highly reactive M^{III} fragments by means of reversible cyclometalation. This trianilide/metallaziridine hydride system is known to react with N_2,[9a] P_4,[9f] CO,[9h] and CO_2[9i] as well as a variety of unsaturated substrates such as nitriles, isonitriles, and

Chart 1. Selected Cp-Free Metallaziridine Complexes of Titanium, Niobium, Tantalum, and Molybdenum



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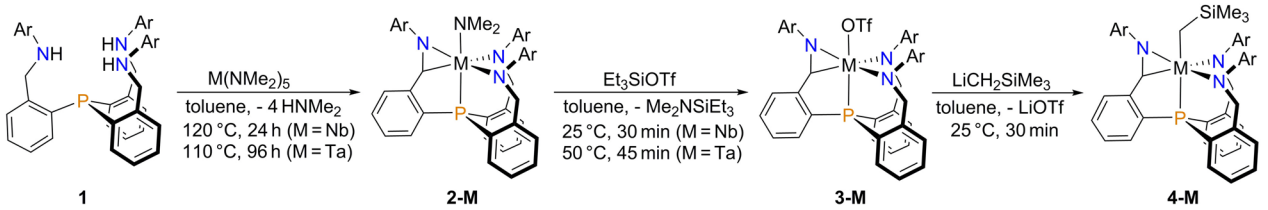
Scheme 1. Synthesis of Metallaziridines 2-M, 3-M, and 4-M (M = Nb, Ta; Ar = 3,5-Xylyl)



alkynes.[9e,h] The third example, the titanaziridine **C** (see Chart 1), was recently synthesized in our laboratory starting from the triamidophosphine-coordinated titanium species [PN_3]Ti-(Me).[10] The apical methyl ligand within the latter complex acts as an internal base upon gentle heating, which leads to the formation of [N_2PCN-κ^5-*N,N,P,C,N*]Ti (**C**). That one of the benzylic positions of the ligand backbone was deprotonated is certainly noteworthy, especially because such backbone cyclometalations are unknown for closely related triamidoamine complexes.[11] Instead, cyclometalation at the peripheral amido substituents with concomitant formation of four-membered metallazetidines was observed in the cases of titanium and zirconium azatranes,[12] while N−C bond cleavage within the tren backbone was noticed for related tantalum tren complexes.[13]

Upon comparison of **B** and **C**, certain structural similarities are obvious because the ligand in **C** (ligand **1**) essentially resembles the three arylamides in **B**, with the major difference being the close proximity of the phosphine anchor that is present in **C**. On the basis of this simple analysis, we decided to investigate the chemistry of ligand **1** in conjunction with group 5 metals in order to clarify whether similarities to **B** are present or whether an independent chemistry of this ligand scaffold is to be found.

RESULTS AND DISCUSSION

Because protonolysis of the homoleptic group 4 tetrakis-(dimethylamido) precursors [$M(NMe_2)_4$, where M = Ti, Zr, Hf] proved to be an efficient starting point for the synthesis of early-transition-metal complexes of ligand **1**,[10] an analogous route for the related group 5 metals was pursued. The reactions of pentakis(dimethylamido)niobium and -tantalum with **1** in toluene both required high temperatures and prolonged reaction times [24 h at 120 °C for $Nb(NMe_2)_5$ and 96 h at 110 °C for $Ta(NMe_2)_5$]. For the latter, it is crucial that the reaction temperature never exceeds 115 °C because the formation of unidentified side products increases significantly at higher temperatures. After workup, complexes [N_2PCN-κ^5-*N,N,P,C,N*]$M(NMe_2)$ (**2-M**) were obtained as orange (M = Nb) or yellow (M = Ta) solids in 75% and 64% yields, respectively (see Scheme 1). Similar to [N_2PCN]Ti (**C**), the ligand binds in a tetraanionic pentadentate fashion because one of the benzylic protons within the ligand backbone suffered from deprotonation. Interestingly, in this case the precursor's dimethylamido ligand is basic enough to allow for this reaction, whereas in the case of titanium, a more basic and more nucleophilic methyl group was required.[10] That formation of the metallaziridine substructure within **2-M** had indeed occurred became evident upon analysis of the ^{1}H, ^{13}C, and ^{31}P NMR spectra and was ascertained by two-dimensional (2D) NMR spectroscopy. The overall C_3 symmetry of the ligand was lost in complexes **2-M**, and only five benzylic protons were detected in the individual ^{1}H NMR spectra [see the Supporting Information (SI) for selected NMR spectra]. For both metals, one of these protons (δ 4.72 ppm for M = Nb and δ 4.63 ppm for M = Ta) was identified as a CH moiety (ascertained by HSQC and DEPT), which resonates at δ 65.0 ppm (M = Nb) and at δ 69.6 ppm (M = Ta) in the corresponding ^{13}C NMR spectra. In combination with the crystallographically characterized products that originate from **2-M** (compounds **3-Nb** and **4-Nb** vide infra), the assignment of this distinct benzylic position to a metallaziridine is unambiguous. The ^{31}P NMR signals of complexes **2-M** are shifted downfield compared to **1** (**2-Nb**, δ −20.7 ppm; **2-Ta**, δ −23.2 ppm; **1**, δ −36.5 ppm), as previously noticed for the related titanium complex **C** [$\delta(^{31}P)$ 46.1 ppm; cf. **C** in Chart 1].

When precursors of the type $Ta(NMe_2)_4X$ (X = Cl, OTf)[14] were used instead of $Ta(NMe_2)_5$, only **2-Ta** and unreacted **1** were formed in equimolar amounts. This finding is interpreted as a result of disproportionation of $Ta(NMe_2)_4X$ into $Ta(NMe_2)_3X_2$ (or the corresponding dimer) and $Ta(NMe_2)_5$.[15] Apparently, only the homoleptic starting material $Ta(NMe_2)_5$ is suitable for the aminolytic synthesis of **2-M**. Because direct entry to the halides or triflates was inaccessible, an exchange of the remaining dimethylamide in **2-M** was pursued. Complexes **2-M** reacted with reagents of the type R_3SiX (X = Cl, OTf, I) by replacement of the apical amido ligand in a straightforward manner. For reaction with triethylsilyl trifluoromethanesulfonate (Et_3SiOTf) with **2-M** in toluene (see Scheme 1), clean conversions to [N_2PCN]M(OTf) (**3-M**, where M = Nb, Ta) were observed directly after addition for **2-Nb** or after gentle heating for **2-Ta** (45 min at 50 °C). After workup, the complexes were obtained as deep-red (**3-Nb**) or yellow (**3-Ta**) solids in good yields (95% for M = Nb and 88% for M = Ta).[16] Both reactions are accompanied by a large downfield shift of around 45 ppm in the respective ^{31}P NMR spectra (**3-Nb**, δ 25.5 ppm;[17] **3-Ta**, δ 22.0 ppm). In these complexes, the ^{31}P NMR chemical shift is quite sensitive toward the ligand in the trans position to the phosphine, which has been observed in related triamidophosphine complexes as well.[18] With respect to the ^{1}H NMR signals of the metallaziridine motif, the ^{1}H NMR spectra of complexes **3-M** are somewhat similar to the corresponding spectra of complexes **2-M**, with the expected difference being that the signals assigned to the apical dimethylamido ligand in **2-M** are, of course, absent in the ^{1}H NMR spectra of complexes **3-M**. X-ray-quality single crystals of **3-Nb** were obtained from a saturated solution of the complex in a toluene/pentane mixture at −40 °C. The solid-state molecular structure and relevant metric parameters are provided in Figure 1.

The solid-state structure of **3-Nb** is consistent with the NMR data acquired in solution and shows the pentadentate coordination of **1** with one phosphorus, one carbon, and the three amido donor atoms bound to the central metal. As expected, the triflate is bound to the metal and completes its coordination sphere. An elongated Nb−O2 bond (d = 2.31 Å)

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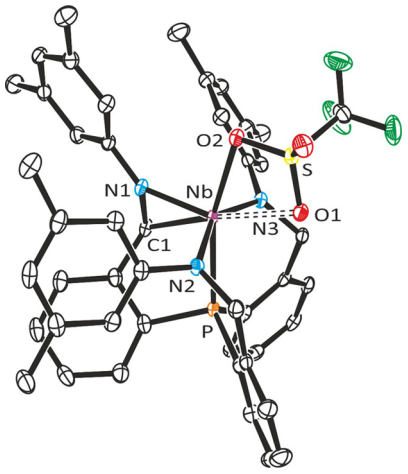

Figure 1. ORTEP diagram of **3-Nb** (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (deg): Nb−N1 1.980(2), Nb−N2 2.056(2), Nb−N3 2.058(2), Nb−C1 2.210(3), Nb−P 2.5210(8), Nb−O2 2.310(2) Nb···O1 2.425(2); N2−Nb−N3 140.70(1), N2−Nb−C1 106.30(1), N3−Nb−C1 90.45(1), N1−Nb−C1 38.54(1), N2−Nb−P 76.41(7), N3−Nb−P 84.17(7), C1−Nb−P 69.85(8), P−Nb−O2 162.64(5), N1−Nb−O2 91.28(9), N3−Nb−O2 93.35(9), O1−S−O2 107.75(12).

