Mono-anionic acetophenone imine ligands: synthesis, *ortho*-lithiation and first examples of group (V) metal complexes†

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A series of niobium and tantalum imido complexes with mono-anionic *ortho*-metallated acetophenone imine ligands have been prepared and characterized using NMR spectroscopy, mass spectrometry and elemental analysis. These low symmetry complexes are produced with only one or two structural isomers in all cases and display interesting correlations between the steric bulk of the ligands employed and the isomers formed. Crystal structures of several new niobium and tantalum complexes are presented as confirmation of the connectivity in these structural isomers.

Introduction

Among nitrogen donor ligand systems, imido groups (RN^{2-}; R = aryl, alkyl) have proven to be extremely important in early transition metal chemistry.[1] The strong bonding observed between the doubly anionic nitrogen donor atom and a highly charged early metal lends excellent stability, while broad tuning of the alkyl or aryl substituent provides for control of steric bulk.[1] In addition to supporting a range of interesting reaction chemistry, early work on imido complexes of group (V) metals was driven by their useful luminescence properties.[2–4] The first niobium and tantalum imido complexes, reported by Finn and co-workers in 1980, were synthesized by the reduction of acetonitrile with zinc or through the metathesis reaction of tantalum neopentylidenes with imines.[5] Later, a more economical route to tantalum and niobium imido complexes was reported, utilizing the reaction of silylated alkylamines with MCl_5.[6–8] A similar reaction of metal halides with silylanilines in the presence of 1,2-dimethoxyethane (DME) afforded a more stable series of metal imido precursors with the general formula of $M(NAr)Cl_3(DME)$ (M = Nb, Ta).[3,9–11] The lability of DME and halide ligands in these imido complexes has provided for a variety of intriguing niobium and tantalum metal complexes.[12–15] Herein, we describe their use as precursors in the synthesis of mono-anionic acetophenone imine group (V) complexes.

The broad use of bidentate ligands in transition metal chemistry derives from the stability garnered from the chelate effect, with the option of using two chemically different donor groups available as a means to more rigidly control the reactivity at the metal center. One way to generate a bidentate ligand system is through the regioselective *ortho*-metallation of an aryl group covalently attached to a second donor moiety.[16–18] This process leads to an anionic ligand framework with two dissimilar donor atoms, yielding electronic asymmetry in the resulting complexes that can lead to unique reactivity. *Ortho*-metallation is commonly effected by the direct activation of an aryl C–H bond, through either oxidative addition or direct deprotonation by a strong base.[16–18] With late transition metals, oxidative addition of the *ortho* C–H bond proves to be a very effective pathway to *ortho*-metallated complexes and to catalytically functionalize aryl groups in this position.[19–22] In recent work, Crabtree has utilized this methodology to produce iridium complexes by the *ortho*-metallation of α,β-unsaturated ketones, esters and acetophenone, which have served as useful catalyst precursors for hydroamination and alkyne hydroalkoxylation reactions.[23,24] Given this useful reactivity, many ligand systems based on α,β-unsaturated ketones, esters and acetophenones have been explored in recent years.[24–38]

Our research group has been interested in the reactivity of related *ortho*-metallated imines. *Ortho*-metallation of acetophenone imines with late metals is readily accessible by C–H activation of the aryl moiety, and this type of reaction allows for the synthesis of metal hydrides with potential applications in C–C bond coupling reactions. Unfortunately, this route has proven to be generally inaccessible for early transition metals. Many common early metal starting materials are in their maximum oxidation state, making *ortho*-metallation through oxidative addition of C–H bonds impossible. Alternate routes utilizing lower oxidation state metal centers have been shown to suffer from deleterious side reactions attributed to redox processes linked to ligand reduction, rather than the desired C–H activation.[39,40] Due to these limitations, reports regarding the use of *ortho*-metallated acetophenone imine ligands with early metals are rare. We recently published an effective synthetic route to group (IV) transition metal complexes of mono-anionic *ortho*-metallated acetophenone imine ligands.[30] Prior methods for the synthesis of early-metal complexes of *ortho*-metallated acetophenone imines had been limited to the insertion of cyano groups into metal–benzyne bonds, a reaction that yields dianionic versions of these ligands with very little substitutional flexibility.[41–51] Herein, we report the synthesis of acetophenone imines with a variety of alkyl and aryl substituents that undergo site-specific lithiation upon treatment with ^{n}BuLi. These activated ligands have been reacted with niobium and tantalum imido precursors to generate a series of twelve new metal imido complexes. The structure and bonding in these complexes was determined by NMR and X-ray analyses. We believe that

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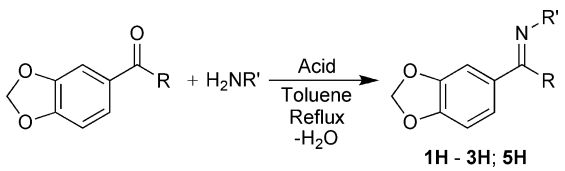
through the combination of the imido moiety and the new mono-anionic *ortho*-metallated acetophenone imine ligand system, a series of niobium and tantalum complexes with exceptional stoichiometric and catalytic reactivity will be uncovered.

Results and discussion

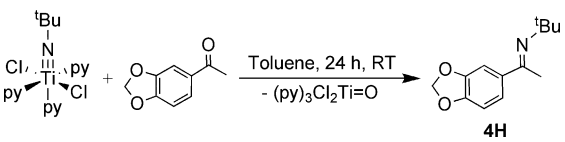
Imine synthesis and *ortho*-lithiation

In our initial communication, we showed that the acetophenone imine (**2H**) produced by the Schiff-base condensation reaction between 3,4-methylenedioxyacetophenone and 2,6-diethylaniline could be regioselectively deprotonated to produce a new mono-anionic bidentate ligand (**2Li**).[30] This new ligand was then successfully utilized in the synthesis of a series of titanium and zirconium complexes.[30] In an effort to lend steric and electronic diversity to this new ligand class, we have expanded the synthesis of these imines to include a much broader array of substituents (Scheme 1). Two new ketimines were formed by the Schiff-base condensation of 3,4-methylenedioxyacetophenone with 2,6-diisopropylaniline (**1H**) and 2,6-dimethylaniline (**3H**). Additionally, a related aldimine was produced by the Schiff-base condensation of piperonal with 2,6-diisopropylaniline (**5H**). Each of these imines was readily synthesized in refluxing toluene using a Dean–Stark trap to drive the reaction to high yield, and purification was effected by vacuum distillation.



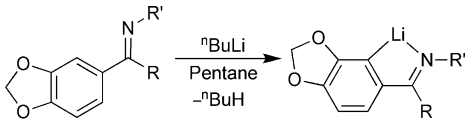
Scheme 1 Imine synthesis proceeds through a Schiff-base condensation reaction (R = Me; R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1H**), 2,6-Et$_2$C$_6$H$_3$ (**2H**), 2,6-Me$_2$C$_6$H$_3$ (**3H**), or R = H; R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5H**)).

In contrast, the Schiff-base condensation of 3,4-methylenedioxyacetophenone with *tert*-butylamine was not successful under any of the conditions tested. In order to overcome these synthetic challenges, the desired imine was produced by an alternative synthetic pathway involving the use of an imido titanium complex as the imine source. Thus, **4H** was synthesized in moderate yield by the reaction of 3,4-methylenedioxyacetophenone with one equivalent of (py)$_3$Cl$_2$Ti(N^{t}Bu),[52] with the poorly soluble titanium oxo byproduct readily removed by filtration (Scheme 2). The strong driving force of metal oxide formation promotes this reaction, yielding the desired imine.



Scheme 2 Synthesis of imine **4H** utilizes an imido titanium reagent.

The imines (**1H–5H**) were lithiated with ^{n}BuLi to produce a series of mono-anionic bidentate ligands (Scheme 3). The electron-withdrawing methylenedioxy moiety (–OCH$_2$O–) helps to activate the adjacent aryl protons toward deprotonation by strong bases.



Scheme 3 *Ortho*-lithiation of the acetophenone imines.

Additionally, the electron pair on the nitrogen atom coordinatively directs the lithiating agent to deprotonate the aromatic ring in an *ortho* position. The combination of these effects allows for regiospecific lithiation of these imines by ^{n}BuLi at the carbon atom *ortho* to both groups. For most of these imines (**1H–3H**, **5H**), the product lithiated species were produced by straightforward room temperature *ortho*-lithiation using ^{n}BuLi; however, in the case of **4H**, these reaction conditions led to substantial formation of byproducts. The observed unwanted products included lithiation at other positions on the aryl ring and addition products resulting from attack at the carbon of the imine moiety. In order to circumvent this problem, lithiation of **4H** was accomplished by using lower reaction temperatures (–78 °C) for longer periods, in addition to more dilute reaction concentrations.

The full range of lithiated products (**1Li–5Li**) has been characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. One notable feature of these materials is that the hydrogen atoms of the –OCH$_2$O– moiety display very large changes in their chemical shifts upon lithiation. For each of the aryl imines (**1Li–3Li**, **5Li**), the two protons of this group remained equivalent and shifted to higher field, while the ^{1}H NMR spectrum of **4Li** (derived from an alkyl imine) showed that these two protons had become inequivalent, with one shifting to higher field and one to lower field. The ^{1}H NMR spectra of both **4H** and **4Li** are shown in Fig. 1 to demonstrate this effect. Note that in the spectrum of **4H** the –OCH$_2$O– protons are equivalent, appearing at 5.28 ppm. After lithiation, the two protons are no longer equivalent and now appear as two resonances at δ 5.48 and 4.51 ppm. The ^{1}H NMR signals derived from the methylenedioxy moiety prove to be quite diagnostic in this ligand set. In fact, these protons are indicative of the ligand's environment in its transition metal complexes, as discussed below for the group (v) metal complexes. It is postulated that upon lithiation, the acetophenone imine ligands form either large clusters or polymerized species in which the ligands gather around groups of lithium ions.[53–56] The formation of aggregates of this type can result in superstructures with lower overall symmetry, explaining the inequivalence of the two ^{1}H NMR resonances for the –OCH$_2$O– moiety. This lack of symmetry can result in one or both of the methylene protons falling in the shielded region due to the ring current of aryl groups from the imines or other acetophenone moieties.[57,58] This shielding causes a high field chemical shift in the ^{1}H NMR spectrum. In the cases where one proton is shifted to lower field, it is possible that one or more of the oxygen atoms of the –OCH$_2$O– moiety are involved in the lithium coordination sphere, leading to the observed deshielding.[57]

Formation of niobium and tantalum complexes

Direct metallation of the lithiated ligands through salt metathesis with group (v) metal halides (MCl$_5$) was problematic, resulting in intractable mixtures which rapidly decomposed to give insoluble

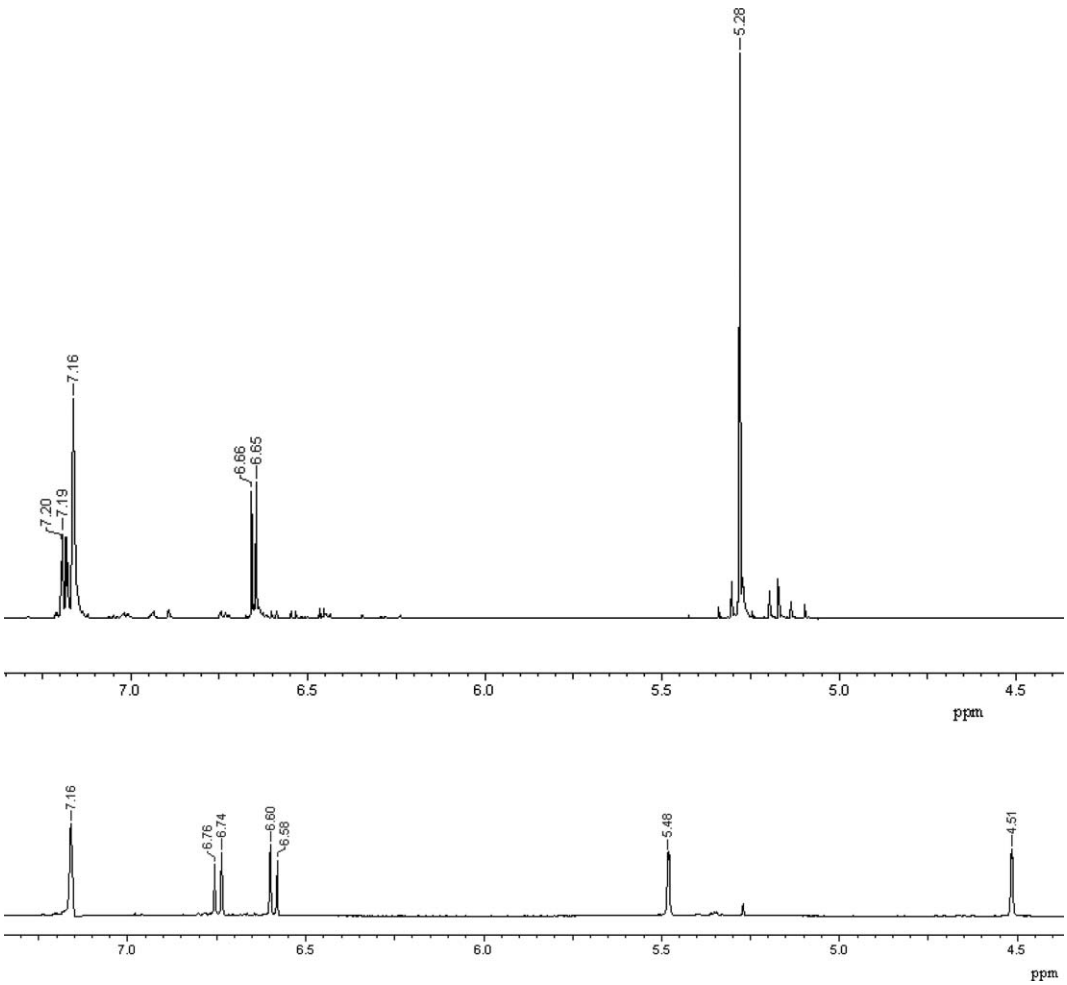
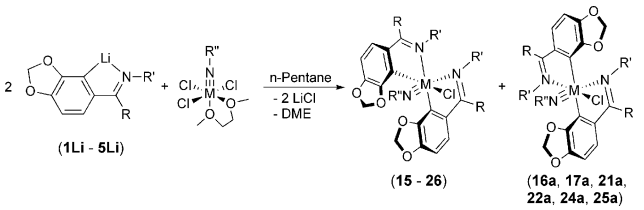


Fig. 1 ^{1}H NMR spectra of **4H** (top) and **4Li** (bottom); methyl groups omitted for clarity.

brown materials. Because of these difficulties, attention was turned to the synthesis of niobium and tantalum complexes containing the imido moiety. Various aryl and alkyl imido complexes of the form $L_2MCl_3(NR)$ (L = neutral donor ligand; M = Nb, Ta; R = aryl, alkyl) are known and thus function as excellent starting materials.[3,8–10,59–61] Use of the imido group allowed access to high-valent (M^{5+}) tantalum and niobium centers that were more stable than the native pentahalides; the strong metal–imido bond gives these species good thermal stability.[1] Furthermore, the substituent on the imido group helped to solubilize the metal precursors, such that low polarity solvents could be used.

