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Synthesis and Reactivity of Novel Niobocene Complexes Containing Allyl or 1-Azaallyl Ligands. X-ray Crystal Structure of [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$

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The lithium 1-azaallyl complex [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (**1**), has been prepared, and its X-ray crystal structure was determined. The niobocene(III) allyl and 1-azaallyl complexes Cp′$_2$Nb[η^3-CH$_2$C(R)CH$_2$] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; R = H (**2**), Me (**3**)) and Cp′$_2$Nb[N(SiMe$_3$)C(^{t}Bu)CH$_2$] (**4**) have been synthesized. Oxidation of **2** and **3** by O$_2$ yields Cp′$_2$Nb[η^1-CH$_2$C(R)CH$_2$](O) (R = H (**5**), Me (**6**)). The complexes CpNb(=N^{t}Bu)[η^1-CH$_2$C(R)CH$_2$]Cl (Cp = η^5-C$_5$H$_5$; R = H (**7**), Me (**8**)) have also been prepared. Oxidation of **2**−**4** by PbCl$_2$ gave Cp′$_2$Nb[η^1-CH$_2$C(R)CH$_2$]Cl (R = H (**9**), Me (**10**)) and Cp′$_2$Nb[N(SiMe$_3$)C(^{t}Bu)CH$_2$]Cl (**11**). Cp′$_2$Nb[η^1-CH$_2$C(R)CH$_2$](L) (L = CO (**12**), CN(2,6-Me$_2$−C$_6$H$_3$) (**13**)) were prepared by the reaction of Cp′$_2$NbCl(L) with ClMg(CH$_2$CHCH$_2$).

The use of 1-azaallyl ligands in the preparation of novel metal complexes has recently received attention.[1] Complexes have been prepared with various metals from differing groups in the periodic table (Li,[2] K,[2] V,[3] Cu,[1b] Zr,[2,4] Mo,[5] Ru,[6] Sn,[1b,7] Ce,[8] Nd,[8] Sm,[8] Yb,[8,9] W,[5] Pb,[7] Th[10]) but there are no examples of Nb complexes. Furthermore, there are only a relatively small number of η^3-allyl complexes of niobium and tantalum despite the synthesis of Cp$_2$Nb(η^3-C$_3$H$_5$) being first reported in 1970.[11] This was followed by the preparation of Cp$_2$M(R) (M = Nb, Ta; R = 1-methylallyl, 2-methylallyl).[12] Nakamura et al have also synthesized a family of allyl niobocene complexes,[13] and more recently the tantalum allyl complexes (η^5-C$_5$Me$_5$)Ta(=NR)[η^1-CH$_2$CHCH$_2$][η^3-CH$_2$CHCH$_2$] (R = Si^{t}Bu$_3$, 2,6-^{i}Pr−C$_6$H$_3$) have also been prepared.[14] In addition, the synthesis of amidinate complexes of niobium[15] and tantalum[16] have been published and in these complexes the amidinate acts as a chelating rather than η^3 ligand. In connection with our studies on the use of unsaturated molecules in the synthesis of new families of niobium organometallics, we report here our results on the reactivity of [Cp′$_2$NbCl]$_2$, Cp′ = η^5-C$_5$H$_4$SiMe$_3$, with lithium 1-azaallyl and allyl reagents to give new niobocene complexes, namely Cp′$_2$Nb[N(SiMe$_3$)C(^{t}Bu)CH$_2$] and Cp′$_2$Nb[η^3-CH$_2$C(R)CH$_2$], and some of their transformations, particularly to oxo- and chloroniobium species. The reactivity of CpNb(=N^{t}Bu)Cl$_2$, Cp = η^5-C$_5$H$_5$, and Cp′$_2$NbCl(L) toward allyl reagents was also considered.

The lithium 1-azaallyl complex, [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (**1**), was prepared by the reaction of ^{t}BuCN and LiCH$_2$SiMe$_3$.[17] The proposed reaction pathway involves initial formation of Li[N=C(CH$_2$SiMe$_3$)^{t}Bu] followed by a 1,3-silicotropic rearrangement to yield the isolated isomer **1** (see Scheme 1). This method is similar to that utilized in the synthesis of the dimeric lithium 1-azaallyl complex [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CHSiMe$_3$}]$_2$.[2]

1 was initially characterized by NMR spectroscopy. Its ^{1}H NMR spectra showed the expected signals for the *tert*-butyl and trimethylsilyl protons (see Experimental Section). In addition, two broad signals, at 3.79 and 4.44 ppm, were observed and assigned to the CH$_2$ protons of

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(1) (a) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203. (b) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Severn, J. R.; Shun, T. *Anales de Química, Int. Ed.* **1996**, *92*, 186.

(2) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637.

(3) de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493.

(4) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Ryan, E. J. *Polyhedron* **1995**, *14*, 2745.

(5) (a) Daff, P. J.; Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1995**, 1925. (b) Daff, P. J.; Monge, A.; Palma, P.; Poveda, M. L.; Ruiz, C.; Valerga, P.; Carmona, E. *Organometallics* **1997**, *16*, 2263. (c) Amador, U.; Daff, P. J.; Poveda, M. L.; Ruiz, C.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1997**, 3145.

(6) Kuhlman, R.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 3188.

(7) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Inorg. Chim. Acta* **1998**, *268*, 181.

(8) Hitchcock, P. B.; Lappert, M. F.; Shun, T. *J. Organomet. Chem.* **1997**, *549*, 1.

(9) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Shun, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2691.

(10) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Shun, T. *J. Organomet. Chem.* **1997**, *536−537*, 473.

(11) Sietger, F. W.; Liefde Meijer, H. J. *J. Organomet. Chem.* **1970**, *23*, 177.

(12) (a) Van Baalen, A.; Groenenboom, C. J.; Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *74*, 240. (b) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.

(13) Yasuda, H.; Arai, T.; Okamoto, T.; Nakamura, A. *J. Organomet. Chem.* **1989**, *361*, 161.