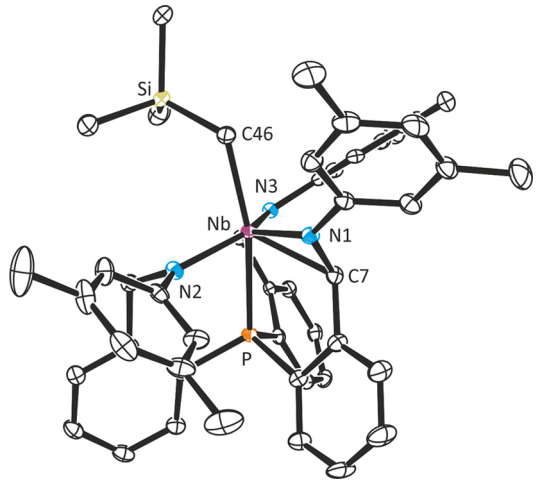

Figure 2. ORTEP diagram of **4-Nb** (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (deg): Nb−N1 1.974(2), Nb−N2 2.006(2), Nb−N3 2.076(2), Nb−C7 2.200(2), Nb−C46 2.240(2), Nb−P 2.6115(6); N2−Nb−N3 132.58(7), N2−Nb−C7 115.24(8), N3−Nb−C7 96.05(8), N1−Nb−C7 39.31(8), N2−Nb−P 77.92(5), N3−Nb−P 79.55(5), C7−Nb−P 71.71(6), P−Nb−C46 162.26(6), N1−Nb−C46 92.49(8), N3−Nb−C46 90.72(8).

and a close contact between Nb and O1 (d = 2.433 Å) are indicative of a chelating triflate (Nb−O bond lengths of approximately 2.1 Å are commonly observed for niobium triflates).[19] The coordination environment of the niobium center is heavily distorted because of the three-membered niobaziridine ring with an N−Nb−C angle of 38.5°. This angle is comparable to other, less preorganized systems,[7c,9d,h] suggesting that severe strains are absent in this complex. With a P−Nb−O2 angle of 162.6°, the triflato ligand is slightly bent away from the ligand's *N*-xylyl rings, possibly to allow for the chelating interaction. The values for the M−N bond lengths vary between 1.98 and 2.06 Å, with the bond to the deprotonated side arm being the shortest. The Nb−C bond (d = 2.21 Å) is found within the expected range,[20a,19a,20b] and a relatively short Nb−P bond (2.52 Å) is noticed.[21] All other bond lengths are within the usual range.

When treated with (trimethylsilyl)methyllithium ($LiCH_2SiMe_3$) in toluene at room temperature, compounds **3-M** were cleanly converted into the corresponding alkyl species $[N_2PCN]M(CH_2SiMe_3)$ (**4-M**) within minutes (see Scheme 1). After removal of the lithium salt byproducts, the complexes were obtained in good yields as deep-red (**4-Nb**, 80% yield) or orange (**4-Ta**, 75% yield) oily liquids, which solidify upon cooling. Both complexes are thermally labile and decompose in an unspecific manner within days if kept at room temperature. The ^{31}P NMR signals are shifted upfield compared to those of **3-M** (**4-Nb**, δ −12.1 ppm; **4-Ta**, δ −18.8 ppm). In the ^{1}H NMR spectra, signals assigned to the metal-bound CH_2 group appear as doublet of doublets (^{31}P and geminal coupling) in addition to trimethylsilyl resonances at 0.27 ppm (**4-Nb**) and 0.08 ppm (**4-Ta**). Single crystals of **4-Nb** suitable for X-ray diffraction were obtained from a saturated solution of the complex in diethyl ether at −40 °C after several days. The molecular structure is shown in Figure 2.

The solid-state structure of **4-Nb** is in agreement with the corresponding NMR data of the complex acquired in solution and the $[N_2PN]Nb$ fragment comparable to the respective fragment in **3-Nb**. The metal center is hexacoordinate and the coordination polyhedron around the niobium metal not easily derived from idealized octahedral or trigonal-prismatic geometries. The niobaziridine ring in **4-Nb** exhibits an N1−Nb−C7 angle of 39.1°, which is slightly larger than the corresponding angle in **3-Nb**. The P−Nb bond is slightly longer (d = 2.61 Å) compared to the triflato complex, owing to the stronger alkyl ligand trans to the phosphine. All other bond lengths are similar to those in **3-Nb**. The Nb−C bond to the apical alkyl ligand (d = 2.24 Å) is found within the expected boundaries.[20a,19a,20b] The apical alkyl ligand in **4-Nb** is slightly bent away from the most proximate *N*-xylyl groups (P−Nb−C46 = 162.3°) possibly because of steric repulsion.

Upon heating of a solution of **4-Nb** or **4-Ta** in the presence of trimethylphosphine, the ligand backbones are once again deprotonated at a second benzylic position, yielding the doubly cyclometalated complexes $[NP(CN)_2$-κ^6-*N,P,C,N,C,N*$]M(PMe_3)$ (**5-M**) and tetramethylsilane (see Scheme 2). After workup, the compounds were obtained as dark-red (**5-Nb**) or orange (**5-Ta**) solids in moderate yields of 48% and 51%, respectively.

The ^{31}P NMR spectra of complexes **5-M** show two coupled doublets with coupling constants of $^{2}J_{P,P} \approx 113$ Hz. The signal of the ligand's phosphorus atom experienced a large downfield shift of about +60 ppm to +45.8 ppm for **5-Nb** and +41.5 ppm for **5-Ta**, while the corresponding resonances of the coordinated trimethylphosphine ligand are found at −27.7 and −19.8 ppm, respectively. For **5-Nb**, both signals are broadened because of unresolved coupling to the ^{91}Nb nucleus and the just-stated ^{31}P NMR shifts were determined from the ^{31}P−^{1}H HMBC NMR spectra.[17] The backbone deprotonation was confirmed by ^{13}C DEPT, ^{1}H−^{13}C HSQC, and ^{1}H NMR spectroscopy, with the ^{1}H NMR spectra displaying two geminally coupled CH_2 protons for the remaining methylene group and two individual singlets for the metal-bound CH groups (see the SI for selected NMR spectra). Single crystals of **5-Ta** suitable for X-ray diffraction were obtained by storing a

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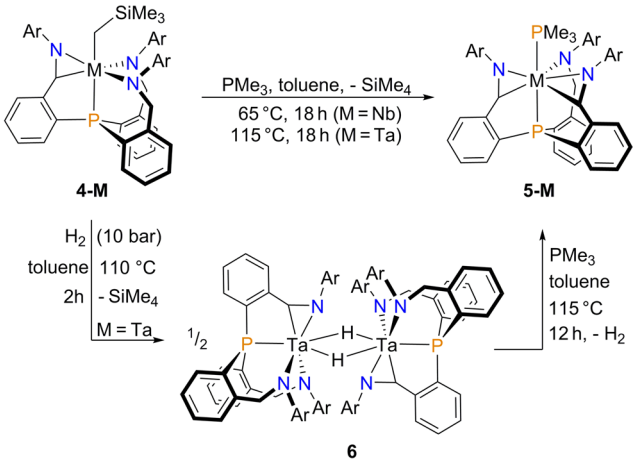
Scheme 2. Synthesis of 5-M (M = Nb, Ta) and 6 (Ar = 3,5-Xylyl)



saturated toluene/pentane solution of the complex for several days at −40 °C (see Figure 3). The C_1 symmetry in **5-Ta**, which is evident from the corresponding NMR spectra obtained in solution, is also found in the solid-state structure. The metal center is coordinated in a 7-fold manner by the now hexadentate ligand and the additional trimethylphosphine donor. A distorted coordination geometry is adopted by the metal center, which is derived neither from pentagonal-bipyramidal nor from capped octahedral or capped trigonal-prismatic polyhedra. Instead, the three amido and one benzylic carbon atom (C22) occupy a plane around the tantalum center. The trimethylphosphine ligand is bound approximately orthogonal to this plane, with angles to the individual corner atoms of the plane ranging from 85° to 98°. The ligand's remaining two donor atoms (P1 and C7) sit beneath this plane with angles to the apical phosphorus atom of trimethylphosphine (P2) of P1−Ta−P2 = 153.2° and C7−Ta−P2 = 134.1°.