Synthesis of the niobium and tantalum imido starting materials was based on previous literature reports. We primarily investigated niobium complexes utilizing $(DME)NbCl_3(NR)$ where R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**9**), 2,6-Et$_2$C$_6$H$_3$ (**10**), 2,6-Me$_2$C$_6$H$_3$ (**11**), Ph (**12**), or ^{t}Bu (**13**).[3,59] To show the applicability of these reactions with tantalum, we also explored complexes derived from $(DME)TaCl_3$(N-2,6-^{i}Pr$_2$C$_6$H$_3$) (**14**).[9] In general, a series of twelve niobium and tantalum imido complexes (**15–26**) were synthesized by reacting the group (V) starting materials (**9–14**) with 2 equiv. of the lithiated ligand (**1Li–5Li**; Scheme 4). The best results were observed when using pentane as solvent, in which case the reaction occurs as a slurry throughout. In all cases, products of the form $(L)_2MCl(NR)$ (L = *ortho*-metallated acetophenone imine) were produced. With



Scheme 4 Synthesis of niobium and tantalum complexes (see Table 1 for definitions of M, R, R′, and R″).

the bidentate anionic acetophenone imine ligands present, these species were characterized as six-coordinate, pseudo-octahedral complexes.

An analysis of the ligands utilized to produce the $L_2MCl(NR)$ complexes (**15–26**) indicates that a number of possible structural isomers exist. The acetophenone imine ligand does not have a large enough bite angle to span *trans* positions around the metal center. Thus, there are only two structural isomers possible where the imido group is oriented *trans* to the chloride ligand. These isomers would necessitate either a two-fold rotation axis (*trans* acetophenone imine ligands) or a mirror plane (*cis* acetophenone imine ligands). In all cases, NMR spectroscopy revealed that no such symmetry operation existed within the observed complexes—that is, in each of these metal complexes, C_1 symmetry was

Table 1 Metal complexes and selected physical properties

Complex	M	R	R′	R″	–OCH_2O– resonances δ/ppm	Number of isomers	Yield (%)
15	Nb	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.141, 5.079, 5.033, 4.950	1	93
23	Ta	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.143, 5.103, 5.056, 4.921	1	85
16	Nb	CH_3	2,6-Et$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.226, 5.211, 5.133, 5.038 (**16**) 5.580, 5.248, 5.083, 4.953 (**16a**)	2	83
24	Ta	CH_3	2,6-Et$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.246, 5.218, 5.162, 5.051 (**24**) 5.638, 5.270, 5.145, 5.019 (**24a**)	2 2	80
17	Nb	CH_3	2,6-Me$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.391, 5.137, 4.812, 4.728 (**17**) 5.365, 5.107, 5.017, 4.843 (**17a**)	2	75
25	Ta	CH_3	2,6-Me$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.250, 5.240, 5.147, 5.077 (**25**) 5.658, 5.293, 5.217, 5.060 (**25a**)	2	80
18	Nb	CH_3	CMe$_3$(^{t}Bu)	2,6-^{i}Pr$_2$C$_6$H$_3$	5.223, 5.210, 5.009, 4.856	1	62
19	Nb	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-Et$_2$C$_6$H$_3$	5.132, 5.100, 4.980, 4.957	1	75
20	Nb	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-Me$_2$C$_6$H$_3$	5.133, 5.108, 5.018, 4.845	1	66
21	Nb	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	Ph	5.387, 5.351, 5.208, 5.169 (**21**) 5.295, 5.093, 4.775, 4.743 (**21a**)	2	33
22	Nb	CH_3	2,6-^{i}Pr$_2$C$_6$H$_3$	CMe$_3$(^{t}Bu)	5.481, 4.832, 4.668, 4.581 (**22**) 5.356, 5.252, 4.730, 4.665 (**22a**)	2	20
26	Ta	H	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	5.161, 5.078, 5.058, 4.953	1	75

observed. This was best indicated by the methylenedioxy resonances of the ligand backbone, where the presence of four inequivalent signals from the four protons (on the two ligands) confirmed the C_1 symmetry of these molecules. Thus, we deduced that the imido ligand was oriented *cis* to the chloride ligand in all complexes formed, while noting that this still left four possible structural isomers (present as racemates). The final important consideration in the analysis of the $L_2MCl(NR)$ complexes involved electronic parameters. Because of the very strong metal–imido bonding, the imido group exerts a significant *trans* influence on the metal center. Thus, very weak bonding *trans* to the imido ligand is expected, favouring dative bonding of the neutral imine donor, rather than the more strongly bound anionic aryl moiety of the acetophenone imine ligand. Thus, by constraining the complexes to those containing a chloride *cis* to the imido group and a neutral imine donor *trans* to the imido group, only two structural isomers are possible (Scheme 4). This was confirmed by the resonances observed in the ^{1}H NMR for the –OCH_2O– groups, as each of the twelve new metal complexes exist as either one or two structural isomers.

In an effort to understand the factors controlling product distribution in the salt metathesis reactions, we investigated two steric aspects in relation to the isomers formed. In complexes **15–18** (Nb) and **23–26** (Ta), the bulkiest imido group (N-2,6-^{i}Pr$_2$C$_6$H$_3$) was used and the size of the ligand substituents was varied. Only one structural isomer was formed when the steric bulk of the ligand was very large (**15**, **23**, **26**) or quite small (**18**). Somewhat surprisingly, based on the X-ray crystal structures of complexes **17**, **18** and **23**, we found that the same isomer was present in both cases (Fig. 2–4). Specifically, this is the structural isomer with an acetophenone imine carbon donor atom oriented *trans* to the chloride ligand. The X-ray structure corresponded well with the solution NMR data. For example, in complex **23**, the only equivalent proton resonances observed by ^{1}H NMR spectroscopy are those resulting from freely spinning methyl groups. The isopropyl groups show diastereotopic methyls and the methylenedioxy moieties yield a total of four inequivalent resonances. Moreover, through analysis of the methylenedioxy chemical shifts while considering the relevant spatial locations

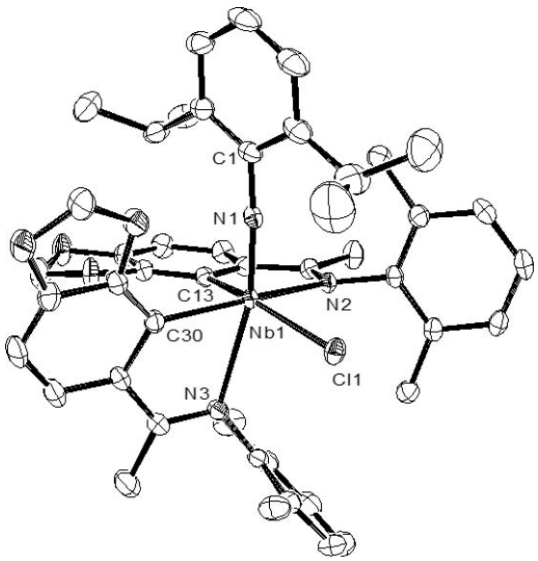


Fig. 2 ORTEP diagram (50% thermal ellipsoids) of (**3**)$_2$Nb(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**17**). Hydrogen atoms omitted for clarity. Bond lengths (Å): Nb1–Cl1 = 2.3881(6), Nb1–N1 = 1.767(2), Nb1–N2 = 2.351(2), Nb1–N3 = 2.486(2), Nb1–C13 = 2.260(2), Nb1–C30 = 2.202(2). Bond angles (°): Nb1–N1–C1 = 174.8(2), N2–Nb1–C13 = 70.51(7), N3–Nb1–C30 = 70.18(7).

in the solid-state structure, it is clear that the significant shielding of these protons is the effect of their location 3.7–4.2 Å above the aryl rings of the imido and acetophenone imine groups.[57,58] The shielding of these protons can be readily attributed to ring current effects from these aromatic systems and their approximate distances parallel their chemical shifts.[57,58]

In contrast, complexes formed from the intermediate sized ligands (Nb: **16**, **17**; Ta: **24**, **25**) yielded a mixture of two structural isomers. Given the preference for the same isomer with both sterically large and sterically small ligands described previously, we were surprised by this result. By carrying out the syntheses of these complexes at various reaction temperatures, we found that different ratios of the two isomers were produced as kinetic products that did not equilibrate in solution. That is, when examining

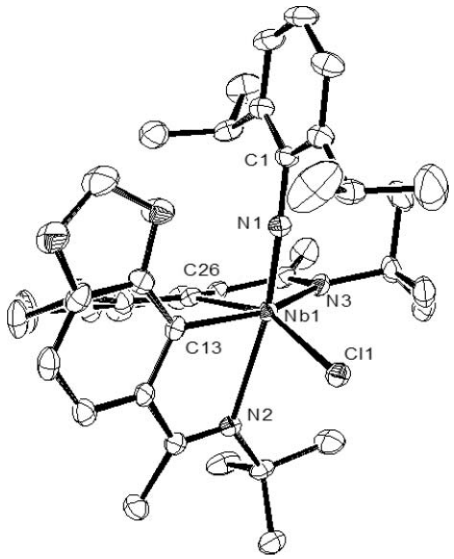


Fig. 3 ORTEP diagram (50% thermal ellipsoids) of $(\mathbf{4})_2$Nb(N-2, 6-^{i}Pr$_2$C$_6$H$_3$)Cl (**18**). Hydrogen atoms omitted for clarity. Bond lengths (Å): Nb1–Cl1 = 2.4489(7), Nb1–N1 = 1.777(2), Nb1–N2 = 2.464(2), Nb1–N3 = 2.358(2), Nb1–C13 = 2.170(3), Nb1–C26 = 2.278(3). Bond angles (°): Nb1–N1–C1 = 177.8(2), N2–Nb1–C13 = 72.82(9), N3–Nb1–C26 = 71.68(9).

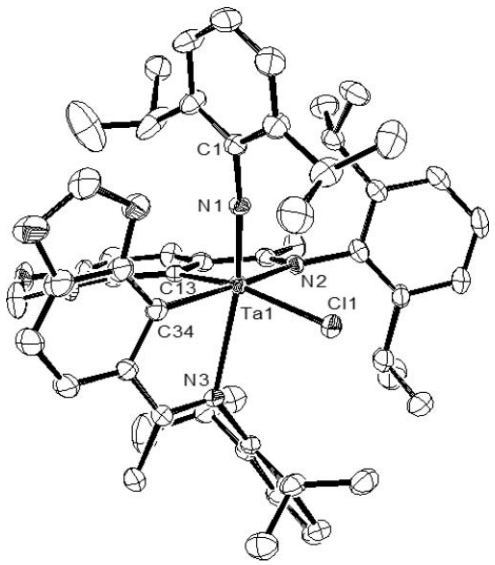


Fig. 4 ORTEP diagram (50% thermal ellipsoids) of $(\mathbf{1})_2$Ta(N-2, 6-^{i}Pr$_2$C$_6$H$_3$)Cl (**23**). Hydrogen atoms, disordered methyl group and toluene solvate molecules are omitted for clarity. Bond lengths (Å): Ta1–Cl1 = 2.3627(9), Ta1–N1 = 1.786(3), Ta1–N2 = 2.360(3), Ta1–N3 = 2.519(3), Ta1–C13 = 2.245(3), Ta1–C34 = 2.195(4). Bond angles (°): Ta1–N1–C1 = 172.7(3), N2–Ta1–C13 = 71.1(1), N3–Ta1–C34 = 70.4(1).

the room temperature NMR spectra of complexes produced under different reaction temperatures, substantially differing product ratios were observed. Variable-temperature NMR showed no change in isomeric ratios upon cooling, although the onset of some equilibration between the isomers was commonly observed near 60 °C for most isomers. The high temperature coalescence point was not reached at 100 °C for any of these four complexes. In the case of complexes **16** and **24**, we were able to grow X-ray quality crystals and determine the solid-state structure of these complexes (Fig. 5 and 6). Subsequent NMR of these crystals revealed the presence of only a single isomer (no equilibration observed), confirming that the major isomer in **16** and **24** is the same structural isomer that we observed in the previous cases. We postulate that the second isomer was observed because of the steric congestion at the metal center in the case of intermediate steric

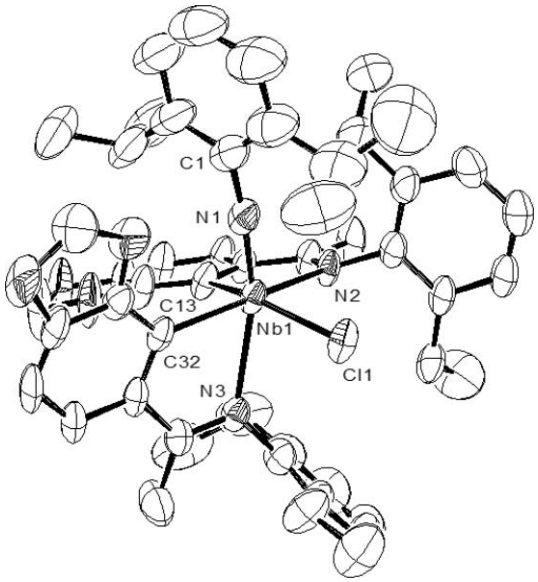


Fig. 5 ORTEP diagram (50% thermal ellipsoids) of $(\mathbf{2})_2$Nb(N-2, 6-^{i}Pr$_2$-C$_6$H$_3$)Cl (**16**). Hydrogen atoms, disordered methyl group, and diethyl ether molecule have been omitted for clarity. Bond lengths (Å): Nb1–Cl1 = 2.390(1), Nb1–N1 = 1.760(4), Nb1–N2 = 2.330(3), Nb1–N3 = 2.528(4), Nb1–C13 = 2.261(4), Nb1–C32 = 2.196(4). Bond angles (°): Nb1–N1–C1 = 173.3(3), N2–Nb1–C13 = 70.5(2), N3–Nb1–C32 = 70.1(2).

