The Reactivity of Allyl and Olefin-Hydride Niobocene Derivatives Towards Isocyanides. X-ray Crystal Structure of [Nb(η^5-$C_5H_4SiMe_3$)$_2${η^3-CH(R)CHCH(R)}] (R = $SiMe_2tBu$)

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The new allylniobocene complexes [NbCp′$_2$(η^3-CHRCHCHR′)] [Cp′ = η^5-$C_5H_4SiMe_3$; R = R′ = $SiMe_2tBu$ (**1**); R = H, R′ = $SiPh_3$ (**2**)] have been prepared and characterised. The molecular structure of **1** has been determined by X-ray diffraction studies, which confirm that the allyl ligand is η^3-bonded to the metal centre. The reactivity of the niobocene complexes **1**, **2**, [NbCp′$_2$H(η^2-CH_2=CH_2)] (**3**), and [NbCp′$_2$(η^3-CH_2CHCH_2)] (**4**) towards aliphatic, *t*BuNC, *n*BuNC, and aromatic, $CNC_6H_3Me_2$-2,6, isocyanide compounds has been studied. From these reactions the new alkylniobocene [NbCp′$_2$(CH_2CH_3)(CNR)] [R = *t*Bu (**5**), $C_6H_3Me_2$-2,6 (**6**), *n*Bu (**7**)], η^1-allylniobocene derivatives [NbCp′$_2$(η^1-$CH_2CHCHSiPh_3$)($CNC_6H_3Me_2$-2,6)] (**8**), and a family of the first neutral η^1-iminoacylniobocene complexes [NbCp′$_2${η^1-C(=NR)R′}(CNR)] (R = $C_6H_3Me_2$-2,6, R′ = Et (**9**); R = *n*Bu, R′ = Et (**10**); R = $C_6H_3Me_2$-2,6, R′ = CH_2CH=$CHSiPh_3$ (**11**); R = $C_6H_3Me_2$-2,6, R′ = CH_2CH=CH_2 (**12**)] were prepared.

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Introduction

The chemistry of η^3-allyl complexes of transition metals is well documented.[1] However there are only a relatively small number of η^3-allyl complexes of niobium and tantalum despite the synthesis of [Nb(η^5-C_5H_5)$_2$(η^3-C_3H_5)] being first reported in 1970.[2] This was followed by the preparation of [M(η^5-C_5H_5)$_2$R] (M = Nb, Ta; R = 1-methylallyl, 2-methylallyl).[3] Several related systems such as the metallacyclic (η^3-allyl)metallocene cations have also been published.[4] Nakamura et al. have also synthesised a family of allylniobocene complexes,[5] and more recently the allyltantalum complexes [Ta(=NR)(η^5-C_5Me_5)(η^1-CH_2CHCH_2)(η^3-CH_2CHCH_2)] (R = Si*t*Bu_3, 2,6-*i*PrC_6H_3) were reported.[6]

Our research group's contribution in this field describes the synthesis and reactivity of η^3-allyl, [NbCp′$_2$(η^3-C_3H_5)], and chelate azaallyl [NbCp′$_2${N($SiMe_3$)C(*t*Bu)CH_2}], niobocene derivatives[7] and forms part of our ongoing studies in the use of unsaturated molecules in the synthesis of new families of niobium organometallic compounds.[8]

The behaviour of isocyanide molecules towards alkyl or aryl transition-metal compounds is well documented and insertion reactions are usually observed.[9] Varying the alkyl or aryl substituent of the isocyanide compound allows fine tuning of the electronic and steric properties of the metal complex. Isocyanides are able to bind to the metal through either or both the carbon and nitrogen atom. η^2-Coordination normally occurs at electron deficient metal centres and is characteristic for high valence early transition metal complexes.