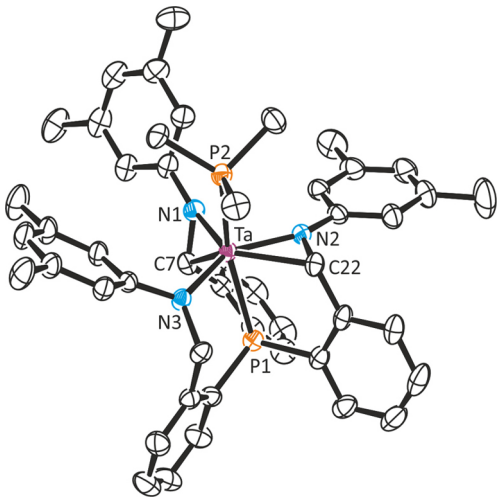


Figure 3. ORTEP diagram of **5-Ta** (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (deg): Ta−N1 2.031(2), Ta−N2 1.970(2), Ta−N3 2.088(2), Ta−C7 2.215(2), Ta−C22 2.280(2), Ta−P1 2.4876(7); Ta−P2 2.6874(7); P1−Ta−P2 153.15(2), N1−Ta−P2 98.73(7), N2−Ta−P2 94.38(6), N3−Ta−P2 84.62(6), C22−Ta−P1 75.27(7), C22−Ta−P2 85.47(6), N2−Ta−P1 82.48(6), N1−Ta−P1 108.11(7), C7−Ta−P1 71.96(5), C7−Ta−P2 134.06(7).

Interestingly, P1, C7, and P2 span a second plane that also includes the central metal. The C−M and N−M bond lengths are within the expected range and compare well to those of the structures discussed above. A relatively short tantalum phosphorus distance of 2.49 Å (Ta−P1) is found for the respective bond to the central phosphine of the triamidophosphine ligand. The Ta−P bond length to the apical trimethylphosphine (Ta−P2 = 2.69 Å) is found within the expected region.[21]

If complexes **4-M** were heated without trimethylphosphine or in the presence of different coligands such as pyridine or tetrahydrofuran (THF), conversion to the expected doubly cyclometalated products still took place but was incomplete and accompanied by the formation of unidentified side products. In this context, it is worth noting that transformation to **5-M** could not be achieved starting from **2-M** ($[N_2PCN]M(NMe_2)$, where M = Nb, Ta), not even after keeping solutions of these complexes at high temperatures for weeks.[22] It appears that elimination of an alkane is necessary to allow for the second deprotonation step. Such alkane eliminations are often achieved by hydrogenation, leaving a reactive hydride species behind.[23,1e] Therefore, we decided to examine the reactivity of complexes **4-M** toward dihydrogen, keeping in mind that these alkyl complexes offer two positions viable for hydrogenation, namely, the apical alkyl ligand and the metallaziridine ring in the ligand's backbone. After a H_2 pressure of 10 bar was applied to a high-pressure NMR tube containing a solution of **4-Ta**, no reaction was observed at room temperature. After the solution was heated to 110 °C for 90 min, a new diamagnetic compound was formed and identified as the tantalum hydride complex $\{[N_2PCN\text{-}\kappa^5\text{-}N,N,P,C,N]Ta(\mu\text{-}H)\}_2$ (**6**). Apart from the expected resonances of the ligand, one additional multiplet at 16.1 ppm corresponding to the metal-bound hydride is found in the ^{1}H NMR spectrum of **6**. This signal collapses to a singlet upon ^{31}P decoupling. ^{1}H and 2D NMR spectra also revealed that the tantalaziridine ring was intact, while no signals for the (trimethylsilyl)methyl ligand were found. Accordingly, 1 equiv of tetramethylsilane was detected in the ^{1}H NMR spectrum of the crude reaction mixture.

Single crystals suitable for X-ray diffraction were collected after the reaction mixture was allowed to cool to room temperature. The solid-state molecular structure of **6** is shown in Figure 4. Because of the presence of Fourier ripples in the vicinity of the metal atoms (mainly arising from absorption effects), the bridging hydrogen atoms could not be located unambiguously in the difference electron density map. However, the dimeric assembly in conjunction with the spectroscopic data suggests the existence of two bridging hydride ligands. Their positions were modeled based on the atom−atom repulsion potential energy surface using *X-Hydex*.[24] In agreement with NMR data, the presence of the tantalaziridine substructure is confirmed by X-ray diffraction analysis and the ligand is found in its tetraanionic pentadentate coordination mode. Thus, the presence of one hydride ligand per metal ion is in line with two tantalum(V) centers, while an alternative interpretation of this structure as a Ta^{IV}−Ta^{IV} dimer is in conflict with the observed ^{1}H NMR hydride signal and the long M−M distance (d = 3.26 Å).[25] The metric parameters are comparable to those of the related tantalaziridine hydride complex $(^t$BuCH$_2$NAr$)_2(\eta^2$-^{t}BuC(H)NAr)TaH (**B**, where Ar = 3,5-xylyl; Chart 1) reported by Cummins and co-workers.[9i] A noteworthy deviation is the Ta−C bond, which is slightly longer in **6** (2.18 vs 2.24 Å).

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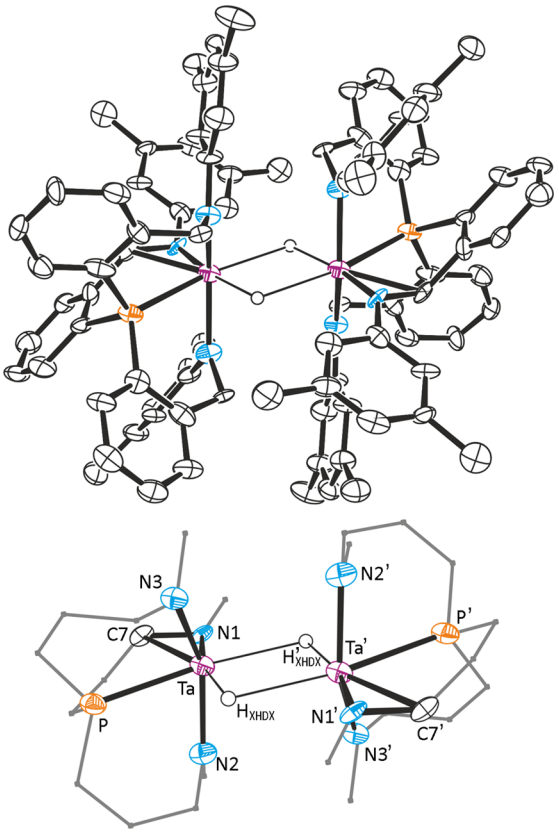
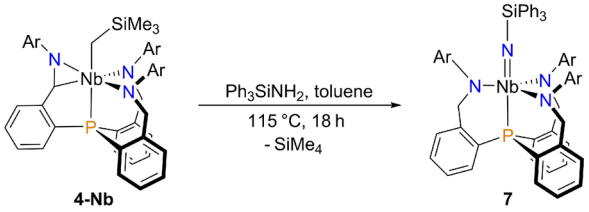


Figure 4. Molecular structure of **6**: ORTEP diagram (top) and numbering scheme (bottom) (hydrogen atoms are omitted for clarity with exception of the calculated hydride positions, and thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (deg): Ta···Ta′ 3.2613(10), Ta−P 2.558(3), Ta−N1 1.950(8), Ta−N2 2.069(7), Ta−N3 2.068(8), Ta−C7 2.240(10); N1−Ta−P 106.2(2), N2−Ta−P 73.7(2), N3−Ta−P 81.5(2), N1−Ta−C7 39.9(3),P−Ta···Ta′ 137.04(6). Half of the dimer is generated by symmetry transformations ($-x + 2, -y, -z$). The bridging hydride H_{XHDX} was modeled using *XHydex* (Ta−H_{XHDX} of approximately 1.75 Å, Ta′−H_{XHDX} of approximately 2.41 Å, and Ta−H_{XHDX}−Ta′ of approximately 102°).