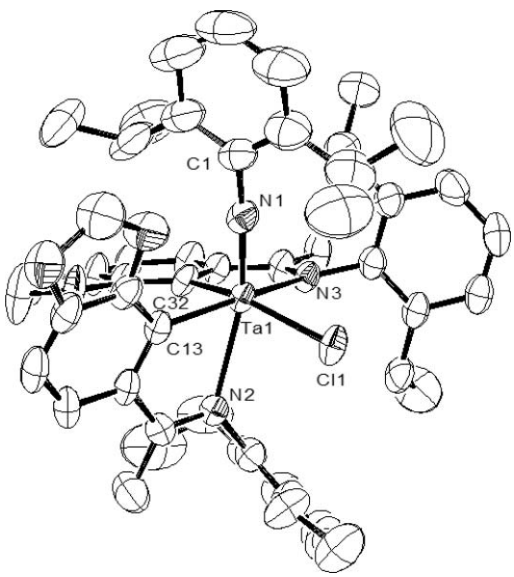


Fig. 6 ORTEP diagram (50% thermal ellipsoids) of $(\mathbf{2})_2$Ta(N-2, 6-^{i}Pr$_2$C$_6$H$_3$)Cl (**24**). Hydrogen atoms and ether solvate molecule omitted for clarity. Bond lengths (Å): Ta1–Cl1 = 2.377(1), Ta1–N1 = 1.783(4), Ta1–N2 = 2.513(4), Ta1–N3 = 2.315(3), Ta1–C13 = 2.191(4), Ta1–C32 = 2.243(4). Bond angles (°): Ta1–N1–C1 = 173.4(3), N2–Ta1–C13 = 70.1(2), N3–Ta1–C32 = 71.0(2).

bulk. With the reduced steric bulk, we suggest that isomerization pathways in the reaction intermediates are lower in energy and under the reaction conditions employed, small amounts of the minor product are formed that are unable to thermally equilibrate at room temperature. Our current investigations involve alkylation of these complexes, which may shed further insight into the production of two isomers using these intermediate sized ligands.

In a second series of experiments, the bulkiest ligand was used and the imido group on the niobium was varied in size (**15**, **19–22**). Similar to the previous set of experiments, each of these complexes was formed as either one or two structural isomers. The number of structural isomers produced during each reaction was entirely dependent upon the size of the imido group used. Complexes **15**, **19** and **20** had very bulky arylimido moieties (2,6-$R_2C_6H_3$; R = ^{i}Pr, Et, Me), resulting in the formation of only one structural isomer, while two isomers were formed when smaller imido moieties were used, as evidenced by **21** and **22**. The preferred isomer had the same relative configuration as that observed in the earlier cases, as confirmed by the X-ray crystal structure of complex **20** (Fig. 7) For reactions where two isomers were observed, the synthesis was carried out a second time at 0 °C, rather than room temperature. This did not prevent the formation of two isomers, but changed the ratios of the two isomers present. For example, the room temperature synthesis of **21** results in a 1 : 1 ratio of the two isomers, while low temperature synthesis (0 °C) of the same complex results in a 5 : 2 ratio. Thus, again we conclude that the structural isomers are not interconverting in solution at room temperature. Rather, their formation reflects the kinetic control of the products of these reactions at the employed temperatures. The major isomer for complexes **21** and **22** is the same as that described previously with the chloride ligand located *trans* to the anionic carbon of an acetophenone imine ligand, while the minor isomer contains the nitrogen atom of an acetophenone imine *trans* to the chloride. Overall, the synthesis of complexes **15–26** reveal that the salt metathesis reactions are controlled by more than just the steric size of the ligands, including such factors as reaction temperature, type of imido moiety, and the steric bulk of the ligand system.

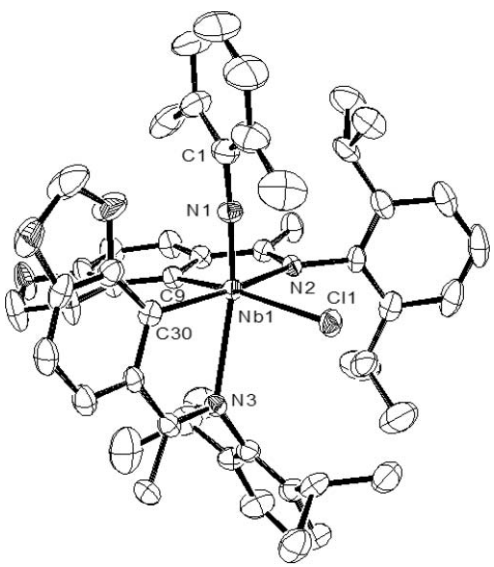


Fig. 7 ORTEP diagram (50% thermal ellipsoids) of one of the two independent molecules of (**1**)$_2$Nb(N-2,6-$Me_2C_6H_3$)Cl (**20**) in the asymmetric unit. Hydrogen atoms and ether solvate molecules are omitted for clarity. Bond lengths (Å): Nb1–Cl1 = 2.3989(8), Nb1–N1 = 1.764(3), Nb1–N2 = 2.389(3), Nb1–N3 = 2.538(3), Nb1–C9 = 2.250(3), Nb1–C30 = 2.207(3). Bond angles (°): Nb1–N1–C1 = 172.7(2), N2–Nb1–C9 = 70.7(1), N3–Nb1–C30 = 70.4(1).

Conclusions

Herein, we demonstrate that mono-anionic acetophenone imine ligands can be produced with a wide diversity of imine substituents. These ligands have proven to be strong chelating ligands for the synthesis of niobium and tantalum imido complexes of the form (L)$_2$MCl(NR) (L = *ortho*-metallated acetophenone imine; M = Nb, Ta; R = aryl, alkyl). Primarily, the complexes are synthesized as only a single structural isomer (out of at least six possible isomers). Exceptions where two isomers are observed suggest the formation of kinetic products and careful fractional crystallization allowed for the isolation of a single major isomer in several cases. These complexes are quite robust—stable to temperatures of at least 150 °C in all cases. Our ongoing investigations involve the substitution of the chloride ligand with alkyl and amido groups. Further, we are pursuing the stoichiometric and catalytic chemistry of these new complexes.

Experimental

General considerations

All moisture and air sensitive manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques and dried glassware. Diethyl ether was dried by passage through an activated alumina column. Toluene, dichloromethane and pentane were dried over 4 Å activated molecular sieves. The dried solvents were sparged with nitrogen. 1,2-Dimethoxyethane (DME), *tert*-butylamine, cyclohexylamine, and triethylamine were vacuum transferred under nitrogen from anhydrous CaH_2(s) and degassed with 3 freeze–evacuate–thaw cycles. Aniline, 2,6-diisopropylaniline, 2,6-diethylaniline and 2,6-dimethylaniline were distilled and stored over 4 Å molecular sieves. $NbCl_5$, $TaCl_5$, $ZnCl_2$, $CDCl_3$, chlorotrimethylsilane, piperonal, 3,4-methylenedioxyacetophenone and ^{n}BuLi (1.5 M in hexanes) were used as purchased. Benzene-d_6 and toluene-d_8 were vacuum transferred under nitrogen from purple Na/benzophenone ketyl and degassed with 3 freeze–evacuate–thaw cycles. Me_3SiNH(2,6-$^i Pr_2C_6H_3$) (**6**),[9] Me_3SiNH(2,6-$Et_2C_6H_3$) (**7**),[62] Me_3SiNH(2,6-$Me_2C_6H_3$) (**8**),[63] Nb(N-2,6-$^i Pr_2C_6H_3$)Cl_3(DME) (**9**),[3] Nb(N-C_6H_5)Cl_3(DME) (**12**),[59] Nb(NCMe_3)Cl_3(DME) (**13**),[59] Ta(N-2,6-$^i Pr_2C_6H_3$)Cl_3(DME) (**14**),[9] (py)$_3Cl_2$Ti(N^{t}Bu),[52] **2H**[30] and **2Li**[30] were prepared as previously described. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in benzene-d_6, $CDCl_3$, or toluene-d_8 at ambient temperature on a VXRS 400 or an Inova 600 MHz spectrometer and referenced internally to residual proton peaks at δ 7.16 ppm (C_6D_6), 2.09 ppm (C_7D_8), or 7.27 ppm ($CDCl_3$) and δ 128.0 ppm (C_6D_6), 20.4 ppm (C_7D_8), or 77.23 ppm ($CDCl_3$) for ^{13}C. Unless otherwise specified, given coupling constants are for $^3J_{HH}$. ^{7}Li{^{1}H} NMR data were obtained on a 400 MHz NMR spectrometer at ambient temperature and externally referenced to δ 0.00 ppm with LiCl (3.00 M in D_2O). IR samples were prepared as Nujol mulls between KBr plates. Melting points were performed

on a Mel-Temp; those compounds that were air sensitive were taken in a capillary tube sealed under a nitrogen atmosphere and are uncorrected. Elemental analysis of a representative series from each group of compounds was performed by Columbia Analytics, Tucson, Arizona or Galbraith Laboratories, Knoxville, Tennessee. X-ray structure determinations were performed at the Ohio Crystallographic Consortium housed at the University of Toledo. High resolution mass spectra were obtained using electron impact ionization by the Mass Spectroscopy Laboratory at the University of Illinois, Urbana, IL.

Synthesis

I. Ligand synthesis. Imines (**1H–3H**, **5H**) were synthesized according to the procedure described below:

To a solution of 3,4-methylenedioxyacetophenone (5.00 g, 30.4 mmol) or piperonal (5.00 g, 33.3 mmol) in toluene (300 mL) was added the appropriate amine (45.6 mmol) along with *p*-toluenesulfonic acid monohydrate (1.50 g). After heating the solution to 110 °C in a Dean–Stark trap for 2 d, the solution was neutralized with saturated $NaHCO_3$(aq), washed with deionized water (2 × 30 mL) and the organic portion dried over anhydrous $MgSO_4$(s). Volatiles were distilled under reduced pressure (120 °C, 200 mtorr), leaving the desired product behind. Each oil was recrystallized from methanol at −25 °C, yielding a pale yellow crystalline solid (**1H**: 8.0 g, 81%; **3H**: 6.8 g, 84%; **5H**: 8.0 g, 85%).

Lithiation of the imines (**1H–5H**) was accomplished following the general procedure:

To a solution of the imine (10 mmol) in pentane (100 mL) at 0 °C, ^{n}BuLi (7.0 mL, 1.4 M in hexanes, 9.8 mmol) was added dropwise *via* syringe. Upon addition of the ^{n}BuLi, the solution turned red. The solution was stirred for 1 h at −78 °C and brought to room temperature and stirred for 3 h. The solution was filtered and the solid was dried under vacuum, yielding a dark orange solid. The solid was washed with copious amounts of pentane to give analytically pure material.

1H. (8.0 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.691 (d, 1 H, $^4J_{HH}$ = 2.0 Hz), 7.482 (dd, 1 H, J = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz), 7.21–7.00 (m, 3 H), 6.891 (d, 1 H, J = 8.0 Hz), 6.042 (s, 2 H), 2.732 (sept, 2 H, J = 7.0 Hz), 2.051 (s, 3 H), 1.145 (d, 6 H, J = 7.0 Hz), 1.135 (d, 6 H, J = 7.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.61, 148.12, 136.65, 133.77, 129.12, 128.62, 124.16, 123.73, 122.72, 108.17, 107.94, 101.72, 29.09, 23.76, 23.28, 17.95. IR: 2952 (s), 2924 (s), 2854 (s), 2722 (w), 1859 (w), 1625 (m), 1604 (s), 1590 (m), 1506 (m), 1488 (s), 1460 (s), 1459 (s), 1438 (s), 1378 (s), 1363 (s), 1328 (w), 1288 (s), 1254 (s), 1221 (m), 1188 (m), 1039 (s), 933 (m), 898 (m), 881 (m), 817 (m), 808 (m), 775 (m), 726 (w), 690 (w), 635 (m). Anal. calcd for $C_{21}H_{25}NO_2$: C 77.98, H 7.79, N 4.33. Found: C 77.41, H 8.05, N 4.14. Melting point: 82–85 °C.

1Li. (2.6 g, 80%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.257 (d, 1 H, J = 8.4 Hz), 7.030–6.984 (m, 3 H), 6.652 (d, 1 H, J = 8.4 Hz), 4.799 (s, 2 H), 2.753 (sept, 2 H, J = 6.6 Hz), 1.900 (s, 3 H), 0.978 (d, 6 H, J = 6.6 Hz), 0.882 (d, 6 H, J = 6.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 177.41, 155.65, 146.32, 144.11, 143.67, 138.30, 125.12, 124.56, 123.54, 105.50, 97.73, 28.54, 23.52, 23.25, 18.37. ^{7}Li{^{1}H} NMR (C_6D_6, 155 MHz): δ 4.121. IR: 2955 (s), 2921 (s), 2854 (s), 1614 (m), 1588 (w), 1558 (m), 1464 (s), 1459 (s), 1380 (s), 1320 (m), 1283 (m), 1278 (m), 1242 (s), 1186 (w), 1140 (w), 1129 (w), 1109 (w), 1094 (w), 1086 (w), 1055 (w), 1037 (m), 981 (w), 933 (w), 923 (w), 873 (w), 836 (w), 800 (w), 788 (w), 778 (w), 773 (w), 721 (w). Anal. calcd for $C_{21}H_{24}LiNO_2$: C 76.58, H 7.34, N 4.25. Found: C 76.34, H 7.56, N 4.39. Melting point: 130–135 °C.

3H. (6.8 g, 84%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.893 (s, 1 H), 7.246 (d, 1 H, J = 8.0 Hz), 7.050 (d, 2 H, J = 8.0 Hz), 6.953 (t, 1 H, J = 8.0 Hz), 6.638 (d, 1 H, J = 8.0 Hz), 5.300 (s, 2 H), 1.985 (s, 6 H), 1.659 (s, 3 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 159.23, 145.32, 143.11, 142.74, 129.31, 128.42, 126.09, 122.84, 122.17, 108.32, 101.65, 98.11, 18.42, 17.21. IR: 3069 (w), 3015 (w), 2941 (m), 2901 (m), 1639 (s), 1607 (s), 1593 (s), 1504 (s), 1488 (s), 1472 (s), 1440 (s), 1365 (s), 1344 (s), 1291 (s), 1251 (s), 1222 (s), 1203 (s), 1156 (w), 1113 (m), 1092 (m), 1039 (s), 936 (m), 899 (m), 881 (m), 858 (w), 820 (m), 810 (m), 778 (m), 764 (m). Anal. calcd for $C_{17}H_{17}NO_2$: C 76.38, H 6.41, N 5.24. Found: C 76.27, H 6.18, N 4.90. Melting point: 85–92 °C.