Our well documented studies of the first insertion reaction of CO into the niobium−carbon bond of alkylniobocene complexes which give the corresponding η^1-acyl derivatives,[10] have led us to consider the insertion reactions of isocyanide compounds. The isolobal relationship between carbon monoxide and isocyanide compounds suggests that similar types of reactivity can be expected although isocyanides are generally regarded as better σ donors and weaker π acceptors than carbon monoxide.[11]

We report here the synthesis and characterisation of new allylniobocene complexes and their reactivity as well as that of olefin-hydride species towards aliphatic and aromatic isocyanide reagents. We also present the molecular structure of an η^3-allylniobocene complex, which to the best of our knowledge is only the second reported example.

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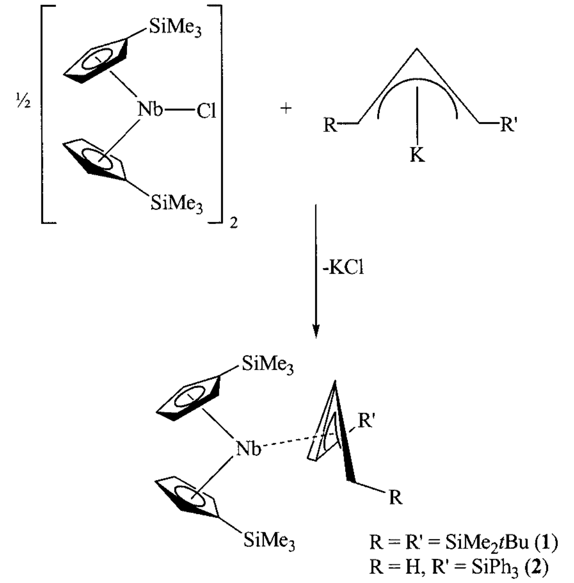
Results and Discussion

The eighteen-electron allyl complexes [NbCp'$_2$(η^3-CHRCHCHR')] [Cp' = η^5-C$_5$H$_4$SiMe$_3$; R = R' = SiMe$_2$*t*Bu (**1**); R = H, R' = SiPh$_3$ (**2**)] were prepared by the metathesis reaction of [{NbCp'$_2$Cl}$_2$] and the corresponding potassium salt [K(η^3-CHRCHCHR')] (Scheme 1).



Scheme 1

Complexes **1** and **2** were characterised by NMR and mass spectroscopy (see Exp. Sect.). The ^{1}H NMR spectrum of **1** showed two sets of allylic proton signals, a doublet for the terminal allylic protons (two H$_{anti}$) and a triplet for the central allylic proton. Four signals were observed for the protons of the two cyclopentadienyl rings. The σ_v symmetry of **1** makes the protons 2-H, 5-H and 3-H, 4-H in each cyclopentadienyl ring equivalent (see Figure 1). The η^3-coordination of the allyl ligand results in the inequivalency of the two cyclopentadienyl rings and thus two sets of signals corresponding to the distinct cyclopentadienyl ligands were observed. In addition the two methyl groups of the allyl silyl substituents were found to be magnetically inequivalent and this was attributed to the greater restriction to rotation about the silicon−allyl−carbon bond of the allyl ligand.[12] The ^{13}C NMR spectrum observed was in accordance with the proposed structure (see Exp. Sect.).

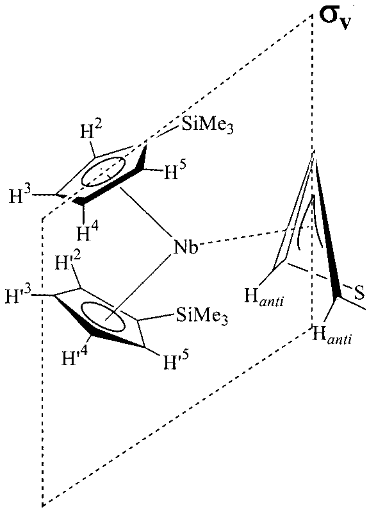


Figure 1. Proposed structure for [NbCp'$_2$(η^3-*t*BuMe$_2$SiCHCHCH-SiMe$_2$*t*Bu)] (**1**)

The ^{1}H NMR spectrum of **2** showed eight signals for the protons of the cyclopentadienyl ligands and two singlets for the SiMe$_3$ ring substituents in accordance with an asymmetrical environment about the niobium centre. The inequivalence of the two cyclopentadienyl rings indicates an η^3 coordination of the allyl ligand (see Figure 2). Three sets of signals for the allylic group were observed, a doublet at $\delta = -0.09$ ppm assigned to the H$_{anti}$ proton bonded to the silicon atom, a doublet of doublets at $\delta = 0.89$ ppm assigned to the H$_{anti}$ of the unsubstituted terminal carbon and a multiplet at $\delta = 2.73$ ppm assigned to the central proton which overlaps with the signal assigned to the H$_{syn}$ proton. The ^{13}C NMR spectrum observed was in accordance with the proposed structure (see Exp. Sect.).