The isotopically labeled complex **6-D** was prepared in an analogous manner using deuterium gas. The ^{2}H NMR spectrum of this compound shows the expected resonances at 16 ppm for the tantalum-bound deuteride and at 0 ppm for tetramethylsilane-d_1, as well as a broad signal in the region of the methylene protons (3−5 ppm) and reasonably sharp signals in the aromatic domain. A comparison with the ^{1}H NMR spectrum of **6** suggests that the latter belongs to the ortho protons of the ligand's xylyl substituents, hinting at hydrogen/deuterium exchange not only at the benzylic positions but also at the *o*-xylyl positions.[26] A similar reactivity was found for a dinuclear diamidophosphine-coordinated tantalum tetrahydrido complex and reported recently by Fryzuk and co-workers.[23,25m] Because a clean reaction of the latter dimeric ditantalum tetrahydride with dinitrogen has been reported, compound **6** was exposed to dinitrogen as well, but no reaction was detected at room temperature. Although numerous species were formed upon heating (as judged by ^{31}P NMR spectroscopy), it seems noteworthy that the resulting product mixture was not identical with the decomposition products that formed upon heating of **6** under an atmosphere of dry argon. During the formation of **6** via hydrogenation of **4-Ta**, one additional product was formed in amounts of 5−15%, depending on the reaction times and temperatures. While we did not succeed in the isolation of this compound, NMR spectroscopic investigations of the crude reaction mixture revealed the minor product to be spectroscopically similar to **6** (i.e., a dimeric assembly with intact tantalaziridine substructures and one ^{1}H NMR signal for two bridging hydrides). When a mixture containing the minor species was subjected to combustional analysis, results identical with those of the combustional analysis of single crystals of **6** were obtained (within the margin of error), implying that the elemental composition of the two products is identical, at least with respect to the non-hydrogen atoms. Together with the spectroscopic similarities, these findings indicate that the minor product is, in fact, an isomer of **6**, although no temperature-dependent equilibrium was detectable by ^{31}P NMR spectroscopy. Upon treatment of crude **6** with trimethylphosphine, the doubly cyclometalated tantalum complex **5-Ta** formed (see Scheme 2). The presence of a C_{2v}-symmetric isomer of **6** is in agreement with these observations (see the SI for details).

When a sample of **4-Nb** in toluene was pressurized with H_2 (10 bar) and heated to 70 °C for 60 min, the ^{31}P NMR signal disappeared, and only one signal corresponding to tetramethylsilane was found in the ^{1}H NMR spectrum. Thus, hydrogenation of **4-Nb** resulted in the formation of one or more paramagnetic products, but all attempts to isolate or crystallize a well-defined species were unsuccessful. Common analytical methods gave no insight into the nature of this material (see the SI for details),[21] and the question arose as to whether the Nb−CH_2SiMe_3 moiety in **4-Nb** could be eliminated via protonation instead of hydrogenation. Because the niobium imido complex [PN_3]Nb=$NSiMe_3$(py) is easily prepared via the reaction of K_3[PN_3] with Me_3SiN=$NbCl_3(py)_2$[27] (see the SI for experimental details and crystallographic analysis), we decided to probe the reactivity of complexes **4-M** toward acidic primary amines, expecting that related imido complexes would form. While **4-Ta** reacted in an unspecific manner upon treatment with triphenylsilylamine (Ph_3SiNH_2), the reaction of **4-Nb** with Ph_3SiNH_2 resulted in a relatively clean conversion to the desired triphenylsilylimido complex [PN_3]Nb=$NSiPh_3$ (**7**), although prolonged heating was required (see Scheme 3). The ^{1}H NMR spectrum of **7** reveals only one set of signals per ligand side arm, indicating the existence of a C_3-symmetric species in solution. As expected, the three phenyl groups of the silylimido fragment appear as multiplets in the aromatic region. The methylene protons resonate as two doublet of doublets at 4.81 and 5.19 ppm and integrate for six protons. This pattern is indicative of a C_3-symmetric complex, with the geminally coupled methylene protons ($^2J_{H,H}$ = 15.6 Hz) being chemically inequivalent because of the helical twist of the molecular cage structure. The second coupling within this doublet of doublets pattern is due to a ^4J coupling to the ^{31}P nucleus ($^4J_{P,H}$ = 3.4 Hz). Compared

Scheme 3. Synthesis of 7 Starting from 4-Nb (Ar = 3,5-Xylyl)



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to the starting material **4-Nb**, the ^{31}P NMR signal of **7** is shifted upfield and found at −51.4 ppm.

Single crystals of **7** suitable for X-ray diffraction were obtained from a concentrated solution of the complex in pentane at room temperature. The corresponding molecular structure is shown in Figure 5.

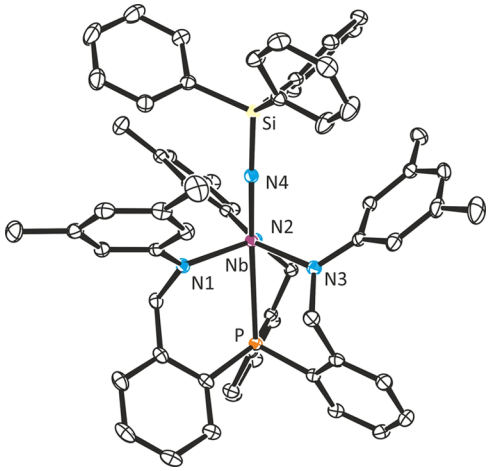

Figure 5. ORTEP diagram of **7** (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (deg): Nb−N1 2.057(1), Nb−N2 2.043(1), Nb−N3 2.062(1), Nb−N4 1.794(2), Nb−P 2.8727(4) N4−Si 1.7279(13); N1−Nb−N2 115.35(5), N2−Nb−N3 112.73(5), N1−Nb−N3 117.87(5), P−Nb−N4 177.23(4), N1−Nb−N4 101.10(5), Nb−N4−Si 178.13(8).

In agreement with NMR data, the solid-state structure exhibits the expected C_3 symmetry, with the coordination geometry around the metal center being trigonal-bipyramidal. The niobium atom is positioned somewhat above the equatorial plane (d = 0.45 Å), and a slight deviation from the principal axis is noticed (N4−Nb−P = 177.2°). While the amido−Nb bond lengths are only slightly larger than those in **3-Nb** and **4-Nb**, the P−Nb distance is considerably elongated to d = 2.87 Å (cf. d = 2.52 Å for **3-Nb** and d = 2.61 Å for **4-Nb**). The distance between the metal and imido nitrogen is found within the usual range for silylimidoniobium species (Nb−N4 = 1.79 Å).[28] A substantial triple-bond character of the Nb−N4 bond is inferred from an approximately linear Nb−N4−Si array (Nb−N4−Si = 178.1°), which is indicative of π donation from the imido nitrogen into empty metal-centered orbitals. The three nitrogen atoms of the ligand are nearly planar because of π donation, although simultaneous donation of all six amido π electrons is disallowed by orbital symmetry.[11] A similar situation is found not only in related niobium azatranes (cf. $[N(CH_2CH_2NEt)_3]Nb{=}N^tBu$)[29] but also in conformationally unrestricted niobium trianilide complexes [cf. $(^tBuNAr)_3Nb{=}NC(O)^tBu$, where Ar = 3,5-xylyl].[9g] Thus, far, the most important conclusion to be drawn from the molecular structure of **7** is that the metallaziridine in **4-Nb** was indeed ring-opened via protonation. Keeping in mind that high temperatures were required for this conversion, it seems that reversible cyclometalation with concomitant hydride migration as observed in $M(^tBuCH_2NAr)_3$ (M = Nb, Ta, Mo; Ar = 3,5-xylyl; cf. **B** in Chart 1) is unlikely to occur with our systems at ambient temperatures. In conjunction with the observed formation of bis(metallaziridines) (cf. complexes **5-M**), we arrive at the conclusion that the niobium and tantalum triamidophosphine complexes reported herein exhibit a distinct reactivity, which is only loosely related to tren-[30,13,11,29] or trianilide-coordinated complexes[7c,9c,d,f,h−j] of these metals.