(14) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500.

(15) Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982.

(16) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111.

(17) Lappert, M. F.; Liu, D.-S. Unpublished work.

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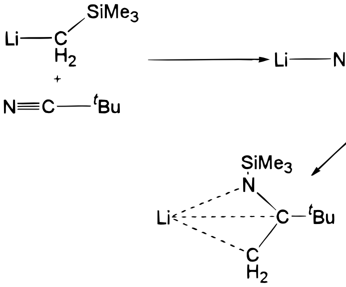
Scheme 1. Proposed Mechanism in the Synthesis of [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (1)



the azaallyl ligand with the broadening of these signals being due to the close proximity of lithium. However, in the ^{7}Li and ^{13}C NMR spectra of **1** Li−C coupling was not observed.

The molecular structure of **1** was established by X-ray crystal studies. The molecular structure and atomic numbering scheme are shown in Figure 1. A summary of X-ray and refinement data can be found in Table 1.

The structure reveals a trimer made up of three mutually bonded Li atoms, with each being linked to an azaallyl ligand. The nitrogen atom of this ligand bridges two Li atoms of the central core with essentially the same bond distances (1.99(1)−2.092(9) Å). The azaallyl ligand is bonded to the Li atom in form η^3 with average bond distances of Li−N 2.010 (10) Å, Li−C$_{central}$ 2.296 (11) Å, and Li−C$_{terminal}$ 2.361(11) Å. The C−N and C−C bond distances for the three azaallyl ligands are normal for this type of ligand and comparable with other related compounds.[2] The Li$_3$N$_3$ trimeric unit consists of alternate Li and N atoms forming an approximately planar six-membered ring. Li(1) and Li(2) are situated furthest from the average plane at distances of −0.13(1) and 0.17(1) Å, respectively. The average Li−Li distance is 2.970(12) Å, and the average N−Li−N and Li−N−Li angles are 143.9(9) and 95.2(4)°, respectively. The bonding mode in **1** clearly indicates η^3 character nevertheless the compound can also be regarded as a lithium amide with additional Li−C contacts.[18] It should be noted that the crystal data collected is poor and is due to the low intensity of diffraction of the crystal and the disorder of ^{t}Bu and SiMe$_3$ groups.

1 is one of the very few examples of a Li$_3$ cluster. Only three other compounds of this type have previously been reported, [LiN(SiMe$_3$)$_2$]$_3$,[19] trimeric [α-(1,13,3-tetramethyl-2-indanyline)benzyl]lithium[20] and a trimeric bis(trimethylsilyl)phenylamidinato cyanobenzene lithium compound.[21]

The rarity of allyl complexes of the heavy group 5 elements has led us to prepare allyl complexes of niobium and to study their reactivity. The eighteen electron allyl complexes Cp′$_2$Nb[η^3-CH$_2$C(R)CH$_2$] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) (R = H (**2**), Me (**3**)) were prepared by the reaction of [Cp′$_2$NbCl]$_2$ and the corresponding Grignard reagent (eq 1; see Chart 1).

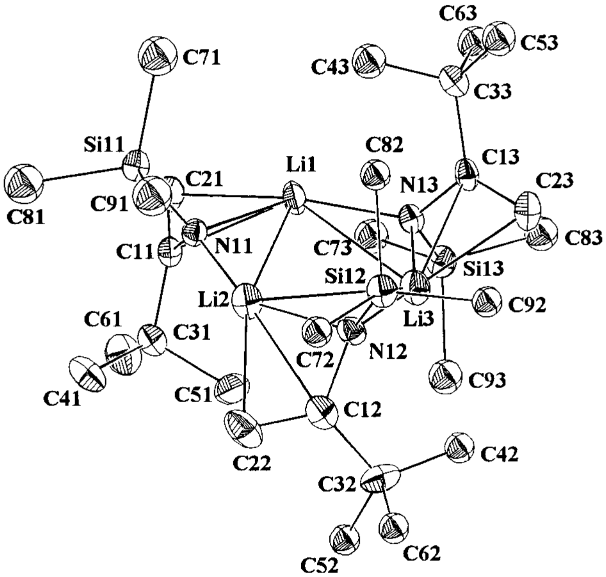


Figure 1. Molecular structure and atom-labeling scheme for [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (**1**). Selected average distances (Å): Li−Li, 2.970(12); Li−N$_a$, 2.002(9); Li−N$_d$, 2.018(10); Li−C$_c$, 2.296(11); Li−C$_t$, 2.361(11); C$_c$−N$_a$, 1.411(8); C$_c$−C$_t$, 1.350(8). Selected average angles (deg): Li−Li−Li, 60.0(3); N−Li−N, 143.9(5); Li−N−Li, 95.2(4); Li−N$_a$-C$_c$, 81.4(4); Li−C$_t$−C$_c$, 70.5(4); Li−C$_c$−C$_t$, 75.8(4); Li−C$_c$−N$_a$, 61.3(3); N$_a$−C$_c$−C$_t$, 121.2(5); C$_c$−N$_d$−Li, 123.3(4) (C$_c$ and C$_t$ are the central and terminal carbon atoms, respectively, of the azaallyl ligand; N$_a$ is the nitrogen atom pertaining to the same azaallyl ligand and N$_d$ to that of a neighboring ligand). The ^{t}Bu and SiMe$_3$ groups show rotational disorder and have been refined isotropically.