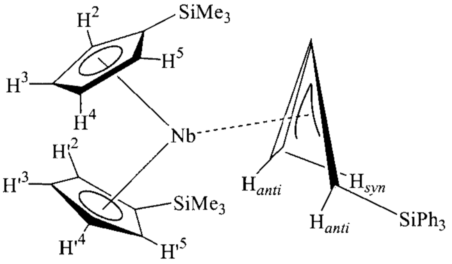


Figure 2. Proposed structure for [NbCp'$_2$(η^3-CH$_2$CHCHSiPh$_3$)] (**2**)

The molecular structure of **1** was established by single crystal X-ray diffraction and confirmed the η^3-coordination of the allyl ligand. The molecular structure and atom numbering scheme are shown in Figure 3. Selected bond lengths and angles for **1** are given in Table 1.

The structure of **1** shows the typical bent metallocene confirmation observed in niobocene complexes, with both cyclopentadienyl ligands bound to the metal in an η^5 mode. The environment of the niobium atom is completed by the η^3-allyl ligand. If the terminal carbon atoms of the allyl ligand are regarded as occupying two coordination sites, then the niobium metal centre can be considered as having a distorted tetrahedral geometry. The angle defined by Cent(1), Nb and Cent(2) is 131.48(1)°, by Cent(1), Nb and Cent(3) 113.13(2)°, and by Cent(2), Nb and Cent(3) 115.35(1)° [Cent(1) and Cent(2) are the centroids of the cyclopentadienyl ligands and Cent(3) is the centroid of the allyl ligand). The sum of these three angles is exactly 360° indicating that the vectors connecting the Nb atom with Cent(1), Cent(2) and Cent(3) are all in one plane.

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Table 1. Selected bond lengths [Å] and angles [°] for **1**

Bond lengths		Bond angles	
av Nb(1)−C[Cent(1)][a][b]	2.398	Cent(1)−Nb(1)−Cent(2)	131.48(1)
av Nb(1)−C[Cent(2)][a][b]	2.429	Cent(1)−Nb(1)−Cent(3)	113.13(2)
Nb(1)−C(1)	2.395(4)	Cent(2)−Nb(1)−Cent(3)	115.35(1)
Nb(1)−C(2)	2.366(4)	C(2)−Nb(1)−C(1)	34.4(1)
Nb(1)−C(3)	2.377(5)	C(3)−Nb(1)−C(1)	64.2(2)
Si(1)−C(1)	1.869(5)	C(2)−C(1)−Si(1)	118.9(3)
Si(1)−C(10)	1.914(5)	C(2)−C(1)−Nb(1)	71.6(2)
Si(2)−C(3)	1.839(5)	Si(1)−C(1)−Nb(1)	137.9(2)
Si(2)−C(4)	1.904(6)	C(1)−C(2)−C(3)	127.3(4)
C(1)−C(2)	1.408(6)	C(1)−C(2)−Nb(1)	74.0(3)
C(2)−C(3)	1.421(6)	C(3)−C(2)−Nb(1)	73.0(3)
		C(2)−C(3)−Si(2)	124.1(4)
		C(2)−C(3)−Nb(1)	72.1(2)
		Si(2)−C(3)−Nb(1)	133.7(2)

[a] Cent(1), Cent(2) and Cent(3) are the centroids of C(21)−C(25), C(31)−C(35) and C(1)−C(3), respectively. [b] Refers to the average bond length between Nb(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