CONCLUSION

In summary, it was shown that the triamidophosphine **1** forms cyclometalated complexes of the general type $[N_2PCN]M(X)$ [X = NMe_2 (**2-M**), OTf (**3-M**), CH_2SiMe_3 (**4-M**); M = Nb, Ta] with the ligand binding in a tetraanionic pentadentate form. For both alkyl complexes **4-M** (M = Nb, Ta), a second cyclometalation process was observed, affording complexes **5-M**, which comprise two metallaziridine substructures. In the case of tantalum, hydrogenation of **4-Ta** resulted in formation of the dinuclear hydrido-bridged complex **6** without concomitant ring opening (i.e., hydrogenation) of the metallaziridine. For niobium, however, such a ring-opening process was observed upon protonation of **4-Nb** with triphenylsilylamine, which led to the isolation of **7**. Thus, it was demonstrated that **1** can act as a trianionic tetradentate (cf. **7**), as a tetraanionic pentadentate (cf. **2**, **3**, **4**, and **6**), or as a pentaanionic hexadentate (cf. **5**) ligand scaffold. Whether this unique reactivity is of use in catalysis or small-molecule activation is currently under investigation.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an atmosphere of dry and oxygen-free argon by means of standard Schlenk or glovebox techniques. Toluene, THF, pentanes, hexanes, and diethyl ether were purified by passing the solvents over activated alumina columns (MBraun Solvent Purification System). Toluene-d_8, THF-d_8, and benzene-d_6 were refluxed over sodium and purified by distillation; CD_2Cl_2 was dried over CaH_2 and distilled prior to use. NMR spectra were recorded on a Bruker Avance II 400 MHz or a Bruker Avance III 600 MHz spectrometer at room temperature. ^{1}H and ^{13}C NMR spectra were referenced to residual ^{1}H NMR signals of the lock solvent. ^{31}P NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). Microanalyses (C, H, and N) were performed at the Department of Chemistry at the University of Heidelberg. Protioligand **1**, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$ were synthesized according to the literature.[31,10] Triethylsilyl trifluoromethanesulfonate, trimethylsilyl chloride, trimethylphosphine, (triphenylsilyl)amine, and (trimethylsilyl)methyllithium (1.6 M solution in diethyl ether) were purchased from commercial suppliers and used as received.

*$[N_2PCN]Ta(NMe_2)$ (**2-Ta**).* Pentakis(dimethylamido)tantalum (1.67 g, 4.15 mmol, 1.10 equiv) and protioligand **1** (2.50 g, 3.78 mmol, 1.00 equiv) were suspended in toluene (100 mL) and heated to 110 °C for 96 h. All volatiles were removed in vacuo, and the crude product was washed with diethyl ether (3 × 10 mL) to afford the complex as a yellow solid (2.16 g, 2.45 mmol, 64%). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.88 (t, J = 5.9 Hz, 1 H, Ar−H), 7.58 (t, J = 7.1 Hz, 1 H, Ar−H), 7.51 (t, J = 7.1 Hz, 2 H, Ar−H), 7.32 (s, 2 H, Ar−H), 7.21 (s, 2 H, Ar−H), 7.18 (d, J = 7.7 Hz, 1 H, Ar−H), 7.03−6.94 (m, 5 H, Ar−H), 6.93 (s, 2 H, Ar−H), 6.73 (m, 3 H, Ar−H), 6.63 (s, 1 H, Ar−H), 6.54 (s, 1H, Ar−H), 6.40 (s, 1 H, Ar−H), 5.19 (d, J = 15.0 Hz, 1 H, CH_2), 4.97 (d, J = 15.0 Hz, 1 H, CH_2), 4.88 (d, J = 15.4 Hz, 1 H, CH_2), 4.78 (d, J = 15.4 Hz, 1 H, CH_2), 4.63 (s, 1 H, CH), 3.33 (s, 6 H, NMe_2), 2.26 (s, 12 H, Ar−CH_3), 2.14 (s, 6 H, Ar−CH_3). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 158.8 (d, J = 24.6 Hz, Ar−C), 155.7 (s, Ar−C), 153.1 (s, Ar−C), 150.6 (s, Ar−C), 148.2 (d, J = 17.0 Hz, Ar−C), 146.2 (d, J = 16.8 Hz, Ar−C), 138.8 (s, Ar−C), 138.5 (s, Ar−C), 137.1 (s, Ar−C), 134.0 (s, Ar−C), 134.1 (s, Ar−C), 134.4 (s, Ar−C), 130.2 (s, Ar−C), 129.7 (d, J = 17.0 Hz, Ar−C), 129.2 (s, Ar−C), 128.0 (s, Ar−C), 127.5 (s, Ar−C), 126.9 (s, Ar−C), 125.6 (s, Ar−C), 124.0 (s, Ar−C), 123.4 (s, Ar−C), 123.2 (s, Ar−C), 122.1 (s, Ar−C), 119.1 (s, Ar−C), 118.5 (s, Ar−C), 118.4 (s, Ar−C), 69.9 (d, J = 7.4 Hz, CH), 62.3 (d, J = 16.9 Hz, CH_2), 52.7 (d, J = 17.1 Hz, CH_2), 48.6

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(s, NMe_2), 22.0 (s, Ar−CH_3), 21.9 (s, Ar−CH_3), 21.8 (s, Ar−CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −23.2 (s). Anal. Calcd for $C_{47}H_{50}N_4PTa$: C, 63.94; H, 5.71; N, 6.35. Found: C, 63.57; H, 6.18; N, 6.16.

*[N_2PCN]Nb(NMe_2) (**2-Nb**).* Pentakis(dimethylamido)niobium (1.30 g, 4.15 mmol, 1.10 equiv) and protioligand **1** (2.50 g, 3.78 mmol, 1.00 equiv) were suspended in toluene (50 mL) and heated to 120 °C for 24 h. All volatiles were removed in vacuo, and the crude product was washed with diethyl ether (3 × 10 mL) to afford the complex as an orange solid (2.22 g, 2.83 mmol, 75%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.87−7.91 (m, 1 H, Ar−H), 7.48−7.59 (m, 3 H, Ar−H), 7.37 (s, 2 H, Ar−H), 7.18 (s, 2 H, Ar−H), 6.92−7.08 (m, 6 H, Ar−H), 6.87 (s, 2 H, Ar−H), 6.78 (t, J = 7.5 Hz, 1 H, Ar−H), 6.74 (t, J = 7.6 Hz, 1 H, Ar−H), 6.61 (s, 1 H, Ar−H), 6.59 (s, 1 H, Ar−H), 6.41 (s, 1 H, Ar−H), 5.01 (d, J = 15.3 Hz, 1 H, CH_2), 4.87 (d, J = 15.0 Hz, 1 H, CH_2), 4.71−4.78 (m, 3 H, CH, CH_2), 3.22 (s, 6 H, NMe_2), 2.26 (s, 12 H, Ar−CH_3), 2.16 (s, 6 H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 155.1 (d, J = 36.5 Hz, Ar−C), 154.9 (s, Ar−C), 152.2 (s, Ar−C), 149.5 (s, Ar−C), 146.7 (d, J = 17.5 Hz, Ar−C), 144.9 (d, J = 15.6 Hz, Ar−C), 137.6 (s, Ar−C), 137.5 (s, Ar−C), 135.9 (s, Ar−C), 133.3 (d, J = 1.9 Hz, Ar−C), 133.2 (d, J = 1.9 Hz, Ar−C), 132.9 (d, Ar−C), 132.0 (d, J = 12.4 Hz, Ar−C), 129.3 (d, J = 8.9 Hz, Ar−C), 129.1 (d, J = 8.7 Hz, Ar−C), 128.9 (d, J = 8.6 Hz, Ar−C), 128.2 (s, Ar−C), 127.1 (s, Ar−C), 126.5 (d, J = 4.4 Hz, Ar−C), 125.9 (d, J = 4.5 Hz, Ar−C), 124.9 (d, J = 4.5 Hz, Ar−C), 123.8 (s, Ar−C), 122.2 (s, Ar−C), 120.8 (s, Ar−C), 117.5 (s, Ar−C), 117.4 (s, Ar−C), 116.2 (s, Ar−C), 65.3 (s, CH), 51.1 (d, J = 17.8 Hz, CH_2), 51.7 (d, J = 18.6 Hz, CH_2), 48.6 (d, J = 2.0 Hz, NMe_2), 20.8 (s, Ar−CH_3), 20.7 (s, Ar−CH_3), 20.6 (s, Ar−CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −20.7 (s). Anal. Calcd for $C_{47}H_{50}N_4NbP$: C, 71.02; H, 6.34; N, 7.05. Found: C, 71.19; H, 6.85; N, 6.88.