Table 1. Crystal Data and Structure Refinement for [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (1)

empirical formula	C$_{27}$H$_{60}$Li$_3$N$_3$Si$_3$
fw	531.87
wavelength (Å)	0.71070
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	9.530(10)
b (Å)	12.346(6)
c (Å)	16.90(2)
α (deg)	79.11(7)
β (deg)	80.70(10)
γ (deg)	67.89(6)
volume (Å^3)	1800(3)
Z	2
density (calculated) (g/cm^3)	0.981
absorption coefficient (cm^{-1})	1.49
F(000)	588
cryst size (mm)	0.20 × 0.17 × 0.13
θ range for data collection (deg)	2.03 to 28.00
index ranges	$0 \le h \le 12$, $-14 \le k \le 16$, $-21 \le l \le 22$
no. of indep reflcns	8684
no. of obsd reflcns [$I > 2\sigma I$]	3213
GOF	0.916
R1 [$I > 2\sigma I$]	0.0919
wR2 [$I > 2\sigma I$]	0.2442
largest diff. Peak and hole (e/Å^3)	0.355 and −0.374

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

2 and **3** were characterized spectroscopically, and their ^{1}H NMR spectra showed a system corresponding to that associated with metal complexes with η^3 coordination of the allyl ligand, namely the presence of syn

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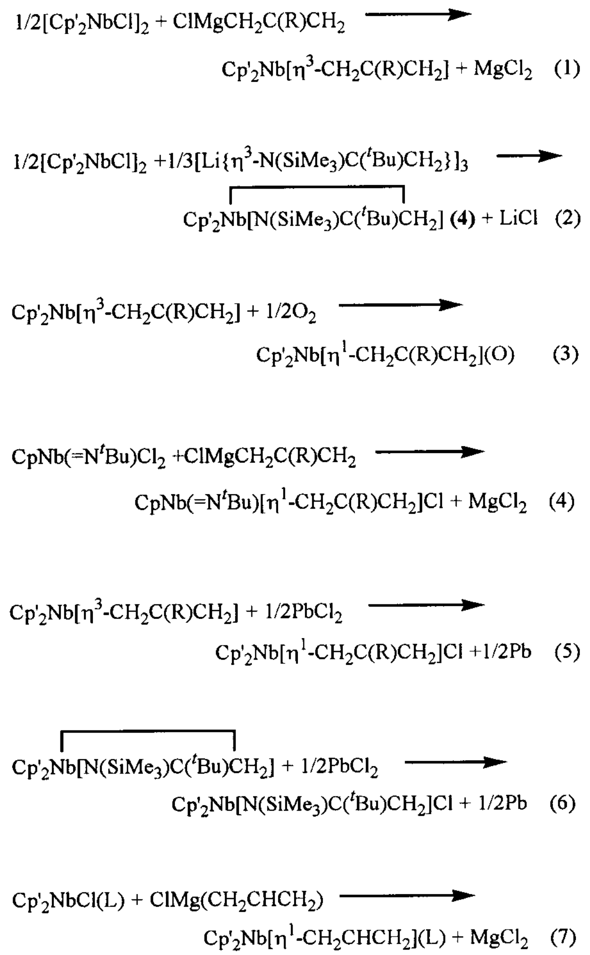
(18) See, for example: (a) Setzer, W. N.; Schleyer, P. v. R.; *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (c) *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience Publications: New York, 1995. (d) Mulvey, R. E.; *Chem. Soc. Rev.* **1991**, *20*, 167.

(19) Rogers, R. D.; Atwood J. L.; Gruening, R. *J. Organomet. Chem.* **1978**, *157*, 229.

(20) Knorr, R.; Hoang, T. P.; Nöth, H.; Linti, G. *Organometallics* **1992**, *11*, 2669.

(21) Gabauer, T.; Deknicke, K.; Goesmann, H.; Feuske, D. *Z. Naturforsch., Teil B* **1994**, *49*, 1444.

Chart 1



$$1/2[Cp'_2NbCl]_2 + ClMgCH_2C(R)CH_2 \longrightarrow Cp'_2Nb[\eta^3\text{-}CH_2C(R)CH_2] + MgCl_2 \qquad (1)$$

$$1/2[Cp'_2NbCl]_2 + 1/3[Li\{\eta^3\text{-}N(SiMe_3)C(^tBu)CH_2\}]_3 \longrightarrow Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]\ (\mathbf{4}) + LiCl \qquad (2)$$

$$Cp'_2Nb[\eta^3\text{-}CH_2C(R)CH_2] + 1/2O_2 \longrightarrow Cp'_2Nb[\eta^1\text{-}CH_2C(R)CH_2](O) \qquad (3)$$

$$CpNb(=N^tBu)Cl_2 + ClMgCH_2C(R)CH_2 \longrightarrow CpNb(=N^tBu)[\eta^1\text{-}CH_2C(R)CH_2]Cl + MgCl_2 \qquad (4)$$

$$Cp'_2Nb[\eta^3\text{-}CH_2C(R)CH_2] + 1/2PbCl_2 \longrightarrow Cp'_2Nb[\eta^1\text{-}CH_2C(R)CH_2]Cl + 1/2Pb \qquad (5)$$

$$Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2] + 1/2PbCl_2 \longrightarrow Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]Cl + 1/2Pb \qquad (6)$$

$$Cp'_2NbCl(L) + ClMg(CH_2CHCH_2) \longrightarrow Cp'_2Nb[\eta^1\text{-}CH_2CHCH_2](L) + MgCl_2 \qquad (7)$$

and anti protons. In addition this type of coordination of the allyl ligand results in the inequivalency of the two cyclopentadienyl rings and thus two signals are observed in ^1H NMR spectra for the $SiMe_3$ substituents (see Experimental Section). Four signal are observed in ^1H NMR spectra for the protons of the cyclopentadienyl ring. This is due to a plane of symmetry (σ_v) which makes the protons H2 and H5 and H3 and H4 in each ring equivalent (see Figure 2).

To explore the differences between allyl and azaallyl compounds of niobium the preparation of the niobocene(III) 1-azaallyl complex, $Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]$ (**4**), was carried out. Complex **4** offers the first example of a 1-azaallyl complex of niobium and was synthesized by the reaction of $[Cp'_2NbCl]_2$ and $[Li\{\eta^3\text{-}N(SiMe_3)C(^tBu)CH_2\}]_3$ (**1**) in THF (eq 2).