3Li. (1.8 g, 67%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.228 (d, 1 H, J = 8.0 Hz), 7.059 (d, 2 H, J = 7.2 Hz), 6.963 (t, 1 H, J = 7.2 Hz), 6.856 (d, 1 H, J = 8.0 Hz), 4.810 (s, 2 H), 1.801 (s, 6 H), 1.645 (s, 3 H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 144.03, 143.52, 129.33, 128.57, 125.92, 125.09, 123.64, 123.01, 122.38, 107.76, 107.73, 104.89, 101.38, 97.79, 18.20, 17.33, 16.91. ^{7}Li{^{1}H} NMR (C_6D_6, 155 MHz): δ 3.671. IR: 3150 (m), 2875 (s), 1913 (w), 1837 (w), 1611 (s), 1561 (s), 1381 (s), 1321 (s), 1280 (s), 1236 (s), 1200 (s), 1164 (w), 1131 (m), 1082 (s), 1037 (s), 986 (w), 932 (s), 866 (w), 837 (m), 805 (m), 787 (s), 761 (s), 730 (w). Melting point: 136 °C (decomposition).

4H. 3,4-Methylenedioxyacetophenone (2.0 g, 12 mmol) and $(py)_3Cl_2Ti(N^tBu)$[52] (5.0 g, 12 mmol) were dissolved separately in toluene (50 mL). Then, the reactants were mixed at 0 °C and stirred for 1 h. The solution was brought to room temperature and stirred for 24 h, forming a red slurry. The slurry was filtered and the liquid portion dried under vacuum. The yellowish oil was dissolved in pentane (30 mL), filtered and concentrated, yielding a light green oil (1.7 g, 64%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.825 (s, 1 H), 7.189 (d, 1 H, J = 8.4 Hz), 6.652 (d, 1 H, J = 8.4 Hz), 5.281 (s, 2 H), 1.899 (s, 3 H), 1.328 (s, 9 H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 159.77, 149.34, 148.57, 138.10, 121.40, 108.06, 107.64, 101.45, 55.27, 31.20, 18.64. IR: 3078 (s), 2965 (m), 2780 (m), 2359 (m), 2050 (w), 1963 (w), 1845 (m), 1640 (s), 1609 (s), 1491 (s), 1434 (s), 1362 (s), 1275 (s), 1111 (m), 1039 (s), 936 (m), 884 (m), 813 (m). $HRMS_{calcd}$: 219.1259 for $C_{13}H_{17}NO_2$. $HRMS_{measd}$: 219.1263.

4Li. (0.9 g, 40%). ^{1}H NMR (C_6D_6, 400 MHz): δ 6.744 (d, 1 H, J = 7.8 Hz), 6.591 (d, 1 H, J = 7.8 Hz), 5.485 (d, 1 H, $^2J_{HH}$ = 1.8 Hz), 4.520 (d, 1 H, $^2J_{HH}$ = 1.8 Hz), 2.185 (s, 3 H), 1.001 (s, 9 H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 178.21, 157.18, 151.80, 142.47, 120.82, 107.96, 97.28, 55.57, 33.49, 30.66, 22.86. ^{7}Li{^{1}H} NMR (C_6D_6, 155 MHz): δ 2.820. IR: 2924 (s), 2855 (s), 2723 (w), 2361 (m), 1618 (m), 1559 (m), 1460 (s), 1375 (s), 1302 (s), 1268 (m), 1042 (s), 942 (m), 799 (w), 721 (w). Melting point: 125 °C (decomposition).

5H. (8.0 g, 85%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.901 (s, 1 H), 7.741 (s, 1 H), 7.191-7.154 (m, 3 H), 6.942 (d, 1 H, J = 7.2 Hz), 6.570 (d, 1 H, J = 7.2 Hz), 5.201 (s, 2 H), 3.15 (sept, 2 H, J = 8.0 Hz), 1.18 (d, 12 H, J = 8.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 161.21, 151.10, 150.31, 149.23, 138.11, 131.83, 125.82, 124.74, 123.62, 108.53, 107.12, 101.75, 28.64, 23.82; IR:

2904 (s), 2729 (w), 1845 (w), 1765 (w), 1625 (m), 1597 (m), 1452 (s), 1375 (s), 1251 (s), 1194 (m), 1173 (m), 1091 (m), 1039 (s), 933 (m), 887 (w), 853 (w), 807 (m), 783 (m), 750 (m), 722 (m). Anal. calcd for $C_{20}H_{23}NO_2$: C 77.64, H 7.50, N 4.53. Found: C 77.40, H 7.59, N 4.52. Melting point: 88–94 °C.

5Li. (2.1 g, 68%). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.036 (s, 1 H), 7.045 (m, 3 H), 6.899 (d, 1 H, J = 7.2 Hz), 6.616 (d, 1 H, J = 7.2 Hz), 4.975 (s, 2 H), 2.953 (sept, 2 H, J = 8.0 Hz), 0.990 (d, 12 H, J = 8.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 175.22, 161.21, 155.53, 149.34, 139.12, 129.53, 126.01, 124.32, 123.53, 105.91, 102.01, 98.84, 28.94, 24.14; ^{7}Li{^{1}H} NMR (C_6D_6, 155 MHz): δ 3.897; IR: 3061 (w), 2854 (s), 2725 (w), 2361 (w), 1622 (s), 1588 (m), 1553 (s), 1504 (w), 1486 (m), 1460 (s), 1382 (s), 1369 (s), 1323 (s), 1254 (s), 1174 (s), 1134 (w), 1114 (w), 1094 (s), 1046 (s), 934 (m), 861 (m), 788 (s). Anal. calcd for $C_{20}H_{22}LiNO_2$: C 76.18, H 7.03, N 4.44. Found: C 76.64, H 7.06, N 4.73. Melting point: 143 °C (decomposition).

II. Metal precursor synthesis.

Nb(N-2,6-Et$_2$C$_6$H$_3$)Cl$_3$(DME) (***10***) (*ref. 64*). Toluene (40 mL) was added to $NbCl_5$ (5.0 g, 19 mmol) and the solution was cooled to 0 °C. Dimethoxyethane (2.0 mL) was added to **7** (8.40 g, 37.4 mmol). The **7**/DME solution was slowly added to the $NbCl_5$/toluene forming a purple solution and stirred for 1 h at 0 °C. After stirring overnight at room temperature, the solution was filtered, concentrated to half volume, and cooled to −30 °C. The purple precipitate was washed with pentane to yield a purple powder (5.7 g, 69%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.031 (d, 2 H, J = 8 Hz), 6.952 (t, 1 H, J = 8 Hz), 4.164–4.092 (m, 4 H), 3.493 (s, 3 H), 3.162 (s, 3 H), 2.655 (q, 4 H, J = 8 Hz), 1.354 (t, 6 H, J = 8 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz):[65] 145.40, 128.07, 126.98, 75.43, 70.67, 68.37, 62.62, 26.40, 17.60.

Nb(N-2,6-Me$_2$C$_6$H$_3$)Cl$_3$(DME) (***11***) (*ref. 64*). Toluene (40 mL) was added to $NbCl_5$ (5.0 g, 19 mmol) and the solution was cooled to 0 °C. Dimethoxyethane (2.0 mL) was added to **8** (7.3 g, 38 mmol). The **8**/DME solution was slowly added to the $NbCl_5$/toluene forming a red solution and stirred for 1 h at 0 °C. After stirring overnight at room temperature, the solution was filtered, concentrated to half volume, and cooled to −30 °C. The red precipitate was washed with pentane to yield a red powder (5.4 g, 72%). ^{1}H NMR (C_6D_6, 600 MHz): δ 6.730 (d, 2 H, J = 7 Hz), 6.595 (t, 1 H, J = 7 Hz), 3.430 (s, 3 H), 3.090 (s, 3 H), 3.019-2.996 (m, 4 H), 2.941 (s, 6 H). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz):[65] 138.75, 128.25, 127.29, 75.20, 70.55, 68.40, 62.40, 20.08.

III. Metal complex synthesis.

*(**1**)$_2$Nb(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl* (***15***). To a flask containing both **9** (2.0 g, 4.3 mmol) and **1Li** (2.8 g, 8.6 mmol), pentane (100 mL) was added. The mixture was stirred overnight at ambient temperature. Then, the orange precipitate was filtered and remaining ligand was removed by washing with pentane (3 × 30 mL). Lithium chloride was readily removed by extracting the product into toluene (100 mL) and filtering. The solution was then dried under vacuum. The resulting oil was recrystallized from ether at −25 °C, yielding an orange crystalline solid (3.8 g, 93%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.208 (dd, 1 H, J = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.145 (d, 1 H, J = 7.8 Hz), 7.069–7.049 (m, 4 H), 7.017 (d, 1 H, J = 7.8 Hz), 7.005 (d, 1 H, J = 7.8 Hz), 6.931 (t, 1 H, J = 7.8 Hz), 6.883 (d, 1 H, J = 8.0 Hz), 6.819 (d, 1 H, J = 8.0 Hz), 6.607 (d, 1 H, J = 8.0 Hz), 6.498 (d, 1 H, J = 8.0 Hz), 5.141 (s, 1 H), 5.079 (s, 1 H), 5.033 (s, 1 H), 4.950 (s, 1 H), 4.731 (sept, 1 H, J = 7.2 Hz), 3.951 (sept, 1 H, J = 6.6 Hz), 3.330 (sept, 1 H, J = 6.6 Hz), 3.280 (sept, 1 H, J = 6.6 Hz), 2.816 (sept, 1 H, J = 6.6 Hz), 2.452 (sept, 1 H, J = 6.6 Hz), 1.783 (s, 3 H), 1.690 (s, 3 H), 1.427 (d, 3 H, J = 6.6 Hz), 1.339 (d, 3 H, J = 6.6 Hz), 1.185 (d, 3 H, J = 6.6 Hz), 1.073 (d, 3 H, J = 6.6 Hz), 1.038 (d, 3 H, J = 7.2 Hz), 0.930 (d, 3 H, J = 6.6 Hz), 0.844–0.804 (m, 12 H), 0.703 (d, 3 H, J = 6.6 Hz), 0.631 (d, 3 H, J = 6.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 183.12, 180.20, 156.76, 152.44, 150.10, 149.23, 148.36, 148.07, 148.05, 146.78, 143.60, 143.59, 143.41, 143.40, 142.25, 142.24, 141.69, 141.68, 140.81, 140.59, 127.32, 126.89, 126.80, 125.48, 125.00, 124.76, 123.64, 123.07, 122.36, 122.11, 108.38, 106.15, 99.82, 99.62, 29.90, 29.28, 28.92, 28.46, 28.37, 27.95, 26.98, 26.74, 26.21, 25.49, 25.41, 25.25, 25.15, 25.11, 25.08, 24.53, 23.78, 23.29, 22.11, 21.51. IR: 3403 (m), 2854 (s), 2726 (w), 1635 (w), 1549 (w), 1463 (s), 1406 (m), 1367 (s), 1298 (m), 1250 (m), 1243 (m), 1172 (w), 1150 (w), 1122 (w), 1092 (w), 1052 (w), 985 (w), 952 (w), 860 (w). Anal. calcd for $C_{54}H_{65}ClN_3NbO_4$: C 65.85,[66] H 6.91, N 4.43. Found: C 66.21, H 6.51, N 4.22. Melting point: >250 °C.

*(**2**)$_2$Nb(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl* (***16***). To a flask containing both **9** (0.500 g, 1.07 mmol) and **2Li** (0.736 g, 2.44 mmol), pentane (50 mL) was added. The mixture was stirred at room temperature for 30 h forming an orange slurry. Volatiles were removed under vacuum, and the resulting solid was washed with pentane (2 × 50 mL) and extracted into toluene (50 mL). After filtration, drying under vacuum yielded a fine orange solid (0.80 g, 83%). ^{1}H NMR spectroscopic data of this product revealed a non-interconverting mixture of two isomers in a 1 : 1 ratio. The separation of ^{1}H NMR and ^{13}C NMR peaks was possible by variable temperature NMR spectra of the product at 80 °C in toluene-d$_8$, which leads to 3 : 1 peak ratios assignable as major and minor isomers. ^{1}H NMR (C_7D_8, 400 MHz): **major isomer** (**16**): δ 7.193 (d, 2 H, J = 7.8 Hz), 7.123 (s, 2 H), 7.045 (d, 2 H, J = 7.8 Hz), 6.991–6.940 (m, 5 H), 6.523 (d, 1 H, J = 7.8 Hz), 6.490 (d, 1 H, J = 7.8 Hz), 5.226 (s, 1 H), 5.211 (s, 1 H), 5.133 (s, 1 H), 5.038 (s, 1 H), 4.586 (sept, 1 H, J = 6.8 Hz), 4.217 (sept, 1 H, J = 6.8 Hz), 2.179 (dq, 2 H, $^2J_{HH}$ = 15 Hz, J = 7.0 Hz), 2.105 (s, 3 H), 2.083 (d, 6 H, J = 6.8 Hz), 1.815 (dq, 2 H, $^2J_{HH}$ = 15 Hz, J = 7.0 Hz), 1.738 (s, 3 H), 1.731 (d, 3 H, J = 7.0 Hz), 1.699 (dq, 2 H, $^2J_{HH}$ = 15 Hz, J = 7.0 Hz), 1.577 (dq, 2 H, $^2J_{HH}$= 15 Hz, J = 7.0 Hz), 1.238 (d, 3 H, J = 7.0 Hz), 1.201 (d, 3 H, 7.0 Hz), 1.107 (d, 3 H, J = 7.0 Hz), 1.092 (d, 6 H, J = 6.8 Hz); **minor isomer** (**16a**): 6.930–6.872 (m, 8 H), 6.836 (d, 1 H, J = 7.6 Hz), 6.785 (d, 1 H, J = 7.6 Hz), 6.545 (d, 1 H, J = 7.6 Hz), 6.417 (d, 1 H, J = 7.6 Hz), 6.278 (d, 1 H, J = 7.6 Hz), 5.580 (s, 1 H), 5.248 (s, 1 H), 5.083 (s, 1 H), 4.953 (s, 1 H), 4.493 (sept, 1 H, J = 6.4 Hz), 3.816 (sept, 1 H, J = 6.4 Hz), 3.166 (dq, 2 H, $^2J_{HH}$= 15 Hz, J = 7.0 Hz), 2.547 (dq, 2 H, $^2J_{HH}$= 15 Hz, J = 7.0 Hz), 2.430 (dq, 2 H, $^2J_{HH}$= 15 Hz, J = 7.0 Hz), 2.374 (dq, 2 H, $^2J_{HH}$= 15 Hz, J = 7.0 Hz), 2.101 (s, 3 H), 1.897 (s, 3 H), 1.405 (d, 3 H, J = 7.0 Hz), 1.261 (d, 3 H, J = 6.4 Hz), 1.141 (d, 3 H, J = 7.0 Hz), 1.040 (d, 3 H, J = 7.0 Hz), 0.839 (d, 3 H, J = 7.0 Hz), 0.730 (d, 3 H, J = 6.4 Hz), 0.683–0.646 (m, 6 H). ^{13}C{^{1}H} NMR (C_7D_8, 100 MHz): **major isomer** (**16**): δ 195.15, 182.70, 182.46, 180.36, 179.59, 156.21, 152.40, 150.07, 149.87, 148.23, 147.60, 143.15, 140.00, 138.04, 137.35, 135.89, 135.55, 129.15, 126.86, 126.45, 126.18, 126.00, 124.99, 124.69, 122.33, 121.93,