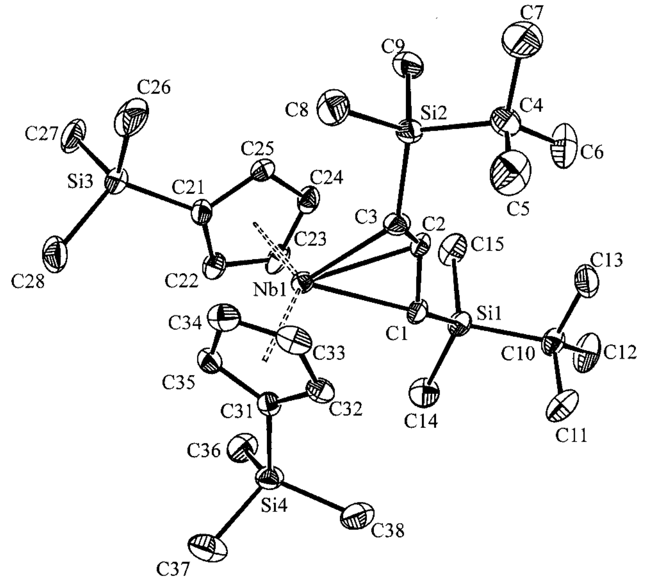
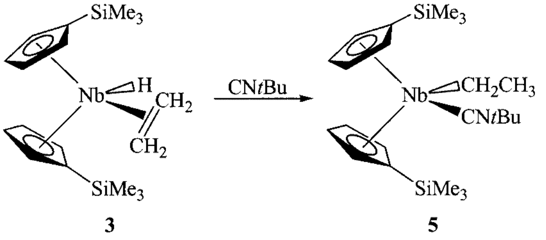


Figure 3. Molecular structure and atom-labelling scheme for $[NbCp'_2(\eta^3\text{-}t\text{BuMe}_2\text{SiCHCHCHSiMe}_2t\text{Bu})]$ (**1**), with thermal ellipsoids at 30% probability

The allyl ligand assumes a planar *cis-syn* geometry and shows η^3-coordination to the metal centre. The carbon atoms of the allyl ligand are nearly planar with C−C distances of 1.408(6) Å and 1.421(6) Å, which are similar to the only other X-ray characterised allylniobocene complex, namely $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_5)]$.[13] The plane of the allyl group in **1** is not perpendicular to the plane defined by Nb(1), C(2) and C(3) but at an angle of 116.0(4)°, typically tilted away from perpendicular to maximize orbital overlap. These structural features are consistent with a strong bonding interaction between the allyl nonbonding orbital and the empty metal orbital, and little back-bonding from the metal to the allyl.[13] The close structural similarity between the niobium derivatives **1**, and $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_5)]$ (d^2 metal centre) with $[Ti(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_3\text{-}1,3\text{-}Me_2)]$[14] ($d^1$ metal centre) is also an indication that the metal-to-ligand back donation is negligible. The effect of alkyl substitution at the terminal carbons of the allyl ligand is reflected in the elongated Nb−C(1) and Nb−C(3) distances 2.395(4) Å and 2.377(5) Å, respectively. These values are greater than the Nb−C(2) distance [2.366(4) Å] and longer that observed in the unsubstituted allyl compound.[13]