A green oil was obtained which was shown to be chemically pure by NMR spectroscopy. The ^1H NMR spectrum of **4** reveals that the cyclopentadienyl ligands are equivalent due to a σ_h plane of symmetry and thus rules out the possible η^3 coordination of the 1-azaallyl ligand that was observed in the allyl complexes **2** and **3**. The proposed structure of **4** (see Figure 3), with the 1-azaallyl ligand adopting a chelating mode of coordination to the metal center is in complete agreement with the spectroscopic data.

The oxidation of **2** and **3** by O_2 (eq 3) yielded the eighteen electron complexes $Cp'_2Nb[\eta^1\text{-}CH_2C(R)CH_2](O)$ (R = H (**5**), Me (**6**)) which result in a change of bonding mode of the allyl ligand from η^3 to η^1.

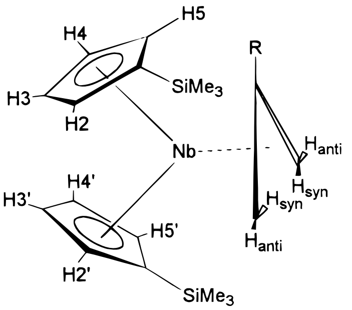


Figure 2. Proposed structure for $Cp'_2Nb[\eta^3\text{-}CH_2C(R)CH_2]$ (R = H (**2**), Me (**3**)).

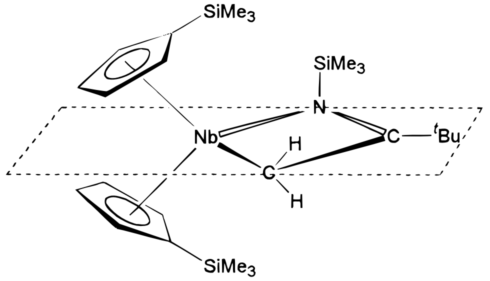


Figure 3. Proposed structure for $Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]$ (**4**).

The compounds were characterized by IR and NMR spectroscopy. The ^1H NMR spectra of **5** and **6** reveal the two cyclopentadienyl rings to be equivalent indicating a change in the plane of symmetry from σ_v to σ_h. The disappearance of the anti and syn proton signals is also observed. The signals associated with the allyl ligand are typical to those normally seen for η^1-allyl systems (e.g. $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu)[\eta^1\text{-}CH_2CHCH_2]$[22]), namely, three signals corresponding to the CH_2 bonded to the metal center, the central group C(R) and the olefinic protons for the terminal CH_2. The various coupling constants are given in Table 2.

To prepare allyl complexes of niobium(V) imides the sixteen electron half-sandwich complexes, $CpNb(=N^tBu)[\eta^1\text{-}CH_2C(R)CH_2]Cl$ (R = H (**7**), Me (**8**)), were prepared (eq 4) by the action of $CpNb(=N^tBu)Cl_2$[23] with the corresponding allylmagnesium chloride.

The expected eighteen electron species $CpNb(=N^tBu)[\eta^3\text{-}CH_2C(R)CH_2]Cl$ were not observed. ^1H NMR spectra of **7** and **8** are very similar to those recorded for **5** and **6** indicating that the allyl ligand is η^1 coordinated to the metal center (see Experimental Section). The various coupling constants are given in Table 2. It should be noted that **7** and **8** possess chirality about the niobium atom.

The one-electron oxidation of **2**−**4** by $PbCl_2$ has also been carried out and led to the formation of the niobium(IV) complexes $Cp'_2Nb[\eta^1\text{-}CH_2C(R)CH_2]Cl$ (R = H (**9**), Me (**10**)) (eq 5) and $Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]Cl$ (**11**) (eq 6).

In addition to IR spectroscopy and microananalysis, **9**−**11** were characterized by ESR spectroscopy. The ESR spectra for the paramagnetic niobium(IV) complex **9** gave a value of $g_{iso} = 1.9913$ with a hyperfine splitting $\langle a_{^{93}Nb}\rangle$ of 99.7 G, analogous to other niobocene(IV) complexes, with the unpaired electron mainly located

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[22] Antiñolo, A.; Otero, A.; Prashar, S.; Rodriguez, A. M. *Organometallics* in press (MS#OM980561N).

Table 2. Coupling Constants for the η^1- and η^3-Allyl Complexes 2, 3, 5−8, 12, and 13

	$^2J_{\mathrm{anti-syn}}$	$^3J_{\mathrm{anti-H}}$	$^3J_{\mathrm{syn-H}}$
$Cp'_2Nb[\eta^3\text{-}CH_2CHCH_2]$ (**2**)	6.1 Hz	15.1 Hz	9.8 Hz
$Cp'_2Nb[\eta^3\text{-}CH_2C(Me)CH_2]$ (**3**)	4.8 Hz		

	$^3J(^1H-^1H)$	$^2J_{\mathrm{gem}}(^1H-^1H)$	$^3J_{\mathrm{cis}}(^1H-^1H)$	$^3J_{\mathrm{trans}}(^1H-^1H)$
$Cp'_2Nb[\eta^3\text{-}CH_2CHCH_2](O)$ (**5**)	8.3 Hz	3.5 Hz	8.4 Hz	16.8 Hz
$Cp'_2Nb[\eta^3\text{-}CH_2C(Me)CH_2](O)$ (**6**)		3.0 Hz		
$CpNb({=}N^tBu)[\eta^1\text{-}CH_2CHCH_2]Cl$ (**7**)	8.1 Hz	2.6 Hz	9.9 Hz	16.8 Hz
$CpNb({=}N^tBu)[\eta^1\text{-}CH_2C(Me)CH_2]Cl$ (**8**)		3.0 Hz		
$Cp'_2Nb[\eta^1\text{-}CH_2CHCH_2](CO)$ (**12**)	8.5 Hz	2.5 Hz	10.3 Hz	16.7 Hz
$Cp'_2Nb[\eta^1\text{-}CH_2CHCH_2](CNAr)$ (**13**)	8.4 Hz	2.8 Hz	9.8 Hz	16.6 Hz

at the metal center.[24] Similar results were obtained for **10** and **11**. Reduction of **9**−**11** by Na/Hg recuperated the starting products **2**−**4**. In the case of **11** it was not possible to determine if the η^1-azaallyl ligand was bonded to the metal center by the nitrogen or carbon atom of said ligand.