121.76, 107.97, 105.79, 99.81, 28.36, 27.58, 25.30, 24.62, 24.45, 24.30, 24.25, 24.08, 23.79, 23.64, 23.52, 19.18, 18.82, 18.52, 15.55, 15.35, 14.79, 12.85; **minor isomer** (**16a**): 200.40, 152.27, 151.71, 149.69, 149.30, 149.25, 149.14, 148.58, 148.41, 147.45, 142.63, 138.90, 137.84, 137.25, 136.97, 136.88, 135.14, 126.31, 125.54, 124.82, 124.57, 124.25, 123.91, 123.75, 123.26, 123.08, 121.67, 106.83, 105.59, 100.99, 29.53, 28.73, 28.53, 26.30, 25.83, 24.16, 23.19, 21.58, 20.69, 20.48, 19.23, 18.05, 15.52, 14.55, 13.84, 12.19. IR: 1915 (s), 1549 (w), 1459 (s), 1375 (m), 1302 (w), 1244 (m), 1176 (w), 1147 (w), 1115 (w), 1046 (m), 941 (m), 860 (w), 804 (w), 778 (w), 725 (w). Anal. calcd for $C_{50}H_{57}ClN_3NbO_4$: C 67.30, H 6.44, N 4.71. Found: C 66.58, H 6.76, N 4.33. Melting point: 205 °C (decomposition).

*(**3**)$_2$Nb(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**17**).* To a flask containing both **9** (0.500 g, 1.07 mmol) and **3Li** (0.638 g, 2.44 mmol), pentane (50 mL) was added, forming a pale yellow slurry. The mixture was stirred at room temperature for 30 h forming a brown slurry. Volatiles were removed under vacuum, and the resulting solid was washed with pentane (3 × 50 mL) and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was dried under vacuum. The resulting oil was recrystallized from ether at −25 °C, yielding an orange crystalline solid (0.67, 75%). ^{1}H NMR showed a non-interconverting mixture of two isomers with a 1 : 1 ratio of peak heights. ^{1}H NMR signals assignable to each isomer was achieved by repetition of the above synthetic procedure at 0 °C, which leads to a 3 : 1 ratio of the isomers. ^{1}H NMR (C_6D_6, 400 MHz): **major isomer** (**17**): δ 7.194 (d, 1 H, J = 7.6 Hz), 7.185 (d, 1 H, J = 7.6 Hz), 6.998 (t, 1 H, J = 7.6 Hz), 6.951 (t, 1 H, J = 7.6 Hz), 6.814–6.775 (m, 6 H), 6.673 (d, 1 H, J = 7.6 Hz), 6.636 (d, 1 H, J = 7.6 Hz), 6.441 (d, 1 H, J = 7.6 Hz), 5.391 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 5.137 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.812 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.728 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 3.814 (sept, 1 H, J = 6.8 Hz), 3.683 (sept, 1 H, J = 6.8 Hz), 2.894 (s, 3 H), 2.135 (s, 3 H), 2.028 (s, 3 H), 1.794 (s, 3 H), 1.712 (d, 3 H, J = 6.8 Hz), 1.172 (d, 3 H, J = 6.8 Hz), 1.139 (s, 3 H), 1.122 (s, 3 H), 1.007 (d, 3 H, J = 6.8 Hz), 0.741 (d, 3 H, J = 6.8 Hz); **minor isomer** (**17a**): 7.274 (d, 1 H, J = 7.6 Hz), 7.079–7.051 (m, 3 H), 6.966–6.941 (m, 5 H), 6.746 (d, 1 H, J = 7.6 Hz), 6.703 (d, 1 H, J = 7.6 Hz), 6.595 (d, 1 H, J = 7.6 Hz), 6.520 (d, 1 H, J = 7.6 Hz), 5.365 (s, 1 H), 5.107 (s, 1 H), 5.017 (s, 1 H), 4.843 (s, 1 H), 3.376 (sept, 1 H, J = 6.8 Hz), 2.952 (sept, 1 H, J = 6.8 Hz), 2.802 (s, 3 H), 2.236 (s, 3 H), 1.885 (s, 3 H), 1.760 (s, 3 H), 1.614 (d, 3 H, J = 6.8 Hz), 1.104 (s, 3 H), 0.880 (s, 3 H), 0.850 (d, 3 H, J = 6.8 Hz), 0.587 (d, 3 H, J = 6.8 Hz), 0.476 (d, 3 H, J = 6.8 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): **major isomer** (**17**): δ 182.90, 179.60, 156.35, 152.58, 150.32, 150.15, 150.07, 149.55, 149.36, 148.12, 147.67, 143.15, 140.03, 133.11, 132.09, 130.70, 130.50, 129.93, 129.52, 128.86, 128.02, 126.24, 125.67, 125.28, 125.09, 122.58, 122.19, 108.32, 106.23, 100.23, 99.90, 28.68, 27.91, 25.22, 24.38, 24.31, 24.09, 20.49, 18.75, 18.27, 18.02, 17.81, 17.25; **minor isomer** (**17a**): 183.23, 181.12, 152.90, 151.93, 150.25, 149.91, 149.63, 149.53, 147.31, 142.84, 138.86, 132.75, 132.16, 131.28, 129.76, 127.58, 125.38, 124.78, 124.32, 123.90, 123.64, 123.32, 122.72, 122.29, 108.07, 108.00, 107.29, 106.06, 101.70, 100.83, 29.91, 29.10, 29.01, 26.18, 24.74, 22.25, 21.09, 20.09, 19.67, 19.53, 18.86, 18.53. IR: 1923 (s), 1552 (m), 1459 (s), 1403 (m), 1377 (w), 1306 (m), 1242 (s), 1190 (w), 1147 (w), 1117 (w), 1091 (w), 1049 (m), 942 (w), 861 (w), 792 (w), 764 (w). Anal. calcd for $C_{46}H_{49}ClN_3NbO_4$: C 66.07, H 5.91, N 5.02. Found: C 66.43, H 6.82, N 5.49. Melting point: 195–200 °C.

*(**4**)$_2$Nb(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**18**).* A flask containing both **9** (0.321 g, 0.684 mmol) and **4Li** (0.315 g, 1.38 mmol) was cooled to 0 °C. Then, pentane (50 mL) was added and the mixture was stirred cold for 30 min. After warming to room temperature and stirring for 24 h, a pale yellow slurry formed. The mixture was dried under vacuum and washed with pentane (3 × 50 mL), leaving a brown solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was then dried under vacuum. The resultant oil was recrystallized from ether at −25 °C, yielding a dark brown crystalline solid (0.32, 62%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.134 (d, 1 H, J = 7.6 Hz), 7.064 (d, 1 H, J = 7.6 Hz), 7.024 (d, 1 H, J = 7.6 Hz), 6.920 (t, 1 H, J = 7.6 Hz), 6.801 (d, 1 H, J = 7.6 Hz), 6.629 (d, 1 H, J = 7.6 Hz), 6.543 (d, 1 H, J = 7.6 Hz), 5.223 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 5.210 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 5.009 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.856 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.069 (sept, 1 H, J = 7.2 Hz), 2.646 (sept, 1 H, J = 7.2 Hz), 2.088 (s, 3 H), 2.021 (s, 3 H), 1.585 (d, 3 H, J = 7.2 Hz), 1.519 (s, 9 H), 1.390 (d, 3 H, J = 7.2 Hz), 1.335 (s, 9 H), 1.035 (d, 3 H, J = 7.2 Hz), 1.018 (d, 3 H, J = 7.2 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 179.80, 173.15, 149.63, 148.14, 147.87, 147.15, 141.49, 125.23, 123.75, 123.46, 122.97, 122.21, 120.13, 119.26, 107.27, 105.76, 101.95, 99.87, 99.20, 59.72, 58.07, 32.66, 32.15, 31.18, 28.49, 28.42, 27.94, 25.30, 25.07, 24.66, 23.67, 22.92, 22.56, 21.32. IR: 1683 (w), 1459 (s), 1375 (s), 1301 (w), 1256 (w), 1152 (w), 1043 (w), 941 (w), 804 (w), 724 (w). Anal. calcd for $C_{38}H_{49}ClN_3NbO_4$: C 61.66, H 6.67, N 5.68. Found: C 61.98, H 6.66, N 5.62. Melting point: 150 °C (decomposition).

*(**1**)$_2$Nb(N-2,6-Et$_2$C$_6$H$_3$)Cl (**19**).* To a flask containing both **10** (0.40 g, 0.99 mmol) and **1Li** (0.744 g, 1.82 mmol), pentane (50 mL) was added, forming an orange slurry. The mixture was stirred at room temperature for 30 h, forming a brown slurry. The mixture was dried under vacuum and washed with pentane (3 × 50 mL), leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was dried under vacuum. The resultant oil was recrystallized from ether at −25 °C, yielding an orange crystalline solid (0.65 g, 75%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.208 (d, 1 H, J = 8.0 Hz), 7.157 (t, 1 H, J = 8.0 Hz), 7.065 (d, 1 H, J = 8.0 Hz), 7.08–7.04 (m, 3 H), 6.932 (d, 1 H, J = 7.0 Hz), 6.909 (d, 1 H, J = 7.0 Hz), 6.885 (d, 1 H, J = 8.0 Hz), 6.855 (t, 1 H, J = 7.0 Hz), 6.829 (d, 1 H, J = 8.0 Hz), 6.610 (d, 1 H, J = 8.0 Hz), 6.518 (d, 1 H, J = 8.0 Hz), 5.132 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.100 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 4.980 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 4.957 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 3.588 (sept, 1 H, J = 7.0 Hz), 3.520 (dt, 1 H, $^2J_{HH}$ = 23 Hz, J = 8.0 Hz), 3.441 (dt, 1 H, $^2J_{HH}$ = 23 Hz, J = 8.0 Hz), 3.361 (sept, 1 H, J = 7.0 Hz), 3.066 (dt, 1 H, $^2J_{HH}$ = 23 Hz, J = 8.0 Hz), 2.853 (sept, 1 H, J = 7.0 Hz), 2.461 (dt, 1 H, $^2J_{HH}$ = 23 Hz, J = 8.0 Hz), 2.430 (sept, 1 H, J = 7.0 Hz), 1.731 (s, 3 H), 1.703 (s, 3 H), 1.418 (d, 3 H, J = 7.0 Hz), 1.190 (t, 3 H, J = 8.0 Hz), 1.009 (t, 3 H, J = 8.0 Hz), 0.893 (d, 3 H, J = 7.0 Hz), 0.881 (d, 3 H, J = 7.0 Hz), 0.869 (d, 3 H, J = 7.0 Hz), 0.802 (d, 3 H, J = 7.0 Hz), 0.791 (d, 3 H, J = 7.0 Hz), 0.668 (d, 3 H, J = 7.0 Hz), 0.656 (d, 3 H, J = 7.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 183.30, 180.36, 156.97, 152.28, 150.02, 149.22, 148.55, 148.17 (×2), 146.02, 143.66 (×2), 143.39, 142.14,

141.99, 141.78 (×2), 140.89, 140.27, 127.20, 126.95, 126.75, 125.75, 125.32, 124.96, 124.80, 124.45 (×2), 123.65, 122.35, 108.42, 106.18, 99.90, 99.59, 29.72, 29.25, 28.50, 28.04, 26.75, 26.68, 26.09, 25.89, 25.50, 25.22 (×2), 24.69 (×2), 23.28, 21.93, 21.21, 15.62, 14.97. IR: 2854 (s), 1655 (m), 1635 (m), 1549 (m), 1462 (s), 1406 (m), 1377 (s), 1351 (w), 1298 (w), 1250 (w), 1172 (w), 1150 (w), 1092 (w), 1052 (w), 942 (w), 860 (w). Anal. calcd for $C_{52}H_{61}ClN_3NbO_4$: C 67.86, H 6.68, N 4.57. Found: C 67.28, H 7.19, N 4.26. Melting point: 180–187 °C.

*(**1**)$_2$Nb(N-2,6-Me$_2$C$_6$H$_3$)Cl (**20**).* To a flask containing both **11** (0.40 g, 0.98 mmol) and **1Li** (0.796 g, 2.44 mmol), pentane (50 mL) was added, forming a pale yellow slurry. The mixture was stirred at room temperature for 30 h, forming a brown slurry. The mixture was dried under vacuum and washed with pentane (3 × 50 mL), leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was then dried under vacuum. The resultant oil was recrystallized from ether at −25 °C, yielding an orange crystalline solid (0.58 g, 66%). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.208 (dd, 1 H, J = 8.0 Hz, $^4J_{HH}$ = 1 Hz), 7.162 (t, 1 H, J = 8.0 Hz), 7.08–7.04 (m, 4 H), 6.868 (d, 1 H, J = 8.0 Hz), 6.820 (d, 1 H, J = 7.0 Hz), 6.819 (d, 1 H, J = 8.0 Hz), 6.800 (d, 1 H, J = 7.0 Hz), 6.695 (t, 1 H, J = 7.0 Hz), 6.595 (d, 1 H, J = 8.0 Hz), 6.521 (d, 1 H, J = 8.0 Hz), 5.133 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.108 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.018 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 4.845 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 3.668 (sept, 1 H, J = 7.0 Hz), 3.373 (sept, 1 H, J = 7.0 Hz), 2.938 (sept, 1 H, J = 7.0 Hz), 2.799 (s, 3 H), 2.434 (sept, 1 H, J = 7.0 Hz), 2.233 (s, 3 H), 1.721 (s, 3 H), 1.706 (s, 3 H), 1.411 (d, 3 H, J = 7.0 Hz), 0.923 (d, 3 H, J = 7.0 Hz), 0.914 (d, 3 H, J = 7.0 Hz), 0.874 (d, 3 H, J = 7.0 Hz), 0.800 (d, 3 H, J = 7.0 Hz), 0.788 (d, 3 H, J = 7.0 Hz), 0.754 (d, 3 H, J = 7.0 Hz), 0.677 (d, 3 H, J = 7.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 151.85, 149.90, 149.36 (×2), 148.64 (×2), 147.96, 143.68, 143.22, 142.03 (×2), 141.70 (×2), 141.00, 140.70, 139.85 (×2), 136.23 (×2), 127.48, 127.22, 127.11, 127.02, 126.70, 125.71, 124.85, 124.40, 123.89, 123.68, 122.39, 108.40, 106.27, 99.91, 99.64, 29.75, 29.26, 28.53, 28.02, 26.78, 26.60, 25.49, 25.29, 25.01, 24.77, 24.57, 23.20, 21.80, 21.08, 21.03, 19.63. IR: 2905 (s), 1650 (m), 1635 (m), 1509 (m), 1444 (s), 1401 (w), 1357 (m), 1345 (w), 1280 (m), 1238 (w), 1154 (w), 1144 (w), 1087 (w), 1052 (w), 938 (w), 802 (w). Anal. calcd for $C_{50}H_{57}ClN_3NbO_4$: C 67.30, H 6.44, N 4.71. Found: C 67.05, H 6.69, N 4.36. Melting point: 149 °C (decomposition).