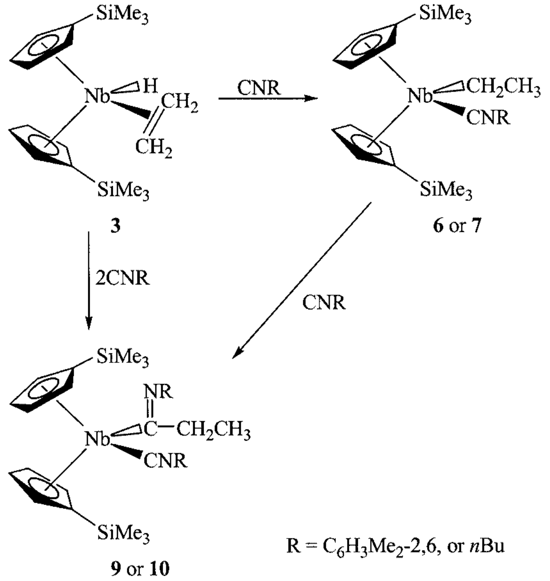
The reaction of the niobocene derivatives **1**, **2**, $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**)[10] and $[NbCp'_2(\eta^3\text{-}CH_2CHCH_2)]$ (**4**)[7] with isocyanide compounds has been studied. The hydrido(ethylene)niobocene complex $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) was found to react slowly at room temperature with *tert*-butyl isocyanide to give the ethyl isocyanide derivative $[NbCp'_2(CH_2CH_3)(CNt\text{Bu})]$ (**5**) in quantitative yield as a red oil (Scheme 2). The isocyanide ligand promotes the insertion of the olefin into the niobium−hydride bond and no further reaction was observed even when an excess of isocyanide was used or the reaction was carried out the at higher temperatures. Complex **5** was characterised spectroscopically. The most significant IR band for **5** corresponds to the isocyanide stretching mode ν(CN) at 2095 cm^{-1}. In the ^{13}C NMR spectrum of **5** the most interesting feature was the extremely low field resonance (δ = 270.0 ppm) which was observed for the metal-bonded isocyanide carbon. This resonance appears as a broad singlet due to the high relaxation time in the NMR time scale.[15]



3 **5**

Scheme 2

In contrast with the behaviour observed in the synthesis of **5**, an equimolar amount of 2,6-dimethylphenyl isocyanide reacts at room temperature with **3** to give, initially the ethyl isocyanide derivative $[NbCp'_2(CH_2CH_3)(CNC_6H_3Me_2\text{-}2,6)]$ (**6**) which evolves rapidly at room temperature with the insertion of a second equivalent of the isocyanide ligand into the niobium-carbon bond to yield the neutral iminoacyl compound $[NbCp'_2\{\eta^1\text{-}C(=N-C_6H_3Me_2\text{-}2,6)(CH_2CH_3)\}(CNC_6H_3Me_2\text{-}2,6)]$ (**9**) (Scheme 3). Compound **6** could not be isolated as a pure sample, but as part of a mixture containing, in addition, **3** and **9**. However, **9** could be prepared and isolated as a pure sample by the reaction of **3** with two equivalents of the isocyanide reagent.



Scheme 3

Compound **6** was characterised by ^1H NMR spectroscopy where typical resonances corresponding to the cyclopentadienyl, ethyl and isocyanide ligands were observed (see Exp. Sect.). Complex **9** showed in the IR spectrum a band corresponding to the stretching mode ν(CN) at 2021 cm^{-1} of the linear isocyanide ligand. The ν(C=N) stretching frequency corresponding to the η^1-iminoacyl ligand was observed at 1657 cm^{-1}.[16] NMR evidence supports the proposal that the iminoacyl ligand in this compound is coordinated in an η^1 fashion. The ^1H NMR resonance of the inserted methylene group of the ethyl ligand observed is displaced to lower field, $\delta = 2.35$ ppm, with respect to that observed in **6**, $\delta = 0.81$ ppm. In the ^{13}C NMR spectrum a low field resonance, $\delta = 218.2$ ppm, was observed for the carbon of the terminal isocyanide ligand bonded to niobium. A second signal shifted to higher field, $\delta = 153.6$ ppm, was assigned to the carbon of the η^1-iminoacyl ligand. The previously reported cationic iminoacylniobium derivatives $[NbCp'_2X(\eta^2\text{-}C(=NPh)\text{-}CHCHRPh)]$[17] (X = Cl, H, CH_3) showed the signal attributed to the η^2-iminoacyl carbon in the range $\delta = 213-219$ ppm which was in accordance with the data reported for complexes of other early transition metals.[18] Adams and co-workers have shown that the η^2-iminoacyl carbon in $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}MeCNMe)]$ resonates approximately $\delta = 40$ ppm downfield of the corresponding resonance in $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{P(OMe)_3\}(\eta^1\text{-}MeCNPh)]$.[19] Royo and co-workers have proposed a related η^1 iminoacyltantalum system as an intermediate in the synthesis of compounds containing imido-η^2-iminoacyl ligands $[Ta(\eta^5\text{-}C_5Me_5)(=NtBu)Cl\{\eta^2\text{-}C[C(Me)=NR]=NR\}]$ (R = $C_6H_3Me_2$-2,6).[20]