Finally, the η^1-allyl eighteen-electron niobocene(III) complexes $Cp'_2Nb[\eta^1\text{-}CH_2CHCH_2](L)$ (L = CO (**12**), CN-(2,6-$Me_2-C_6H_3$) (**13**)) were prepared by the reaction of $Cp'_2NbCl(L)$[25] and $ClMg(CH_2CHCH_2)$ (eq 7).

12 and **13** were characterized spectroscopically. In the ^1H NMR spectra of **12** and **13**, similar to those observed for **5** and **6**, the expected signals for the η^1-allyl ligand and the equivalency of the cyclopentadienyl rings can clearly be seen. The various coupling constants are given in Table 2.

In conclusion, we have prepared novel allyl and 1-azaallyl complexes of niobium in various oxidation states and by NMR spectroscopy we have been able to determine the coordination mode (η^3, η^1, or chelating) of the allyl or azaallyl ligand. In addition, the molecular structure of the lithium 1-azaallyl complex, $[Li\{\eta^3\text{-}N(SiMe_3)C(^tBu)CH_2\}]_3$ (**1**), offers one the very few Li_3-cluster compounds reported to date.

Experimental Section

General Procedures. All reactions were preformed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

The complexes $(\eta^5\text{-}C_5H_5)Nb({=}N^tBu)Cl$,[23] $Cp'_2NbCl(L)$ (L = CO, CN(2,6-$Me_2C_6H_3$)),[25] $[NbCp'_2Cl]_2$,[26] and $Li(CH_2SiMe_3)$[27] were prepared as described earlier. The THF solution of ClMg-(CH_2CHCH_2) and ^tBuCN were purchased from Aldrich and used directly. The Et_2O solution of $ClMg(CH_2C(Me)CH_2)$ was prepared by normal methods. ESR spectra were taken at the X-band with a Bruker ESP 300 spectrometer. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

$[Li\{\eta^3\text{-}N(SiMe_3)C(^tBu)CH_2\}]_3$ (1). ^tBuCN (2.96, mL, 26.79 mmol) was added to a solution of $Li(CH_2SiMe_3)$ (2.52 g, 26.79 mmol) in Et_2O (100 mL) at 0 °C. The resulting green solution was allowed to warm to room temperature and stirred for 12 h. Solvent was removed in vacuo, and the residue was heated (40 °C) for 1 h. The solid was extracted into hexane (100 mL). The solution was concentrated (20 mL) and cooled (−30 °C) to give white crystals of the title compound (3.85 g, 81%). ^1H NMR (200 MHz, C_6D_6): δ 0.23 (9H, s, $SiMe_3$), 1.13 (9H, s, CMe_3), 3.79 (1H), 4.44 (1H) (m, CH_2). $^7Li\{^1H\}$ NMR (300 MHz, C_6D_6): 0.54. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): 4.49 ($SiMe_3$), 31.20 (CMe_3), 38.90 (CMe_3), 92.00 (CH_2), 175.70 (CN). Anal. Calcd for $C_{27}H_{60}Li_3N_3Si_3$: C, 62.97; H, 11.37; N, 7.90. Found C, 62.86; H, 11.16; N, 7.91.

$Cp'_2Nb[\eta^3\text{-}CH_2CHCH_2]$ (2). A 2 M solution of $ClMgCH_2$-$CHCH_2$ in THF (0.87 mL, 1.74 mmol) was added to a stirring solution of $[Cp'_2NbCl]_2$ (0.70 g, 0.87 mmol) in THF (50 mL) at −30 °C. The green solution was allowed to warm to room temperature and stirred for 6 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane. A green crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.59 g, 83%). ^1H NMR (200 MHz, C_6D_6): δ 0.16 (9H), 0.22 (9H) (s, $SiMe_3$), 0.70 (dd, 2H, CH_{2anti}), 2.75 (dd, 2H, 2H, CH_{2syn}) ($^2J_{\mathrm{anti-syn}} = 6.1$ Hz, $^3J_{\mathrm{anti-H}} = 15.1$ Hz, $^3J_{\mathrm{syn-H}} = 9.8$ Hz), 2.40 (m, 1H, CH_2CHCH_2), 3.21 (2H), 3.29 (2H), 4.36 (2H), 5.17 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 1.19, 1.33 ($SiMe_3$), 38.93 (CH_2), 82.69 (CH_2CH-CH_2), 77.34 (C^1), 86.49 (C^1), 92.67, 92.92, 95.78, 97.68 (C_5H_4). Anal. Calcd for $C_{19}H_{31}NbSi_2$: C, 55.86; H, 7.65. Found C, 55.64; H, 7.49.

$Cp'_2Nb[\eta^3\text{-}CH_2C(Me)CH_2]$ (3). The preparation of **3** was carried out in an identical manner to **2** (yield 89%). ^1H NMR (200 MHz, C_6D_6): δ 0.24 (9H), 0.28 (9H) (s, $SiMe_3$), 0.86 (d, 2H, CH_{2anti}), 2.73 (dd, 2H, 2H, CH_{2syn}) ($^2J_{\mathrm{anti-syn}} = 4.8$ Hz), 1.53 (s, 3H, $CH_2C(Me)CH_2$), 3.20 (2H), 3.38 (2H), 4.47 (2H), 5.17 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 1.35, 1.42 ($SiMe_3$), 40.89 (CH_2), 30.55 ($CH_2C(Me)CH_2$), 82.79 (CH_2C(Me)-CH_2), 77.95 (C^1), 85.26 (C^1), 92.86, 94.63, 95.86, 97.04 (C_5H_4). Anal. Calcd for $C_{20}H_{33}NbSi_2$: C, 56.85; H, 7.87. Found C, 56.99; H, 8.00.