*(**1**)$_2$Nb(N-C$_6$H$_5$)Cl (**21**).* To a flask containing both **12** (2.0 g, 7.2 mmol) and **1Li** (2.4 g, 14 mmol), which had been cooled (0 °C), cold pentane (100 mL) was added, forming a yellow slurry. The mixture was kept at 0 °C for 1 h, brought to room temperature and stirred for 3 h. The mixture was filtered and washed with pentane (3 × 30 mL). Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was concentrated under vacuum to precipitate a fine brown solid with a 5 : 2 ratio of the products (1.8 g, 33%). ^{1}H NMR (C_6D_6, 600 MHz): **major isomer** (**21**): δ 7.261 (d, 1 H, J = 8.0 Hz), 7.175 (t, 1 H, J = 8.0 Hz), 7.09–7.02 (m, 3 H), 7.042 (d, 1 H, J = 8.0 Hz), 6.947 (d, 1 H, J = 8.0 Hz), 6.837 (t, 2 H, J = 7.0 Hz), 6.763 (d, 1 H, J = 8.0 Hz), 6.697 (d, 1 H, J = 8.0 Hz), 6.609 (t, 1 H, J = 7.0 Hz), 6.476 (d, 1 H, J = 7.0 Hz), 6.204 (d, 2 H, J = 7.0 Hz), 5.387 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.351 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.208 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 5.169 (d, 1 H, $^2J_{HH}$ = 1.0 Hz), 3.726 (sept, 1 H, J = 7.0 Hz), 3.442 (sept, 1 H, J = 7.0 Hz), 3.281 (sept, 1 H, J = 7.0 Hz), 3.187 (sept, 1 H, J = 7.0 Hz), 1.828 (s, 3 H), 1.796 (s, 3 H), 1.444 (d, 3 H, J = 7.0 Hz), 1.241 (d, 3 H, J = 7.0 Hz), 1.139 (d, 3 H, J = 7.0 Hz), 1.058 (d, 3 H, J = 7.0 Hz), 1.004 (d, 3 H, J = 7.0 Hz), 0.819 (d, 3 H, J = 7.0 Hz), 0.783 (d, 3 H, J = 7.0 Hz), 0.588 (d, 3 H, J = 7.0 Hz); **minor isomer** (**21a**): 7.277 (d, 1 H, J = 8.0 Hz), 7.241 (d, 1 H, J = 8.0 Hz), 7.191 (d, 1 H, J = 8.0 Hz), 7.003 (d, 1 H, J = 8.0 Hz), 6.981 (d, 1 H, J = 8.0 Hz), 6.963 (t, 1 H, J = 8.0 Hz), 6.960 (t, 1 H, J = 8.0 Hz), 6.937 (t, 1 H, J = 8.0 Hz), 6.896 (d, 1 H, J = 8.0 Hz), 6.866 (d, 1 H, J = 8.0 Hz), 6.845 (t, 1 H, J = 8.0 Hz), 6.784 (d, 1 H, J = 8.0 Hz), 6.711 (t, 1 H, J = 8.0 Hz), 6.479 (d, 1 H, J = 8.0 Hz), 6.451 (d, 1 H, J = 8.0 Hz), 5.295 (d, 1 H, $^2J_{HH}$ = 2.0 Hz), 5.093 (d, 1 H, $^2J_{HH}$ = 2.0 Hz), 4.775 (d, 1 H, $^2J_{HH}$ = 2.0 Hz), 4.743 (d, 1 H, $^2J_{HH}$ = 2.0 Hz), 3.761 (sept, 1 H, J = 7.0 Hz), 3.645 (sept, 1 H, J = 7.0 Hz), 2.932 (sept, 1 H, J = 7.0 Hz), 2.804 (sept, 1 H, J = 7.0 Hz), 2.054 (s, 3 H), 1.919 (s, 3 H), 1.597 (d, 3 H, J = 7.0 Hz), 1.077 (d, 3 H, J = 7.0 Hz), 1.029 (d, 3 H, J = 7.0 Hz), 0.895 (d, 3 H, J = 7.0 Hz), 0.878 (d, 3 H, J = 7.0 Hz), 0.798 (d, 3 H, J = 7.0 Hz), 0.599 (d, 3 H, J = 7.0 Hz), 0.563 (d, 3 H, J = 7.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): **major isomer** (**21**): δ 185.12, 184.48, 159.09, 152.14, 150.48, 149.33, 149.24 (x 2), 148.94, 142.13, 141.95, 141.79, 141.74, 141.02, 139.51, 127.90, 127.55, 127.28, 127.14, 125.18, 124.98, 124.61, 124.53, 124.48, 124.19, 123.86, 122.83, 122.74, 106.94, 105.67, 100.51, 100.39, 28.86, 28.67, 28.66, 26.96, 25.77, 25.35, 25.15, 24.79, 24.69, 24.65, 23.77, 23.32, 20.51, 20.11; **minor isomer** (**21a**): 182.27, 180.46, 176.75, 169.34, 153.06, 151.40, 150.14, 149.94, 149.57, 147.17, 144.95, 143.43, 142.03, 141.74, 141.70, 138.76, 128.92, 128.68, 127.28, 126.67, 126.44, 125.55, 124.74, 124.63, 124.40, 124.23, 122.62, 122.06, 107.56, 106.23, 100.68, 100.09, 30.75, 29.90, 29.04, 28.20, 27.36, 26.78, 26.71, 25.59, 25.51 (x 2), 23.07, 22.72, 22.07, 21.73. IR: 1543 (m), 1460 (s), 1408 (m), 1377 (m), 1312 (m), 1245 (m), 1145 (w), 1095 (w), 1047 (m), 937 (w), 860 (w), 802 (m), 778 (w), 688 (w). Anal. calcd for $C_{48}H_{53}ClN_3NbO_4$: C 66.70, H 6.18, N 4.86. Found: C 65.28, H 6.23, N 4.70. Melting point: 195 °C (decomposition).

*(**1**)$_2$Nb(N-CMe$_3$)Cl (**22**).* A flask containing both **13** (1.0 g, 3.9 mmol) and **1Li** (2.6 g, 7.8 mmol) was cooled to 0 °C, followed by the addition of cooled pentane (50 mL). A yellow slurry formed and was stirred at 0 °C for 1 h. The mixture was warmed to room temperature and stirred for an additional 3 h. The mixture was filtered and washed with pentane (3 × 20 mL). Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The resulting solution was then dried under vacuum to yield a fine dark green solid (0.6 g, 20%). The ^{1}H NMR shows a mixture of two isomers in a 3 : 1 ratio. ^{1}H NMR (C_6D_6, 600 MHz): **major isomer** (**22**): δ 7.290 (d, 1 H, J = 7.8 Hz), 7.203 (d, 1 H, J = 7.8 Hz), 7.086 (t, 2 H, J = 7.8 Hz), 7.016 (d, 2 H, J = 7.8 Hz), 6.691 (d, 1 H, J = 7.8 Hz), 6.549 (d, 1 H, J = 7.8 Hz), 6.489 (d, 1 H, J = 7.8 Hz), 6.365 (d, 1 H, J = 7.8 Hz), 5.481 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.832 (d, 1 H, $^2J_{HH}$ = 1.2 Hz), 4.668 (s, 1 H), 4.581 (s, 1 H), 4.250 (sept, 2 H, J = 7.2 Hz), 4.087 (sept, 2 H, J = 7.2 Hz), 3.314 (s, 3 H), 3.118 (s, 9 H), 1.900 (s, 3 H), 1.670 (d, 6 H, J = 7.2 Hz), 1.615 (d, 6 H, J = 7.2 Hz), 1.510 (d, 6 H, J = 7.2 Hz), 0.932 (d, 6 H, J = 7.2 Hz); **minor isomer** (**22a**): 7.338 (d, 1 H, J = 7.8 Hz), 7.257 (d, 1 H, J = 7.8 Hz), 7.191 (d, 1 H, J = 7.8 Hz), 7.092 (d, 2 H, J = 7.8 Hz), 6.977 (t, 2 H, J = 7.8 Hz), 6.921 (d, 1 H, J = 7.8 Hz), 6.849 (d, 1 H, J = 7.8 Hz),

6.646 (d, 1 H, $J = 7.8$ Hz), 5.356 (d, 1 H, $^2J_{HH} = 1.2$ Hz), 5.252 (d, 1 H, $^2J_{HH} = 1.2$ Hz), 4.730 (s, 1 H), 4.665 (s, 1 H), 3.959 (sept, 2 H, $J = 6.6$ Hz), 3.519 (sept, 2 H, $J = 6.6$ Hz), 3.380 (s, 3 H), 3.263 (s, 9 H), 2.110 (s, 3 H), 1.430 (d, 3 H, $J = 6.6$ Hz), 1.405 (d, 3 H, $J = 6.6$ Hz), 1.365 (d, 3 H, $J = 6.6$ Hz), 1.301 (d, 3 H, $J = 6.6$ Hz), 1.172 (d, 3 H, $J = 6.6$ Hz), 1.002 (d, 3 H, $J = 6.6$ Hz), 0.691 (d, 3 H, $J = 6.6$ Hz), 0.510 (d, 3 H, $J = 6.6$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): **major isomer** (**22**): δ 156.12, 151.65, 150.18, 139.39, 137.83, 130.08, 129.84, 128.39, 127.90, 127.20, 126.89, 126.35, 125.94, 125.34, 125.33, 125.30, 125.13, 124.90, 123.90, 109.33, 109.10, 107.37, 101.15, 34.54, 31.96, 30.30, 30.26, 29.95, 29.74, 29.31, 27.10, 26.86, 26.40, 26.29, 25.46, 24.93, 24.45, 22.93, 22.19, 22.09, 19.56; **minor isomer** (**22a**): 153.41, 146.65, 142.93, 142.44, 140.79, 140.73, 135.61, 128.73, 128.30, 126.01, 125.07, 124.85, 124.55, 119.18, 108.71, 108.45, 106.90, 102.87, 102.61, 101.46, 101.40, 100.24, 85.45, 35.15, 32.70, 32.51, 32.42, 31.73, 29.86, 29.08, 28.34, 27.03, 26.96, 26.57, 26.21, 25.61, 24.75, 24.34, 24.23, 22.48, 19.11. IR: 2926 (s), 2853 (s), 2355 (s), 1555 (w), 1492 (m), 1456 (s), 1373 (m), 1243 (m), 1046 (m), 823 (w). Melting Point: 175 °C (decomposition).

*(**1**)$_2$Ta(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**23**).* To a flask containing both **14** (0.30 g, 0.54 mmol) and **1Li** (0.352 g, 1.08 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 × 50 mL), and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL), filtering and removing solvent under vacuum (0.51, 85%). Crystals suitable for X-ray diffraction were recrystallized from a 1 : 1 ratio of toluene and *n*-pentane after two days at –18 °C. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.195 (d, 1 H, $J = 7.2$ Hz), 7.131 (d, 1 H, $J = 7.2$ Hz), 7.114–7.064 (m, 4 H), 7.057 (d, 1 H, $J = 7.8$ Hz), 7.034 (t, 1 H, $J = 7.2$ Hz), 6.913 (d, 1 H, $J = 7.8$ Hz), 6.888 (d, 1 H, $J = 6.0$ Hz), 6.875 (d, 1 H, $J = 6.0$ Hz), 6.621 (d, 1 H, $J = 7.8$ Hz), 6.497 (d, 1 H, $J = 7.8$ Hz), 5.143 (s, 1 H), 5.103 (s, 1 H), 5.065 (s, 1 H), 4.921 (s, 1 H), 4.686 (sept, 1 H, $J = 6.6$ Hz), 3.901 (sept, 1 H, $J = 6.6$ Hz), 3.308 (sept, 1 H, $J = 6.6$ Hz), 3.268 (sept, 1 H, $J = 6.6$ Hz), 2.640 (sept, 1 H, $J = 6.6$ Hz), 2.399 (sept, 1 H, $J = 6.6$ Hz), 1.775 (s, 3 H), 1.658 (s, 3 H), 1.404 (d, 3 H, $J = 6.6$ Hz), 1.359 (d, 3 H, $J = 6.6$ Hz), 1.267 (d, 3 H, $J = 6.6$ Hz), 1.091 (d, 3 H, $J = 6.6$ Hz), 1.043 (d, 3 H, $J = 6.6$ Hz), 0.913 (d, 3 H, $J = 6.6$ Hz), 0.837–0.809 (m, 12 H), 0.679 (d, 3 H, $J = 6.6$ Hz), 0.578 (d, 3 H, $J = 6.6$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): δ 183.93, 181.34, 179.63, 178.38, 154.52, 153.26, 150.73, 150.42, 150.09, 148.29, 147.26, 147.13, 143.85, 143.26, 142.61, 142.36, 141.98, 140.91, 127.57, 126.98, 126.92, 126.15, 124.91, 124.46, 124.26, 123.65, 123.36, 122.42, 121.38, 108.24, 106.14, 99.93, 99.78, 29.82, 29.28, 28.65, 28.45, 27.94, 27.10, 26.80, 26.29, 25.71, 25.56, 25.26, 25.22, 25.09, 25.02, 24.80, 23.51, 23.35, 22.64, 22.04. IR: 1547 (m), 1459 (s), 1408 (w), 1376 (w), 1303 (w), 1248 (m), 1150 (w), 1123 (w), 1094 (w), 1050 (w), 943 (w), 863 (w), 800 (w), 777 (w). Anal. calcd for $C_{54}H_{65}ClN_3O_4Ta$: C 62.57, H 6.32, N 4.04. Found: C 62.66, H 6.11, N 4.02. Melting point: 210 °C (decomposition).