Further evolution of **9** to give the coupling of the isocyanide and the η^1-iminoacyl groups to produce metallacyclic compounds was not observed.[21]

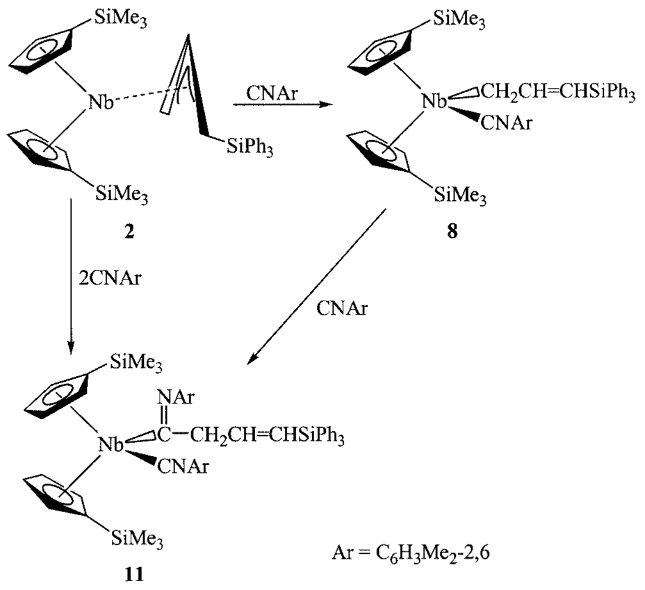
The reaction of *n*-butyl isocyanide with **3** also gave a mixture of products, namely the alkyl compound $[NbCp'_2(CH_2CH_3)(CNnBu)]$ (**7**) and the iminoacyl complex $[NbCp'_2\{\eta^1\text{-}C(=NnBu)(CH_2CH_3)\}(CNnBu)]$ (**10**) (Scheme 3). With an excess of isocyanide further reactions gave a mixture of products which we were unable to identify. **7** was characterised by ^1H NMR spectroscopy where typical resonances corresponding to the cyclopentadienyl, ethyl and isocyanide ligands were observed (see Exp. Sect.). In the ^1H NMR spectrum a second set of signals corresponding to the cyclopentadienyl, ethyl, isocyanide and iminoacyl ligands were assigned to compound **10** (see Exp. Sect.).

In the case of the allylniobocene derivatives, **1**, **2** and **4**, there was no reaction with *tert*-butyl isocyanide (even at 80 °C). Nevertheless the complexes rapidly reacted with *n*-butyl isocyanide although only to give mixtures of products which we were unable to identify.

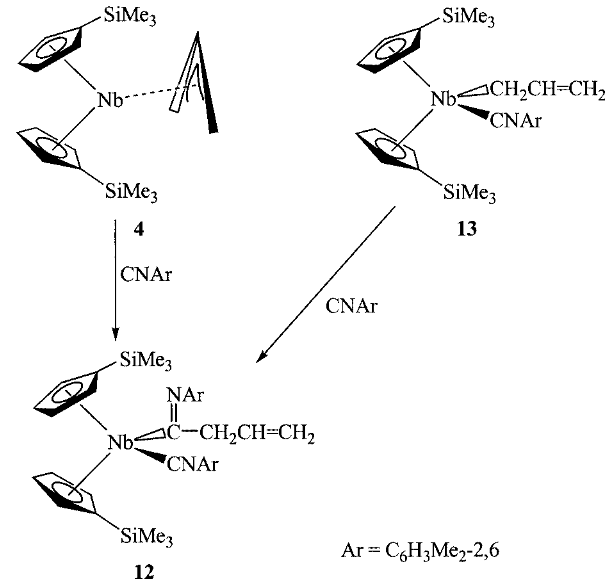
Complex **1** did not react with 2,6-dimethylphenyl isocyanide at room temperature and at 80 °C the products from the reaction could not be identified. However, $[NbCp'_2(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (**2**) reacts with two equivalents of 2,6-dimethylphenyl isocyanide at room temperature to give initially the η^1-allyl isocyanide derivative $[NbCp'_2(\eta^1\text{-}CH_2CH=CHSiPh_3)(CNC_6H_3Me_2\text{-}2,6)]$ (**8**) which undergoes an insertion reaction of further isocyanide to give the iminoacyl derivative $[NbCp'_2\{\eta^1\text{-}C(=NC_6H_3Me_2\text{-}2,6)(CH_2CH=CHSiPh_3)\}(CNC_6H_3Me_2\text{-}2,6)]$ (**11**) (Scheme 4).