$Cp'_2Nb[N(SiMe_3)C(^tBu)CH_2]$ (4). THF (100 mL) was added to a solid mixture of $[Cp'_2NbCl]_2$ (0.96 g, 1.19 mmol) and **1** (0.42 g, 0.79 mmol) and the resulting green solution was allowed to stir at room temperature for 12 h. Solvent was removed in vacuo and the green residue extracted into hexane (75 mL). Hexane was removed under reduced pressure to yield a green oil of the title complex (1.15 g, 90%). ^1H NMR (200 MHz, C_6D_6): δ 0.19 (s, 18H, $C_5H_4SiMe_3$), 0.26 (s, 9H, $NSiMe_3$), 1.05 (9H, s, CMe_3), 1.75 (s, 2H, CH_2),), 4.05 (2H), 4.10 (2H), 4.85 (2H), 5.08 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 1.82 ($C_5H_4SiMe_3$), 6.44 ($NSiMe_3$), 26.32 (CH_2), 30.82 (CMe_3), 38.59 (CMe_3), 89.65 (C^1), 92.72, 97.69, 97.96, 102.28 (C_5H_4), 147.96 (CN).

$Cp'_2Nb[\eta^1\text{-}CH_2CHCH_2](O)$ (5). A solution of **2** (0.28 g, 0.68 mmol) in hexane was stirred for 30 min, at room temperature, under one atmosphere of O_2. A color change was observed from green to yellow. Hexane was removed in vacuo to yield the title complex as a yellow solid (0.29 g, 100%). IR (Nujol) ν-(Nb=O) 906 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.25 (s, 18H, $SiMe_3$), 2.85 (d, 2H, $CH_2-CH{=}CH_2$) $^3J(^1H-^1H) = 8.3$ Hz, 4.80

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[23] Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

[24] Antiñolo, A.; Fajardo, M.; de Jesús, E.; Mugnier, Y.; Otero, A. *J. Organomet. Chem.* **1994**, *470*, 127.

[25] Antiñolo, A.; de Ilarduya, J. M.; Otero, A.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1988**, 2685.

[26] Antiñolo, A.; Espinosa, P.; Fajardo, M.; Gómez-Sal, P.; López-Mardomingo, C.; Martin-Alonso, A.; Otero, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1007.

[27] Tecle, B.; Rahman, A. F. M. M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *317*, 267.

(cis), 4.95 (trans) (dd, 2H, $\mathrm{CH_2{-}CH{=}C}H_2$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 3.5$ Hz, $^{3}J_{\mathrm{cis}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 8.4$ Hz, $^{3}J_{\mathrm{trans}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 16.8$ Hz, 5.00 (2H), 5.38 (2H), 5.98 (2H), 6.00 (2H) (m, $\mathrm{C_5}H_4$), 6.40 (m, 1H, $\mathrm{CH_2{-}C}H\mathrm{{=}CH_2}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.63 ($\mathrm{Si}Me_3$), 37.00 ($C\mathrm{H_2{-}CH{=}CH_2}$), 108.42, 113.16, 115.69, 121.23, 123.17 ($\mathrm{C^1}$) ($C_5\mathrm{H_4}$), 106.27 ($\mathrm{CH_2{-}CH{=}}C\mathrm{H_2}$), 145.66 ($\mathrm{CH_2{-}}C\mathrm{H{=}CH_2}$). Anal. Calcd for $\mathrm{C_{19}H_{31}NbOSi_2}$: C, 53.76; H, 7.36. Found C, 53.49; H, 7.29.

Cp′$_2$Nb[η^1-CH$_2$C(Me)CH$_2$](O) (6). The preparation of **6** was carried out in an identical manner to **5** (yield 100%). IR (Nujol) $\nu(\mathrm{Nb{=}O})$ 905 cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 0.26 (s, 18H, $\mathrm{Si}Me_3$), 1.76 (s, 3H, $\mathrm{CH_2C(}Me\mathrm{){=}CH_2}$), 4.53 (s, 2H, $\mathrm{C}H_2\mathrm{C(Me){=}CH_2}$), 4.85 (cis), 4.98 (trans) (m, 2H, $\mathrm{C}H_2\mathrm{C(Me){=}CH_2}$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 3.0$ Hz, 6.32 (4H), 6.45 (2H), 6.61 (2H), (m, $\mathrm{C_5}H_4$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.30 ($\mathrm{Si}Me_3$), 29.01 ($\mathrm{CH_2C(}Me\mathrm{){=}CH_2}$), 36.68 ($C\mathrm{H_2C(Me){=}CH_2}$), 108.15 ($\mathrm{CH_2C(Me){=}}C\mathrm{H_2}$), 145.66 ($\mathrm{CH_2}C\mathrm{(Me){=}CH_2}$), 114.48, 114.66, 116.65, 121.69, 124.45 ($\mathrm{C^1}$) ($C_5\mathrm{H_4}$). Anal. Calcd for $\mathrm{C_{209}H_{33}NbOSi_2}$: C, 54.77; H, 7.58. Found C, 54.51; H, 7.43.