*[N_2PCN]Ta(OTf) (**3-Ta**).* To a solution of complex **2-Ta** (1.50 g, 1.70 mmol, 1.00 equiv) in toluene (50 mL) was added triethylsilyl trifluoromethanesulfonate (494 mg, 1.87 mmol, 1.10 equiv) in toluene (10 mL), and the resulting solution was stirred for 45 min at 50 °C. All volatiles were removed in vacuo, and the crude product was washed with pentane (3 × 10 mL) to afford the product as a yellow-orange solid (1.48 g, 1.80 mmol, 88%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.55 (t, J = 8.2 Hz, 1 H, Ar−H), 7.45 (t, J = 7.9 Hz, 1 H, Ar−H), 7.31−7.34 (m, 2 H, Ar−H), 7.32 (s, 2 H, Ar−H), 6.82−7.11 (m, 8 H, Ar−H), 6.69 (t, J = 7.5 Hz, 1 H, Ar−H), 6.60 (s, 1 H, Ar−H), 6.44 (s, 2 H, Ar−H), 6.38 (s, 1 H, Ar−H), 6.34 (s, 2 H, Ar−H), 6.17 (s, 1 H, Ar−H), 5.60 (d, J = 17.7 Hz, 1 H, CH_2), 5.14 (d, J = 15.2 Hz, 1 H, CH_2), 4.81 (d, J = 17.9 Hz, 1 H, CH_2), 4.60 (dd, J = 15.3 Hz, J = 4.9 Hz, 1 H, CH_2), 3.78 (s, 1 H, CH), 2.26 (s, 6 H, Ar−CH_3), 1.87 (s, 6 H, Ar−CH_3), 1.83 (s, 6 H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 155.3 (s, Ar−C), 155.0 (s, Ar−C), 152.0 (s, Ar−C), 150.8 (s, Ar−C), 148.1 (s, Ar−C), 146.8 (s, Ar−C), 146.1 (d, J = 12.1 Hz, Ar−C), 138.9 (s, Ar−C), 138.5 (s, Ar−C), 137.6 (s, Ar−C), 135.0 (s, Ar−C), 133.6 (s, Ar−C), 132.7 (s, Ar−C), 132.1 (d, J = 11.0 Hz, Ar−C), 131.6 (d, J = 13.8 Hz, Ar−C), 131.1 (s, Ar−C), 130.2 (d, J = 9.8 Hz, Ar−C), 129.8 (d, J = 9.2 Hz, Ar−C), 128.3 (s, Ar−C), 128.4 (s, Ar−C), 118.5 (s, Ar−C), 118.1 (s, Ar−C), 117.9 (s, Ar−C), 67.2 (d, J = 9.6 Hz, CH), 61.1 (d, J = 19.4 Hz, CH_2), 52.6 (d, J = 11.8 Hz, CH_2), 21.6 (s, Ar−CH_3), 21.5 (s, Ar−CH_3), 21.0 (s, Ar−CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ 22.0 (s). Anal. Calcd for $C_{46}H_{44}F_3N_3O_3PSTa$: C, 55.93; H, 4.49; N, 4.25. Found: C, 56.56, H, 4.90, N, 4.14.

*[N_2PCN]Nb(OTf) (**3-Nb**).* To a solution of complex **2-Nb** (1.50 g, 1.89 mmol, 1.00 equiv) in toluene (50 mL) was added dropwise triethylsilyl trifluoromethanesulfonate (549 mg, 2.08 mmol, 1.10 equiv) in toluene (10 mL), and the resulting solution was stirred for 30 min. All volatiles were removed in vacuo, and the crude product was washed with pentane (3 × 10 mL) to afford the product as a deep-red solid (1.62 g, 1.80 mmol, 95%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.54 (t, J = 8.5 Hz, 1 H, Ar−H), 7.41 (t, J = 7.8 Hz, 1 H, Ar−H), 7.28 (s, 2 H, Ar−H), 7.21 (d, J = 5.8 Hz, 1 H, Ar−H), 7.05 (t, J = 7.4 Hz, 1 H, Ar−H), 6.94−7.00 (m, 3 H, Ar−H), 6.91 (t, J = 6.5 Hz, 1 H, Ar−H), 6.87 (t, J = 7.2 Hz, 1 H, Ar−H), 6.83 (t, J = 6.8 Hz, 1 H, Ar−H), 6.78 (t, J = 7.5 Hz, 1 H, Ar−H), 6.65 (t, J = 7.5 Hz, 1 H, Ar−H), 6.61 (s, 1 H, Ar−H), 6.38 (s, 2 H, Ar−H), 6.36 (s, 2 H, Ar−H), 6.35 (s, 1 H, Ar−H), 6.16 (s, 1 H, Ar−H), 5.73 (d, J = 18.0 Hz, 1 H, CH_2), 5.19 (d, J = 15.3 Hz, 1 H, CH_2), 4.83 (d, J = 18.0 Hz, 1 H, CH_2), 4.25 (dd, J = 15.1 Hz, J = 5.1 Hz, 1 H, CH_2), 3.84 (s, 1 H, CH), 2.25 (s, 6 H, Ar−CH_3), 1.85 (s, 6 H, Ar−CH_3), 1.81 (s, 6 H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 152.7 (d, J = 2.8 Hz, Ar−C), 151.1 (s, Ar−C), 148.1 (s, Ar−C), 136.2 (s, Ar−C), 134.9 (s, Ar−C), 133.3 (s, Ar−C), 132.1 (s, Ar−C), 131.5 (s, Ar−C), 131.4 (s, Ar−C), 131.3 (s, Ar−C), 131.0 (s, Ar−C), 130.4 (s, Ar−C), 130.4 (s, Ar−C), 130.3 (s, Ar−C), 129.9 (s, Ar−C), 129.9 (s, Ar−C), 129.4 (s, Ar−C), 128.6 (s, Ar−C), 127.9 (s, Ar−C), 127.8 (s, Ar−C), 127.7 (s, Ar−C), 127.4 (s, Ar−C), 127.4 (s, Ar−C), 126.2 (s, Ar−C), 125.7 (s, Ar−C), 125.4 (s, Ar−C), 124.7 (s, Ar−C), 118.2 (s, Ar−C), 118.0 (s, Ar−C), 116.8 (s, Ar−C), 67.6 (d, J = 9.6 Hz, CH), 62.3 (d, J = 19.6 Hz, CH_2), 52.7 (d, J = 11.7 Hz, CH_2), 21.6 (s, Ar−CH_3), 21.5 (s, Ar−CH_3), 21.0 (s, Ar−CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ 25.5 (s). Anal. Calcd for $C_{46}H_{44}F_3N_3NbO_3PS$: C, 61.40; H, 4.93; N, 4.67. Found: C, 61.06; H, 5.41; N, 4.71.

*[N_2PCN]Ta(CH_2SiMe_3) (**4-Ta**).* To a solution of complex **3-Ta** (300 mg, 0.30 mmol, 1.00 equiv) in toluene (20 mL) was added dropwise trimethylsilylmethyl lithium (32 mmol, 0.33 mmol, 1.10 equiv) in toluene (5 mL), and the resulting solution was stirred for 30 min. All volatiles were removed in vacuo, and the residue was taken up in diethyl ether and filtered through Celite. The solvent was removed in vacuo, and the crude product was washed with cold pentane (3 × 2 mL) to obtain the complex as an orange oily liquid, which solidified upon cooling (210 mg, 0.23 mmol, 75%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.81 (dd, J = 6.4 Hz, J = 4.2 Hz, 1 H, Ar−H), 7.50−7.55 (m, 2 H, Ar−H), 7.39 (t, J = 7.0 Hz, 1 H, Ar−H), 7.37 (s, 2 H, Ar−H), 7.12 (t, J = 7.3 Hz, 1 H, Ar−H), 7.07 (t, J = 7.5 Hz, 1 H, Ar−H), 7.04 (s, 2 H, Ar−H), 7.00 (t, J = 7.2 Hz, 1 H, Ar−H), 6.96 (t, J = 7.4 Hz, 1 H, Ar−H), 6.92 (t, J = 7.3 Hz, 1 H, Ar−H), 6.87 (t, J = 7.2 Hz, 1 H, Ar−H), 6.84 (t, J = 7.4 Hz, 1 H, Ar−H), 6.80 (t, J = 7.4 Hz, 1 H, Ar−H), 6.61 (s, 2 H, Ar−H), 6.58 (s, 1 H, Ar−H), 6.44 (s, 1 H, Ar−H), 6.43 (s, 1 H, Ar−H), 5.18−5.24 (m, 2 H, CH_2), 4.99 (d, J = 16.0 Hz, 1 H, CH_2), 4.78 (dd, J = 15.0 Hz, J = 4.4 Hz, 1 H, CH_2), 4.17 (d, J = 3.2 Hz, 1 H, CH), 2.27 (s, 6 H, Ar−CH_3), 2.14 (s, 6 H, Ar−CH_3), 2.05 (s, 6 H, Ar−CH_3), 1.15 (d, J = 12.0 Hz, 1 H, Ta−CH_2), 0.80 (d, J = 12.0 Hz, 1 H, Ta−CH_2), 0.07 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 157.8 (d, J = 21.1 Hz, Ar−C), 155.9 (s, Ar−C), 153.1 (s, Ar−C), 150.2 (s, Ar−C), 148.3 (d, J = 17.1 Hz, Ar−C), 146.6 (d, J = 16.7 Hz, Ar−C), 145.5 (s, Ar−C), 145.1 (s, Ar−C), 143.1 (s, Ar−C), 140.1 (s, Ar−C), 139.4 (s, Ar−C), 138.0 (s, Ar−C), 137.9 (d, J = 17.0 Hz, Ar−C), 137.7 (s, Ar−C), 133.4 (s, Ar−C), 130.6 (s, Ar−C), 130.2 (s, Ar−C), 129.4 (s, Ar−C), 127.4 (s, Ar−C), 126.4 (s, Ar−C), 124.3 (s, Ar−C), 124.0 (s, Ar−C), 123.0 (s, Ar−C), 119.7 (s, Ar−C), 118.7 (s, Ar−C), 116.6 (s, Ar−C), 67.5 (s, CH), 62.1 (d, J = 30.3 Hz, Ta−CH_2), 59.0 (d, J = 23.2 Hz, CH_2), 55.5 (d, J = 20.1 Hz, CH_2), 21.6 (s, Ar−CH_3), 21.5 (s, Ar−CH_3), 21.2 (s, Ar−CH_3), 3.49 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −18.8 (s). Anal. Calcd for $C_{49}H_{55}N_3PSiTa$: C, 63.56; H, 5.99; N, 4.34. Found: C, 63.42; H, 6.24; N, 4.76.