*(**2**)$_2$Ta(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**24**).* To a flask containing both **14** (0.20 g, 0.36 mmol) and **2Li** (0.217 g, 0.723 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 × 50 mL), and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (30 mL) and filtering. ^{1}H NMR spectroscopic data of this product revealed a non-interconverting mixture of two isomers in a 2 : 1 ratio. The separation of ^{1}H NMR and ^{13}C NMR peaks was possible by variable temperature NMR studies of the product at 42 °C in C_6D_6 which leads to 3 : 1 peak ratios assignable as major and minor isomers. Crystals suitable for X-ray diffraction were recrystallized from ether after a day at –25 °C (0.28 g, 80%). ^{1}H NMR (C_6D_6, 400 MHz): **major isomer** (**24**): δ 7.216 (d, 2 H, $J = 8.0$ Hz), 7.197 (d, 2 H, $J = 8.0$ Hz), 7.052 (d, 1 H, $J = 8.0$ Hz), 7.013–6.868 (m, 4 H), 6.591 (dd, 2 H, $J = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz), 6.534 (dd, 2 H, $J = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz), 5.246 (s, 1 H), 5.218 (s, 1 H), 5.162 (s, 1 H), 5.051 (s, 1 H), 4.573 (sept, 1 H, $J = 7.2$ Hz), 4.219 (sept, 1 H, $J = 7.2$ Hz), 3.149 (dq, 2 H, $^2J_{HH} = 16$ Hz, $J = 7.2$ Hz), 2.620 (dq, 2 H, $^2J_{HH} = 16$ Hz, $J = 7.2$ Hz), 2.170 (dq, 2H, $^2J_{HH} = 16$ Hz, $J = 7.2$ Hz), 1.720 (dq, 2 H, $^2J_{HH} = 16$ Hz, $J = 7.2$ Hz), 1.622 (s, 3 H), 1.592 (s, 3 H), 1.372 (d, 3 H, $J = 7.2$ Hz), 1.319 (d, 3 H, $J = 7.2$ Hz), 1.139 (t, 3 H, $J = 7.2$ Hz), 1.108 (t, 3 H, $J = 7.2$ Hz), 0.869 (d, 3 H, $J = 7.2$ Hz), 0.813 (d, 3 H, $J = 7.2$ Hz), 0.784 (t, 3 H, $J = 7.2$ Hz), 0.753 (t, 3 H, $J = 7.2$ Hz); **minor isomer** (**24a**): 7.258 (d, 2 H, $J = 7.6$ Hz), 7.094–7.020 (m, 3 H), 6.841 (d, 2 H, $J = 7.6$ Hz), 6.774 (d, 2 H, $J = 8.0$ Hz), 6.742 (d, 2 H, $J = 8.0$ Hz), 6.466 (dd, 1 H, $J = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz), 6.353 (dd, 1 H, $J = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz), 5.638 (s, 1 H), 5.270 (s, 1 H), 5.145 (s, 1 H), 5.019 (s, 1 H), 3.749 (sept, 1 H, $J = 7.2$ Hz), 3.412 (dq, 2 H, $^2J = 16$ Hz, $J = 7.2$ Hz), 3.335 (sept, 1 H, $J = 7.2$ Hz), 2.364 (dq, 2 H, $^2J = 16$ Hz, $J = 7.2$ Hz), 1.896 (dq, 2 H, $^2J = 16$ Hz, $J = 7.2$ Hz), 1.695 (dq, 2 H, $^2J = 16$ Hz, $J = 7.2$ Hz), 1.539 (s, 3 H), 1.530 (d, 3 H, $J = 7.2$ Hz), 1.522 (s, 3 H), 1.253 (d, 3 H, $J = 7.2$ Hz), 1.205 (d, 3 H, $J = 7.2$ Hz), 1.149 (t, 3 H, $J = 7.2$ Hz), 1.104 (t, 3 H, $J = 7.2$ Hz), 0.791 (t, 3 H, $J = 7.2$ Hz), 0.744 (t, 3 H, $J = 7.2$ Hz), 0.714 (d, 3 H, $J = 7.2$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): **major isomer** (**24**): δ 183.59, 181.09, 178.95, 178.90, 158.18, 153.35, 150.76, 150.38, 149.62, 148.32, 148.18, 147.95, 143.19, 138.58, 137.94, 136.55, 136.36, 127.30, 126.97, 126.50, 126.30, 125.82, 125.59, 124.45, 123.25, 122.09, 121.58, 108.20, 106.14, 100.30, 100.08, 30.08, 28.33, 27.50, 25.21, 24.83, 24.77, 24.61, 24.33, 24.03, 23.98, 23.73, 19.35, 16.23, 15.30, 14.68, 13.43; **minor isomer** (**24a**): 182.22, 178.65, 175.98, 172.56, 150.20, 149.62, 147.82, 144.71, 143.04, 141.44, 140.21, 138.41, 137.72, 135.70, 128.40, 128.16, 126.73, 126.08 (x 2), 125.26, 124.87, 124.62, 124.55, 124.42, 123.83, 122.95, 107.25, 105.88, 100.93, 100.24, 28.88, 28.46, 27.75, 26.74, 26.21, 25.77, 25.60, 23.49, 22.02, 20.03, 18.75, 16.28, 15.92, 15.01, 14.37, 12.82. IR: 2923 (s), 2856 (s), 1459 (s), 1375 (m), 1248 (w), 1122 (w), 1050 (w), 943 (w), 805 (w), 723 (w). Anal. calcd for $C_{50}H_{57}ClN_3O_4Ta$: C 61.25, H 5.86, N 4.29. Found: C 61.58, H 6.19, N 4.17. Melting point: 190–195 °C.

*(**3**)$_2$Ta(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**25**).* To a flask containing both **14** (0.133 g, 0.240 mmol) and **3Li** (0.125 g, 0.482 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 × 50 mL), and dried under vacuum, leaving a fine orange solid. The fine powder was redissolved in toluene and the insoluble LiCl was filtered off. Removal of volatiles under vacuum leaves behind a brownish oil. The oil was recrystallized from ether at –25 °C, yielding an orange crystalline solid. ^{1}H NMR shows a mixture of two isomers with a

1 : 1 ratio. Synthesis of this product at 0 °C results in the formation of major and minor isomers in a 3 : 1 ratio (0.18 g, 80%). ^{1}H NMR (C_6D_6, 600 MHz): **major isomer** (**25**): 7.258 (d, 1 H, J = 7.2 Hz), 7.038 (d, 1 H, J = 7.2 Hz), 6.990 (d, 1 H, J = 7.2 Hz), 6.930–6.884 (m, 3 H), 6.882 (d, 1 H, J = 7.8 Hz), 6.862 (d, 1 H, J = 7.2 Hz), 6.855 (d, 1 H, J = 7.8 Hz), 6.815 (d, 1 H, J = 7.8 Hz), 6.688 (t, 1 H, J = 7.8 Hz), 6.588 (d, 1 H, J = 7.8 Hz), 6.533 (d, 1 H, J = 7.8 Hz), 5.250 (s, 1 H), 5.240 (s, 1 H), 5.147 (s, 1 H), 5.077 (s, 1 H), 4.616 (sept, 1 H, J = 6.6 Hz), 4.318 (sept, 1 H, J = 6.6 Hz), 2.354 (s, 3 H), 1.869 (s, 3 H), 1.593 (s, 3 H), 1.481 (s, 3 H), 1.466 (s, 3 H), 1.435 (d, 3 H, J = 6.6 Hz), 1.365 (d, 3 H, J = 6.6 Hz), 1.331 (s, 3 H), 1.222 (d, 3 H, J = 6.6 Hz), 0.810 (d, 3 H, J = 6.6 Hz); **minor isomer** (**25a**): 7.128 (d, 1 H, J = 7.8 Hz), 7.085 (d, 1 H, J = 7.8 Hz), 7.035 (d, 1 H, J = 7.8 Hz), 6.962–6.930 (m, 6 H), 6.741 (t, 1 H, J = 7.8 Hz), 6.507 (d, 1 H, J = 8.4 Hz), 6.481 (d, 1 H, J = 8.4 Hz), 6.342 (d, 1 H, J = 7.8 Hz), 5.658 (s, 1 H), 5.293 (s, 1 H), 5.217 (s, 1 H), 5.060 (s, 1 H), 3.760 (sept, 1 H, J = 6.6 Hz), 3.576 (sept, 1 H, J = 6.6 Hz), 2.403 (s, 3 H), 2.189 (s, 3 H), 2.139 (s, 3 H), 1.897 (s, 3 H), 1.663 (d, 3 H, J = 6.6 Hz), 1.580 (s, 3 H), 1.292 (d, 3 H, J = 6.6 Hz), 1.199 (s, 3 H), 1.157 (d, 3 H, J = 6.6 Hz), 0.710 (d, 3 H, J = 6.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): **major isomer** (**25**): δ 183.68, 180.74, 178.99, 178.90, 158.04, 150.94, 150.74, 150.43, 149.32, 149.10, 148.55, 142.95, 141.24, 133.38, 132.34, 131.34, 130.72, 129.97, 128.89, 128.75, 128.54, 126.44, 125.85, 125.79, 124.47, 123.22, 121.97, 121.53, 108.18, 106.25, 100.37, 100.13, 28.26, 27.58, 25.43, 24.58, 24.22, 24.19, 20.48, 18.64, 18.19, 18.01, 17.13; **minor isomer** (**25a**): 184.30, 182.57, 178.01, 172.39, 150.36, 150.22, 149.68, 149.54, 147.80, 147.21, 133.02, 132.91, 131.71, 130.10, 129.46, 127.97, 127.49, 125.65, 125.42, 125.03, 124.59, 123.70, 123.30, 121.82, 108.06, 107.33, 106.01, 101.71, 100.92, 100.31, 29.96, 28.85, 28.51, 26.24, 24.82, 22.36, 21.16, 20.14, 19.75, 19.63, 19.23, 18.53, 18.05; IR: 3175 (w), 2926 (s), 2864 (s), 1550 (m), 1492 (w), 1456 (s), 1373 (s), 1347 (w), 1243 (m), 1119 (w), 1088 (w), 1046 (m), 937 (w), 823 (w), 761 (w). Anal. calcd for $C_{46}H_{49}ClN_3O_4Ta$: C 59.77, H 5.34, N 4.55. Found: C 59.63, H 5.32, N 4.33. Melting point: 150 °C (decomposition).

*(**5**)$_2$Ta(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (**26**).* To a flask containing both **14** (0.60 g, 1.1 mmol) and **5Li** (0.813 g, 2.58 mmol), pentane (100 mL) was added, forming a yellow slurry. The mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (3 × 30 mL), and dried under vacuum, leaving a fine orange solid. The fine powder was redissolved in toluene and the insoluble LiCl was filtered off. Volatiles were removed under vacuum. The resulting oil was recrystallized from ether at –25 °C, yielding an orange crystalline solid (0.74 g, 75%). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.050 (s, 1 H), 7.957 (s, 1 H), 7.281 (d, 1 H, J = 7.8 Hz), 7.261 (d, 1 H, J = 7.8 Hz), 7.188–6.906 (m, 8 H), 6.639 (d, 1 H, J = 7.8 Hz), 6.573 (d, 1 H, J = 7.8 Hz), 6.440 (d, 1 H, J = 7.8 Hz), 5.161 (s, 1 H), 5.078 (s, 1 H), 5.058 (s, 1 H), 4.953 (s, 1 H), 4.754 (sept, 1 H, J = 6.6 Hz), 4.116 (sept, 1 H, J = 6.6 Hz), 3.739 (sept, 1 H, J = 6.6 Hz), 3.339 (sept, 1 H, J = 6.6 Hz), 2.780 (sept, 1 H, J = 6.6 Hz), 2.685 (sept, 1 H, J = 6.6 Hz), 1.303 (d, 3 H, J = 6.6 Hz), 1.260 (d, 3 H, J = 6.6 Hz), 1.170 (d, 3 H, J = 6.6 Hz), 0.991–0.862 (m, 18 H), 0.826 (d, 3 H, J = 6.6 Hz), 0.721 (d, 3 H, J = 6.6 Hz), 0.671 (d, 3 H, J = 6.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 177.01, 176.35, 153.28, 151.03, 150.53, 150.52, 149.32, 143.78, 142.78, 142.27, 141.26, 141.03, 137.79, 128.93, 127.85, 127.68, 127.45, 126.95, 126.37, 125.94, 125.72, 124.00, 123.93, 123.65, 123.03, 122.86, 122.22, 109.26, 106.66, 100.36, 99.99, 29.88, 29.05, 28.61, 28.27, 28.04, 27.90, 27.78, 27.53, 25.78, 25.47, 25.26, 25.14, 24.58, 24.36, 23.45, 23.13, 23.08, 22.76, 21.89; IR: 2923 (s), 2856 (s), 1608 (w), 1552 (w), 1459 (s), 1410 (w), 1376 (m), 1250 (m), 1167 (w), 1111 (w), 1058 (w), 798 (w), 723 (w). Anal. calcd for $C_{52}H_{61}ClN_3O_4Ta$: C 61.93, H 6.10, N 4.17. Found: C 62.02, H 5.96, N 4.15. Melting point: 185 °C (decomposition).

Crystallography

Summaries of crystal data and collection parameters for crystal structures of **16**, **17**, **18**, **20**, **23** and **24** are provided in Table 2. Detailed descriptions of data collection, as well as data solution, are provided below. ORTEP diagrams were generated with the ORTEP-3 software package.[67] For each sample, a suitable crystal was mounted on a pulled glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART[68] diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to the indicated temperature using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT.[69] The final unit cell parameters were determined by a least-squares refinement of the reflections with $I > 10\sigma(I)$. Data analysis using Siemens XPREP[70] and the successful solution and refinement of the structure determined the space group. An empirical absorption correction was applied using SADABS.[71] Equivalent reflections were averaged, and the structures were solved by direct methods using the SHELXTL software package.[72] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined.

16. X-ray quality crystals were grown from a saturated solution of diethyl ether at –20 °C. The asymmetric unit contains one half molecule of disordered solvent located at an inversion center. Additionally, one ligand methyl group is disordered over two positions. The disordered solvent molecule was refined isotropically. The final cycle of full-matrix least-squares refinement was based on 11 698 observed reflections and 558 variable parameters and converged yielding final residuals: R = 0.0814, R_{all} = 0.1200 and GOF = 1.002.