CpNb(═N^{t}Bu)[η^1-CH$_2$CHCH$_2$]Cl (7). A 2M solution of $\mathrm{ClMgCH_2CHCH_2}$ in THF (0.56 mL, 1.12 mmol) was added to a stirring solution of CpNb(═N^{t}Bu)Cl$_2$ (0.36 g, 0.93 mmol) in THF (25 mL) at −30 °C and allowed to stir for 3 h at room temperature. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane (50 mL). A yellow crystalline solid was obtained by concentrating (15 mL) and cooling (−30 °C) the solution (0.16 g, 43%). IR (Nujol) $\nu(\mathrm{Nb{=}N})$ 1240 cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.90 (s, 9H, $\mathrm{C}Me_3$), 2.65 (d, 2H, $\mathrm{C}H_2\mathrm{{-}CH{=}CH_2}$) $^{3}J(^{1}\mathrm{H}\text{-}^{1}\mathrm{H})$ 8.1 Hz, 4.80 (cis), 4.95 (trans) (dd, 2H, $\mathrm{CH_2{-}CH{=}C}H_2$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 2.6$ Hz, $^{3}J_{\mathrm{cis}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 9.9$ Hz, $^{3}J_{\mathrm{trans}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 16.8$ Hz, 5.45 (s, 5H, $\mathrm{C_5}H_5$), 6.45 (m, 1H, $\mathrm{CH_2{-}C}H\mathrm{{=}CH_2}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$): δ 31.00 ($\mathrm{C}Me_3$), 36.53 ($C\mathrm{H_2{-}CH{=}CH_2}$), 70.05 ($C\mathrm{Me_3}$), 108.61 ($C_5\mathrm{H_5})_2$, 103.72 ($\mathrm{CH_2{-}CH{=}}C\mathrm{H_2}$), 150.67 ($\mathrm{CH_2{-}}C\mathrm{H{=}CH_2}$). Anal. Calcd for $\mathrm{C_{12}H_{19}ClNNb}$: C, 47.16; H, 6.27; N, 4.58. Found C, 46.92; H, 6.22; N, 4.49.

CpNb(═N^{t}Bu)[η^1-CH$_2$C(Me)CH$_2$]Cl (8). The preparation of **8** was carried out in an identical manner to **7** (yield 58%). IR (Nujol) $\nu(\mathrm{Nb{=}N})$ 1255 cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.92 (s, 9H, $\mathrm{C}Me_3$), 1.92 (s, 3H, $\mathrm{CH_2C(}Me\mathrm{){=}CH_2}$), 2.65 (s, 2H, $\mathrm{C}H_2\mathrm{C(Me){=}CH_2}$), 4.76 (cis), 4.82 (trans) (m, 2H, $\mathrm{C}H_2\mathrm{C(Me){=}CH_2}$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 3.0$ Hz, 5.46 (s, 5H, $\mathrm{C_5}H_5$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$): δ 31.27 ($\mathrm{C}Me_3$), 25.29 ($\mathrm{CH_2C(}Me\mathrm{){=}CH_2}$), 35.71 ($C\mathrm{H_2C(Me){=}CH_2}$), 68.70 ($C\mathrm{Me_3}$), 103.71 ($\mathrm{CH_2C(Me){=}}C\mathrm{H_2}$), 156.89 ($\mathrm{CH_2}C\mathrm{(Me){=}CH_2}$), 109.00 ($C_5\mathrm{H_5}$). Anal. Calcd for $\mathrm{C_{12}H_{19}ClNNb}$: C, 47.84; H, 6.62; N, 4.38. Found C, 47.52; H, 6.49; N, 4.40.

Cp′$_2$Nb[η^1-CH$_2$CHCH$_2$]Cl (9). $\mathrm{PbCl_2}$ (0.12 g, 0.44 mmol) was added to a yellow solution of **2** (0.36 g, 0.88 mmol) in THF (50 mL) and left in an ultrasonic bath for 1 h. The mixture was filtered to remove the lead metal. Solvent was removed, from the red filtrate, in vacuo to yield a brown solid of the title complex **9** (0.39 g, 100%). ESR $g_{\mathrm{iso}} = 1.9913$, $\langle a^{93}{}_{\mathrm{Nb}}\rangle$ 99.7 G. IR (Nujol) $\nu(\mathrm{SiMe_3})$ 1246 cm^{-1}, $\nu(\mathrm{C_5H_4})$ 834 cm^{-1}, $\nu(\mathrm{Nb{-}Cl})$ 278 cm^{-1}. Anal. Calcd for $\mathrm{C_{19}H_{31}ClNbSi_2}$: C, 51.40; H, 7.04. Found C, 51.02; H, 6.91.

Cp′$_2$Nb[η^1-CH$_2$C(Me)CH$_2$]Cl (10). The preparation of **10** was carried out in an identical manner to **9** (yield 100%). (0.56 g, 100%). %). ESR $g_{\mathrm{iso}} = 1.9983$, $\langle a^{93}{}_{\mathrm{Nb}}\rangle$ 99.9 G. IR (Nujol) $\nu(\mathrm{SiMe_3})$ 1246 cm^{-1}, $\nu(\mathrm{C_5H_4})$ 834 cm^{-1}, $\nu(\mathrm{Nb{-}Cl})$ 279 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_{33}ClNbSi_2}$: C, 52.45; H, 7.26. Found C, 52.13; H, 7.10.

Cp′$_2$Nb[N(SiMe$_3$)C(^{t}Bu)CH$_2$]Cl (11). The preparation of **11** was carried out in an identical manner to **9** (yield 100%). ESR $g_{\mathrm{iso}} = 1.977$, $\langle a^{93}{}_{\mathrm{Nb}}\rangle$ 110.0 G. IR (Nujol) $\nu(\mathrm{SiMe_3})$ 1245 cm^{-1}, $\nu(\mathrm{C_5H_4})$ 820 cm^{-1}, $\nu(\mathrm{Nb{-}Cl})$ 256 cm^{-1}. Anal. Calcd for $\mathrm{C_{25}H_{46}ClNNbSi_3}$: C, 52.38; H, 8.09; N, 2.44. Found C, 52.52; H, 7.95; N, 2.30.