*[N_2PCN]Nb(CH_2SiMe_3) (**4-Nb**).* To a solution of complex **3-Nb** (300 mg, 0.33 mmol, 1.00 equiv) in toluene (20 mL) was added dropwise trimethylsilylmethyl lithium (35 mg, 0.36 mmol, 1.10 equiv) in toluene (5 mL), and the resulting solution was stirred for 30 min. All volatiles were removed in vacuo, and the residue was taken up in diethyl ether and filtered through Celite. The solvent was removed in vacuo, and the crude product was washed with cold pentane (3 × 2 mL) to obtain the complex as a deep-red solid (220 mg, 0.26 mmol, 80%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.67 (dd, J = 7.6 Hz, J = 3.4 Hz, 1 H, Ar−H), 7.55 (t, J = 7.4 Hz, 2 H, Ar−H), 7.46 (s, 2 H, Ar−H), 7.18 (t, J = 7.5 Hz, 1 H, Ar−H), 6.89−7.08 (m, 7 H, Ar−H), 6.70 (t, J = 7.4 Hz, 1 H, Ar−H), 6.66 (s, 1 H, Ar−H), 6.61 (s, 2 H, Ar−H), 6.33 (s, 1 H, Ar−H), 6.25 (s, 1 H, Ar−H), 6.19 (s, 2 H, Ar−H), 5.50 (d, J = 16.7 Hz, 1 H, CH_2), 5.39 (dd, J = 15.1 Hz, J = 5.3 Hz, 1 H, CH_2), 4.82 (dd, J = 15.0 Hz, J = 5.9 Hz, 1 H, CH_2), 4.81 (d, J = 16.5 Hz, 1 H, CH_2), 3.88 (s, 1 H, CH), 2.28 (s, 6 H, Ar−CH_3), 1.96 (s, 6 H, Ar−CH_3), 1.95 (s, 6 H, Ar−CH_3), 1.54 (dd, J = 12.3 Hz, J = 2.6 Hz, 1 H, Nb−CH_2), 1.27 (d, J = 12.5 Hz, 1 H, Nb−CH_2), 0.26 (s, 9 H, $SiMe_3$).

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$^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 153.7 (d, J = 2.6 Hz, Ar−C), 150.2 (s, Ar−C), 148.4 (s, Ar−C), 138.7 (s, Ar−C), 138.4 (d, J = 12.0 Hz, Ar−C), 138.3 (d, J = 13.1 Hz, Ar−C), 138.1 (s, Ar−C), 135.4 (d, J = 4.0 Hz, Ar−C), 133.9 (s, Ar−C), 133.1−133.2 (m, Ar−C), 132.6 (s, Ar−C), 131.0 (s, Ar−C), 130.9 (s, Ar−C), 130.5 (d, J = 7.3 Hz, Ar−C), 130.4 (s, Ar−C), 130.1 (s, Ar−C), 130.0 (s, Ar−C), 129.6−129.7 (m, Ar−C), 129.0 (s, Ar−C), 128.9 (s, Ar−C), 124.4 (s, Ar−C), 123.3 (s, Ar−C), 122.9 (s, Ar−C), 118.5 (s, Ar−C), 115.8 (s, Ar−C), 115.0 (s, Ar−C), 110.8 (s, Ar−C), 60.4 (d, J = 24.2 Hz, CH_2), 58.9 (s, CH), 52.0 (d, J = 13.7 Hz, CH_2), 49.8 (d, J = 10.2 Hz, Nb−CH_2), 21.4 (s, Ar−CH_3), 21.3 (s, Ar−CH_3), 21.1 (s, Ar−CH_3), 3.53 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −12.3 (s). Anal. Calcd for $C_{49}H_{55}N_3NbPSi$: C, 70.23; H, 6.67; N, 5.01. Found: C, 70.93; H, 6.77; N, 5.04.

[NP(CN)$_2$]Ta(PMe$_3$) (**5-Ta**). A solution of complex **4-Ta** (100 mg, 0.11 mmol, 1.00 equiv) and trimethylphosphine (excess, approximately 0.1 mL) in toluene was heated to 115 °C for 18 h. All volatiles were removed in vacuo, and the crude product was washed with pentane to obtain the complex as a light-orange solid (52 mg, 56 μmol, 51%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.88−7.93 (m, 1 H, Ar−H), 7.72−7.78 (m, 1 H, Ar−H), 7.61 (t, J = 8.4 Hz, 1 H, Ar−H), 7.38 (t, J = 8.1 Hz, 1 H, Ar−H), 7.29 (t, J = 7.4 Hz, 1 H, Ar−H), 7.21 (t, J = 7.6 Hz, 1 H, Ar−H), 7.01−7.14 (m, 5 H, Ar−H), 6.91−6.99 (m, 2 H, Ar−H), 6.88 (t, J = 7.4 Hz, 1 H, Ar−H), 6.81 (t, J = 7.1 Hz, 2 H, Ar−H), 6.72 (t, J = 7.4 Hz, 1 H, Ar−H), 6.56 (s, 2 H, Ar−H), 6.23 (s, 1 H, Ar−H), 6.13 (s, 2 H, Ar−H), 5.53 (d, J = 14.1 Hz, 1 H, CH_2), 4.80 (dd, J = 14.1 Hz, J = 3.0 Hz, 1 H, CH_2), 4.13 (s, 1 H, CH), 3.74 (s, 1 H, CH), 2.29 (s, 6 H, Ar−CH_3), 1.97 (s, 6 H, Ar−CH_3), 1.88 (s, 6 H, Ar−CH_3), 1.00 (d, J = 7.4 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 163.8 (d, J = 29.9 Hz, Ar−C), 157.3 (d, J = 37.7 Hz, Ar−C), 155.8 (s, Ar−C), 152.0 (s, Ar−C), 151.4 (s, Ar−C), 144.9 (d, J = 14.3 Hz, Ar−C), 137.5 (s, Ar−C), 137.0 (s, Ar−C), 136.1 (s, Ar−C), 134.1 (s, Ar−C), 133.1 (s, Ar−C), 132.2 (s, Ar−C), 131.6 (s, Ar−C), 131.3 (s, Ar−C), 129.8 (d, J = 2.2 Hz, Ar−C), 129.4 (d, J = 3.1 Hz, Ar−C), 129.3 (d, J = 2.4 Hz, Ar−C), 128.6 (d, J = 1.5 Hz, Ar−C), 128.3 (d, J = 5.1 Hz, Ar−C), 128.1 (s, Ar−C), 126.0 (d, J = 6.3 Hz, Ar−C), 125.2 (d, J = 6.6 Hz, Ar−C), 122.3 (d, J = 5.9 Hz, Ar−C), 122.2 (s, Ar−C), 120.4 (s, Ar−C), 119.1 (d, J = 5.6 Hz, Ar−C), 116.2 (s, Ar−C), 115.7 (s, Ar−C), 112.2 (d, J = 2.3 Hz, Ar−C), 109.9 (s, Ar−C), 58.3 (d, J = 6.2 Hz, J = 1.7 Hz, CH), 58.0 (s, CH), 56.2 (d, J = 14.4 Hz, CH_2), 20.6 (s, Ar−CH_3), 20.4 (s, Ar−CH_3), 20.3 (s, Ar−CH_3), 12.6 (d, J = 19.5 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −19.7 (d, J = 113 Hz, PMe_3), 41.5 (d, J = 113 Hz, PAr_3). Anal. Calcd for $C_{48}H_{52}N_3P_2Ta$: C, 63.09; H, 5.74; N, 4.60. Found: C, 63.63; H, 6.05; N, 4.58.