17. X-ray quality crystals were grown from a saturated solution of diethyl ether at –20 °C. The final cycle of full-matrix least-squares refinement was based on 10 183 observed reflections and 496 variable parameters and converged yielding final residuals: R = 0.0361, R_{all} = 0.0903 and GOF = 0.928.

18. X-ray quality crystals were grown from a saturated solution of diethyl ether at –20 °C. The final cycle of full-matrix least-squares refinement was based on 9101 observed reflections and 424 variable parameters and converged yielding final residuals: R = 0.0389, R_{all} = 0.0863 and GOF = 0.936.

20. X-ray quality crystals were grown from a saturated solution of diethyl ether at –20 °C. The asymmetric unit contained two independent molecules of compound **20**, as well as two ordered

Table 2 Crystal data and collection parameters

Compound	**16**	**17**	**18**	**20**	**23**	**24**
Formula	$C_{50}H_{57}ClN_3NbO_4\cdot\frac{1}{2}C_4H_{10}O$	$C_{46}H_{49}ClN_3NbO_4$	$C_{38}H_{49}ClN_3NbO_4$	$C_{100}H_{114}Cl_2N_6Nb_2O_8\cdot 2C_4H_{10}O$	$C_{54}H_{65}ClN_3O_4Ta\cdot 2C_7H_8$	$C_{50}H_{57}ClN_3O_4Ta\cdot\frac{1}{2}C_4H_{10}O$
FW	929.41	836.24	740.16	1932.93	1220.76	1017.45
Space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$Pbca$ (#61)	$P2_1/n$ (#14)	$C2/c$ (#15)	$P\bar{1}$ (#2)
T/K	175(2)	140(2)	140(2)	170(2)	140(2)	200(2)
a/Å	9.557(1)	13.4669(6)	17.678(1)	24.0051(8)	20.5332(8)	9.5748(5)
b/Å	12.424(2)	12.2295(5)	11.2151(7)	18.6894(6)	14.7874(6)	12.4236(6)
c/Å	21.471(3)	25.270(1)	36.896(2)	24.3056(8)	39.729(2)	21.464(1)
α/°	106.767(3)	90.000	90.000	90.000	90.000	106.673(1)
β/°	91.047(3)	99.774(1)	90.000	113.790(1)	99.180(1)	91.012(1)
γ/°	101.570(3)	90.000	90.000	90.000	90.000	101.091(1)
V/Å^3	2383.4(5)	4101.4(3)	7314.9(8)	9977.9(6)	11908.6(8)	2393.0(2)
Z	2	4	8	4	8	2
D_{calcd}/g cm^{-3}	1.295	1.354	1.344	1.287	1.362	1.412
Diffractometer	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART
Radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
Detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector
Scan type, width	ω, 0.3°	ω, 0.3°	ω, 0.3°	ω, 0.3°	ω, 0.3°	ω, 0.3°
Scan speed	30 s/frame	40 s/frame	45 s/frame	30 s/frame	30 s/frame	40 s/frame
No. of reflections measured	Hemisphere	Hemisphere	Hemisphere	Hemisphere	Hemisphere	Hemisphere
2θ range/°	2.0–56.9	3.1–56.6	2.2–56.6	2.0–56.6	2.1–56.6	2.0–56.6
Crystal dimensions/mm	0.60 × 0.16 × 0.06	0.20 × 0.10 × 0.10	0.08 × 0.06 × 0.02	0.34 × 0.18 × 0.06	0.14 × 0.10 × 0.08	0.20 × 0.05 × 0.05
No. of reflections measured	25 946	45 419	78 495	112 567	66 517	27 256
No. of unique reflections	11 698	10 183	9101	24 814	14 845	11 859
No. of observations	11 698	10 183	9101	24 814	14 845	11 859
R_{int}	0.0724	0.0727	0.1337	0.0940	0.0614	0.0443
No. of parameters	558	496	424	1153	669	549
R, R_w, R_{all}	0.0814, 0.2050, 0.1200	0.0361, 0.0903, 0.0546	0.0389, 0.0865, 0.0863	0.0586, 0.1287, 0.1117	0.0406,0.0929, 0.0545	0.0451, 0.0976, 0.0623
GOF	1.002	0.928	0.936	1.011	1.044	1.028

diethyl ether solvent molecules. The final cycle of full-matrix least-squares refinement was based on 24 814 observed reflections and 1153 variable parameters and converged yielding final residuals: $R = 0.0586$, $R_{all} = 0.1117$ and GOF = 1.011.

23. X-ray quality crystals were grown from a layered solution of toluene and pentane at –20 °C. In addition to compound **23**, the asymmetric unit contained two molecules of disordered toluene, located in three separate regions. Additionally, one isopropyl methyl group is disordered over two positions. The toluene molecules were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 14 845 observed reflections and 669 variable parameters and converged yielding final residuals: $R = 0.0406$, $R_{all} = 0.0545$ and GOF 1.044.

24. X-ray quality crystals were grown from a saturated solution of diethyl ether at –20 °C. The asymmetric unit contained one half molecule of disordered diethyl ether located at an inversion center. The disordered solvent molecule was refined isotropically. The final cycle of full-matrix least-squares refinement was based on 11 859 observed reflections and 549 variable parameters and converged yielding final residuals: $R = 0.0451$, $R_{all} = 0.0623$ and GOF = 1.028.

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References

1 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, John Wiley & Sons, 1988.
2 D. S. Williams, D. W. Thompson and A. V. Korolev, *J. Am. Chem. Soc.*, 1996, **118**, 6526–6527.
3 K. S. Heinselman, V. M. Miskowski, S. J. Geib, L. C. Wang and M. D. Hopkins, *Inorg. Chem.*, 1997, **36**, 5530–5538.
4 D. S. Williams and A. V. Korolev, *Inorg. Chem.*, 1998, **37**, 3809–3819.
5 P. A. Finn, M. S. King, P. A. Kilty and R. E. McCarley, *J. Am. Chem. Soc.*, 1975, **97**, 220–221.
6 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 1391–1401.
7 T. C. Jones, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc., Chem. Commun.*, 1984, 205–206.
8 H. T. Chiu, S. H. Chuang, C. E. Tsai, G. H. Lee and S. M. Peng, *Polyhedron*, 1998, **17**, 2187–2190.
9 Y. W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.*, 1989, **28**, 3860–3868.

10 J. M. Benito, E. de Jesus, F. J. de la Mata, J. C. Flores, R. Gomez and P. Gomez-Sal, *J. Organomet. Chem.*, 2002, **664**, 258–267.
11 J. M. Benito, E. de Jesus, F. J. de la Mata, J. C. Flores, R. Gomez and P. Gomez-Sal, *J. Organomet. Chem.*, 2006, **691**, 3602–3608.
12 A. Baunemann, D. Bekermann, T. B. Thiede, H. Parala, M. Winter, C. Gemel and R. A. Fischer, *Dalton Trans.*, 2008, 3715–3722.
13 K. R. Gust, M. J. Heeg and C. H. Winter, *Polyhedron*, 2001, **20**, 805–813.
14 S. M. Pugh, A. J. Blake, L. H. Gade and P. Mountford, *Inorg. Chem.*, 2001, **40**, 3992–4001.
15 J. A. R. Schmidt and J. Arnold, *J. Am. Chem. Soc.*, 2001, **123**, 8424–8425.
16 G. W. Parshall, *Acc. Chem. Res.*, 1970, **3**, 139–144.
17 G. W. Parshall, *Acc. Chem. Res.*, 1975, **8**, 113–117.
18 M. I. Bruce, *Angew. Chem., Int. Ed.*, 1977, **16**, 73–86.
19 D. A. Colby, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2006, **128**, 5604–5605.
20 C. S. Cao, Y. H. Li, Y. H. Shi and A. L. Odom, *Chem. Commun.*, 2004, 2002–2003.
21 F. Kakiuchi and S. Murai, *Acc. Chem. Res.*, 2002, **35**, 826–834.
22 V. Ritleng, C. Sirlin and M. Pfeffer, *Chem. Rev.*, 2002, **102**, 1731–1769.
23 X. W. Li, P. Chen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2005, **24**, 4810–4815.
24 R. Y. Lai, K. Surekha, A. Hayashi, F. Ozawa, Y. H. Liu, S. M. Peng and S. T. Liu, *Organometallics*, 2007, **26**, 1062–1068.
25 X. W. Li, A. R. Chianese, T. Vogel and R. H. Crabtree, *Org. Lett.*, 2005, **7**, 5437–5440.
26 S. Basu, S. Dutta, M. G. B. Drew and S. Bhattacharya, *J. Organomet. Chem.*, 2006, **691**, 3581–3588.
27 J. Vicente, M. T. Chicote, I. Vicente-Hernandez and D. Bautista, *Inorg. Chem.*, 2008, **47**, 9592–9605.
28 D. L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S. T. Hilton and D. R. Russell, *Dalton Trans.*, 2003, 4132–4138.
29 B. C. de Pater, E. J. Zijp, H. W. Fruhauf, J. M. Ernsting, C. J. Elsevier and K. Vrieze, *Organometallics*, 2004, **23**, 269–279.
30 T. I. Baiz and J. A. R. Schmidt, *Organometallics*, 2007, **26**, 4094–4097.
31 Y. Y. Scaffidi-Domianello, A. A. Nazarov, M. Haukka, M. Galanski, B. K. Keppler, J. Schneider, P. W. Du, R. Eisenberg and V. Y. Kukushkin, *Inorg. Chem.*, 2007, **46**, 4469–4482.
32 F. Lorenzini, P. Marcazzan, B. O. Patrick and B. R. James, *Can. J. Chem.*, 2008, **86**, 253–260.
33 M. B. Ezhova, B. O. Patrick and B. R. James, *Organometallics*, 2005, **24**, 3753–3757.
34 W. J. Hoogervorst, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, J. M. Ernsting and C. J. Elsevier, *Organometallics*, 2004, **23**, 4550–4563.
35 C. Krug and J. F. Hartwig, *Organometallics*, 2004, **23**, 4594–4607.
36 C. Krug and J. F. Hartwig, *J. Am. Chem. Soc.*, 2004, **126**, 2694–2695.
37 P. Marcazzan, B. O. Patrick and B. R. James, *Organometallics*, 2005, **24**, 1445–1451.
38 M. Martin, E. Sola, S. Tejero, J. L. Andres and L. A. Oro, *Chem.–Eur. J.*, 2006, **12**, 4043–4056.
39 E. J. M. de Boer and J. H. Teuben, *J. Organomet. Chem.*, 1978, **153**, 53–57.
40 J. Scholz, G. A. Hadi, K. H. Thiele, H. Gorls, R. Weimann, H. Schumann and J. Sieler, *J. Organomet. Chem.*, 2001, **626**, 243–259.
41 K. Mashima, Y. Tanaka and A. Nakamura, *Organometallics*, 1995, **14**, 5642–5651, and references therein.
42 S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047–1058.
43 R. Choukroun, C. Lorber and L. Vendier, *Organometallics*, 2007, **26**, 3784–3790.
44 V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau and J. P. Majoral, *Organometallics*, 2002, **21**, 3215–3220, and references therein.
45 D. P. Hsu, E. A. Lucas and S. L. Buchwald, *Tetrahedron Lett.*, 1990, **31**, 5563–5566.
46 K. J. Barr, B. T. Watson and S. L. Buchwald, *Tetrahedron Lett.*, 1991, **32**, 5465–5468.
47 H. Lee, B. M. Bridgewater and G. Parkin, *Dalton Trans.*, 2000, 4490–4493.
48 J. Campora and S. L. Buchwald, *Organometallics*, 1993, **12**, 4182–4187, and references therein.
49 M. Zablocka, K. Owsianik, A. Igau, A. Skowronska and J. P. Majoral, *Eur. J. Inorg. Chem.*, 2002, 801–804.
50 K. Owsianik, M. Zablocka, A. Igau, J. P. Majoral and A. Skowronska, *Eur. J. Inorg. Chem.*, 2001, 1693–1697.
51 K. Owsianik, M. Zablocka, B. Donnadieu and J. P. Majoral, *Angew. Chem., Int. Ed.*, 2003, **42**, 2176–2179, and references therein.
52 A. J. Blake, P. E. Collier, S. C. Dunn, W. S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc., Dalton Trans.*, 1997, 1549–1558.
53 K. Gregory, P. V. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47–142.
54 A. B. Sannigrahi, T. Kar, B. G. Niyogi, P. Hobza and P. V. Schleyer, *Chem. Rev.*, 1990, **90**, 1061–1076.
55 P. V. Schleyer, *Pure Appl. Chem.*, 1983, **55**, 355–362.
56 P. V. Schleyer, *Pure Appl. Chem.*, 1984, **56**, 151–162.
57 J. B. Lambert and E. P. Mazzola, *Nuclear Magnetic Resonance Spectroscopy*, Pearson Education Inc., 2004.
58 D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to Spectroscopy*, Thomson Learning, Inc., 2001.
59 A. V. Korolev, A. L. Rheingold and D. S. Williams, *Inorg. Chem.*, 1997, **36**, 2647–2655.
60 K. C. Jayaratne, G. P. A. Yap, B. S. Haggerty, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1996, **35**, 4910–4920.
61 M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1982, **21**, 223–226.
62 D. P. Phillion, R. Neubauer and S. S. Andrew, *J. Org. Chem.*, 1986, **51**, 1610–1612.
63 A. B. Smith, M. Visnick, J. N. Haseltine and P. A. Sprengeler, *Tetrahedron*, 1986, **42**, 2957–2969.
64 This Nb complex was synthesized in an analogous fashion to Ta complex **14** (see ref. 9).
65 $^{13}C\{^{1}H\}$ NMR spectrum is included in the supplementary information†.
66 Due to metal carbide formation, this compound analyzed as having two fewer carbon atoms (those carbons making direct metal–carbon bonds in the complex).
67 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
68 *SMART: Area-Detector Software Package*, v. 5.625, Bruker AXS, Inc., Madison, WI, 1997–2001.
69 *SAINT: SAX Area-Detector Integration Program, v. 6.22*, Bruker AXS, Inc., Madison, WI, 1997–2001.
70 *XPREP: Reciprocal Space Exploration Program, v. 6.12*, Bruker AXS, Inc., Madison, WI, 2001.
71 *SADABS, Bruker/Siemens Area Detector Absorption Program, v. 2.03*, Bruker AXS, Inc., Madison, WI, 2001.
72 *SHELXL-97, Structure Solution Program, v. 6.10*, Bruker AXS, Inc., Madison, WI, 2000.