Cp′$_2$Nb[η^1-CH$_2$CHCH$_2$](CO) (12). A 2 M solution of $\mathrm{ClMgCH_2CHCH_2}$ in THF (0.70 mL, 1.40 mmol) was added to a stirring solution Cp′$_2$NbCl(CO) (0.50 g, 1.16 mmol) in THF (25 mL) at −30 °C and allowed to stir for 3 h at this temperature. Solvent was removed in vacuo and the remaining brown oil extracted in hexane (50 mL). A reddish brown crystalline solid was obtained by concentrating (15 mL) and cooling (−30 °C) the solution (0.27 g, 53%). IR (Nujol) $\nu(\mathrm{CO})$ 1930 cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.05 (s, 18H, $\mathrm{Si}Me_3$), 1.21 (d, 2H, $\mathrm{C}H_2\mathrm{{-}CH{=}CH_2}$) $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 8.5$ Hz, 4.43 (cis), 4.51 (trans) (dd, 2H, $\mathrm{CH_2{-}CH{=}C}H_2$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 2.5$ Hz, $^{3}J_{\mathrm{cis}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 10.3$ Hz, $^{3}J_{\mathrm{trans}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 16.7$ Hz, 4.35 (2H), 4.41 (2H), 4.68 (2H), 4.87 (2H) (m, $\mathrm{C_5}H_4$), 6.14 (m, 1H, $\mathrm{CH_2{-}C}H\mathrm{{=}CH_2}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.13 ($\mathrm{Si}Me_3$), 38.95 ($C\mathrm{H_2{-}CH{=}CH_2}$), 91.22, 95.79 ($\mathrm{C^1}$), 97.14, 99.66, 100.81 ($C_5\mathrm{H_4}$), 102.87 ($\mathrm{CH_2{-}CH{=}}C\mathrm{H_2}$), 152.93 ($\mathrm{CH_2\text{-}}C\mathrm{H{=}CH_2}$), 265.43 (CO). Anal. Calcd for $\mathrm{C_{20}H_3NbOSi_2}$: C, 55.03; H, 7.16. Found C, 54.72; H, 7.05.

Cp′$_2$Nb[η^1-CH$_2$CHCH$_2$]{CN(2,6-Me$_2$-C$_6$H$_3$)} (13). A 2 M solution of $\mathrm{ClMgCH_2CHCH_2}$ in THF (0.62 mL, 1.24 mmol) was added to a stirring Cp′$_2$NbCl{CN(2,6-Me$_2$C$_6$H$_3$)} (0.55 g, 1.03 mmol) in THF (25 mL) at −30 °C and allowed to stir for 3 h at this temperature. Solvent was removed in vacuo and the remaining brown oil extracted in hexane (50 mL). A reddish brown crystalline solid was obtained by concentrating (15 mL) and cooling (−30 °C) the solution (0.32 g, 57%). IR (Nujol) $\nu(\mathrm{CN})$ 2095 cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.11 (s, 18H, $\mathrm{Si}Me_3$), 1.39 (d, 2H, $\mathrm{C}H_2\mathrm{{-}CH{=}CH_2}$), $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 8.4$ Hz, 2.22 (s, 6H, Me), 4.49 (cis), 4.58 (trans) (dd, 2H, $\mathrm{CH_2{-}CH{=}C}H_2$) $^{2}J_{\mathrm{gem}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 2.8$ Hz, $^{3}J_{\mathrm{cis}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 9.8$ Hz, $^{3}J_{\mathrm{trans}}(^{1}\mathrm{H}{-}^{1}\mathrm{H}) = 16.6$ Hz, 4.61 (4H), 4.94 (2H), 5.16 (2H) (m, $\mathrm{C_5}H_4$), 6.25 (m, 1H, $\mathrm{CH_2{-}C}H\mathrm{{=}CH_2}$), 6.68−6.80 (m, 3H, *Ph*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.47 ($\mathrm{Si}Me_3$), 19.24 (Me), 39.05 ($C\mathrm{H_2{-}CH{=}CH_2}$), 92.27, 96.43, 98.81 ($\mathrm{C^1}$), 103.28, 104.56 ($C_5\mathrm{H_4}$), 103.85 ($\mathrm{CH_2{-}CH{=}}C\mathrm{H_2}$), 153.78 ($\mathrm{CH_2{-}}C\mathrm{H{=}CH_2}$), 124.10, 125.05, 126.93, 130.38, 131.45, 132.16 (Ph) 232.09 (CN). Anal. Calcd for $\mathrm{C_{28}H_{40}NNbSi_2}$: C, 62.31; H, 7.47; N, 2.60. Found C, 62.52; H, 7.55; N, 2.68.

X-ray Structure Determination for [Li{η^3-N(SiMe$_3$)C(^{t}Bu)CH$_2$}]$_3$ (1). Crystals of **1** were grown by cooling (−30 °C) a hexane solution. A crystal of **1** was sealed in Lindemann capillary under dry nitrogen and used for data collection. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator MoKα radiation ($\lambda = 0.7107$ Å). 8684 collected reflections ($2 \le \theta \le 28$), with 3213 observed reflections for $I > 2\sigma(I)$. No absorption correction was applied ($\mu = 1.49$ cm^{-1}). The structure was solved by a combination of direct methods[28] and Fourier synthesis and then refined by full-matrix least-squares on F^2.[29] The ^{t}Bu and SiMe$_3$ groups showed rotational disorder and were refined isotropically with different occupancies. The rest of non-hydrogen atoms were anisotropic, and hydrogen atoms were included in their calculated positions as fixed isotropic contributors. Crystallographic data are given in Table 1. Other detailed data are supplied in the Supporting Information.

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(28) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, 435.

(29) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.

Supporting Information Available: Tables of complete crystal data (Table SI), non-hydrogen atom coordinates (Table SII), complete bond distances and angles (Table SIII), anisotropic displacement parameters (Table SIV), hydrogen atom coordinates (Table SV), and ORTEP and crystal packing drawings (16 pages). Ordering information is given on any current masthead page. A list of structure factors is available on request from the authors.

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