[NP(CN)$_2$]Nb(PMe$_3$) (**5-Nb**). A solution of complex **4-Nb** (100 mg, 0.12 mmol, 1.00 equiv) and trimethylphosphine (excess, approximately 0.1 mL) in toluene was heated to 65 °C for 18 h. All volatiles were removed in vacuo, and the crude product was washed with pentane to obtain the complex as a dark-red solid (48 mg, 58 μmol, 48%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.87 (dd, J = 6.9 Hz, J = 2.7 Hz, 1 H, Ar−H), 7.73 (dd, J = 7.3 Hz, J = 4.2 Hz, 1 H, Ar−H), 7.63 (t, J = 8.6 Hz, 1 H, Ar−H), 7.38 (t, J = 7.7 Hz, 1 H, Ar−H), 7.25 (t, J = 7.7 Hz, 1 H, Ar−H), 7.21 (t, J = 7.5 Hz, 1 H, Ar−H), 7.09 (t, J = 7.6 Hz, 1 H, Ar−H), 7.06 (s, 2 H, Ar−H), 6.91 (m, 2 H, Ar−H), 6.89 (t, J = 7.4 Hz, 1 H, Ar−H), 6.80 (t, J = 7.2 Hz, 1 H, Ar−H), 6.72 (t, J = 7.2 Hz, 1 H, Ar−H), 6.61 (s, 2 H, Ar−H), 6.57 (s, 1 H, Ar−H), 6.23 (s, 1 H, Ar−H), 6.14 (s, 1 H, Ar−H), 5.96 (s, 2 H, Ar−H), 5.38 (d, J = 13.8 Hz, 1 H, CH_2), 4.60 (dd, J = 14.2 Hz, J = 3.0 Hz, 1 H, CH_2), 4.11 (s, 1 H, CH), 4.08 (s, 1 H, CH), 2.30 (s, 6 H, Ar−CH_3), 1.92 (s, 6 H, Ar−CH_3), 1.86 (s, 6 H, Ar−CH_3), 0.91 (d, J = 6.60 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 163.8 (d, J = 31.2 Hz, Ar−C), 157.7 (d, J = 38.5 Hz, Ar−C), 156.4 (s, Ar−C), 153.0 (s, Ar−C), 151.9 (s, Ar−C), 145.6 (d, J = 14.0 Hz, Ar−C), 138.7 (s, Ar−C), 138.0 (s, Ar−C), 136.7 (s, Ar−C), 134.8 (d, J = 2.4 Hz, Ar−C), 132.1 (s, Ar−C), 131.9 (s, Ar−C), 131.5 (d, J = 14.0 Hz, Ar−C), 130.5 (d, J = 2.2 Hz, Ar−C), 130.3 (d, J = 2.2 Hz, Ar−C), 129.4 (s, Ar−C), 129.0 (d, J = 13.9 Hz, Ar−C), 128.8 (d, J = 8.4 Hz, Ar−C), 126.9 (d, J = 5.9, Ar−C), 125.9 (d, J = 6.4 Hz, Ar−C), 123.6 (s, Ar−C), 122.8 (d, J = 5.6 Hz, Ar−C), 120.6 (s, Ar−C), 120.6 (s, Ar−C), 117.1 (s, Ar−C), 115.6 (s, Ar−C), 113.0 (s, Ar−C), 61.2 (d, J = 8.2 Hz, CH_2), 57.7 (d, J = 14.6 Hz, CH_2), 57.1 (d, J = 3.3 Hz, CH), 21.5 (s, Ar−CH_3), 21.1 (s, Ar−CH_3), 21.0 (s, Ar−CH_3), 13.3 (d, J = 16.0 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −27.8 (d, J = 118 Hz, PMe_3), 45.8 (d, J = 108 Hz, PAr_3). In numerous attempts, low carbon values were obtained upon combustional analysis of **5-Nb** ($C_{48}H_{52}N_3NbP_2$).

{[N$_2$PCN]Ta(μ-H)}$_2$ (**6**). A solution of complex **4-Ta** (20 mg, 21.6 μmol, 1.00 equiv) in toluene was pressurized with H_2 (8 bar) and heated to 110 °C for 90 min. Upon cooling of the solution to room temperature, orange crystals formed and were collected and dried in a vacuum (14 mg, 16.6 μmol, 77%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 16.0−16.1 (m, 1 H, Ta−H), 7.90 (t, J = 7.5 Hz, 1 H, Ar−H), 7.82 (t, J = 6.2 Hz, 1 H, Ar−H), 7.54 (d, J = 17.4 Hz, 1 H, CH_2), 7.34−7.42 (m, 2 H, Ar−H), 7.07−7.26 (m, 7 H, Ar−H), 6.70−6.80 (m, 1 H, Ar−H), 6.53−6.60 (m, 1 H, Ar−H), 6.50 (s, 1 H, Ar−H), 6.37 (dd, J = 14.4 Hz, J = 2.8 Hz, 1 H, CH_2), 6.14 (s, 2 H, Ar−H), 6.01 (s, 1 H, Ar−H), 5.96 (s, 1 H, Ar−H), 5.74 (s, 2 H, Ar−H), 4.71 (dd, J = 14.6 Hz, J = 5.4 Hz, 1 H, CH_2), 4.49 (dd, J = 14.6 Hz, J = 4.9 Hz, 1 H, CH_2), 3.31 (s, 1 H, CH), 1.97 (s, 6 H, Ar−CH_3), 1.67 (s, 6 H, Ar−CH_3), 1.66 (s, 6 H, Ar−CH_3). $^{13}C\{^1H\}$ NMR measurements were hampered because of low solubility. $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ 23.2 (s). Anal. Calcd for $C_{90}H_{90}N_6P_2Ta_2{\cdot}2C_6H_6$: C, 66.73; H, 5.60; N, 4.58. Found: C, 66.35; H, 5.64; N, 4.78.

[PN$_3$]Nb=NSiPh$_3$ (**7**). A solution of complex **4-Nb** (100 mg, 0.12 mmol, 1.00 equiv) and triphenylsilylamine (36.2 mg, 0.13 mmol, 1.10 equiv) in toluene was heated to 110 °C for 18 h. The solvent was removed in vacuo, and the crude product was washed with cold pentane to obtain the complex as an orange solid (76 mg, 75 μmol, 62%). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 7.65−7.55 (m, 3 H, Ar−H), 7.33 (t, J = 6.8 Hz, 3 H, Ar−H), 7.24 (t, J = 6.8 Hz, 3 H, Ar−H), 6.90−7.10 (m, 18 H, Ar−H), 6.87 (s, 6 H, Ar−H), 6.55 (s, 3 H, Ar−H), 5.19 (dd, J = 16.0 Hz, J = 3.8 Hz, 3 H, CH_2), 4.81 (dd, J = 15.5 Hz, J = 3.4 Hz, 3 H, CH_2), 1.95 (s, 18 H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 158.1 (s, Ar−C), 146.5 (d, J = 5.9, Ar−C), 137.5 (s, Ar−C), 135.1 (s, Ar−C), 130.8 (d, J = 5.6 Hz, Ar−C), 122.8 (s, Ar−C), 118.4 (s, Ar−C), 65.8 (s, CH_2), 21.9 (s, Ar−CH_3), 0.82 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ −51.4 (s). In numerous attempts, low carbon values were obtained upon combustional analysis of **7** ($C_{63}H_{60}N_4NbPSi$).

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, additional experimental details, selected NMR spectra; crystallographic data, and details of the structure determinations for **3-Nb**, **4-Nb**, **5-Ta**, **6**, **7**, and [PN$_3$]Nb=NSiMe$_3$(py). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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