In contrast $[NbCp'_2(\eta^3\text{-}CH_2CHCH_2)]$ (**4**) did not react with the aryl isocyanide at room temperature, and the reaction had to be carried out at 80 °C in order to obtain the corresponding η^1-iminoacyl compound $[NbCp'_2\{\eta^1\text{-}C(=NC_6H_3Me_2\text{-}2,6)(CH_2CH=CH_2)\}(CNC_6H_3Me_2\text{-}2,6)]$ (**12**) [Scheme (5)]. Under these conditions the corresponding intermediate η^1-allyl derivative $[NbCp'_2(\eta^1\text{-}CH_2CH=CH_2)(CNC_6H_3Me_2\text{-}2,6)]$ (**13**) was not detected. However, we have previously reported its preparation by a distinctive synthetic route.[7] The reaction of **13** with an equimolar amount of aryl isocyanide gave the iminoacyl complex **12** (Scheme 5).

The complexes **8**, **11** and **12** were characterised by IR and NMR spectroscopy (see Exp. Sect.). ^1H NMR spectroscopy for these compounds showed that the two cyclopentadienyl ligands are equivalent indicating a σ_h symmetry plane in



Scheme 4



Scheme 5

the molecule. The disappearance of the *anti* and *syn* protons signals of the starting complexes clearly shows the change of bonding mode of the allyl ligand from η^3 to η^1 in the final product. The η^1-allyl complexes exhibited, in the ^1H NMR spectra, for this group, three sets of signals corresponding to a doublet for the CH_2 bonded to the niobium or iminoacyl carbon atom, a multiplet, at ca. $\delta = 5.7$ ppm, for the central group CH and a multiplet, at ca. $\delta = 4.6$ ppm, for the terminal olefinic protons. One the more important features of the ^1H NMR spectra was the position of the resonance of the methylene group of the η^1-allyl system which was found to resonate at $\delta = 1.65$ ppm for **8** and $\delta = 1.39$ ppm for **13**, when this group is directly bonded to niobium. However, for **11** and **12** where the methylene group is bonded to the iminoacyl carbon atom, the corresponding signal was shifted downfield to $\delta = 3.54$ ppm and 3.26 ppm, respectively.

The IR spectrum for compounds **11** and **12** showed a band corresponding to the stretching mode ν(CN) at 2019 and 2029 cm^{-1}, respectively, corresponding to the isocyanide ligand coordinated to the metal atom. The ν(C=N) stretching frequencies for **11** and **12**, corresponding to the η^1-iminoacyl ligands appeared at 1659 and 1677 cm^{-1}, respectively.

In conclusion, two new allylniobocene complexes have been prepared and the X-ray structure (only the second reported example) for one of these compounds has been determined. η^1-Iminoacylniobocene complexes have been synthesised and characterised by spectroscopic techniques. NMR spectroscopy studies have allowed us to establish the ease of the different isocyanide molecules insertion reactions in the different niobium systems, and corresponds to the following order CN*n*Bu > $CNC_6H_3Me_2$-2,6 > CN*t*Bu for the isocyanide molecules and $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) > $[NbCp'_2(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (**2**) > $[NbCp'_2(\eta^3\text{-}CH_2CHCH_2)]$ (**4**), for the organometallic substrates.

Experimental Section

General Remarks: All reactions were performed using standard Schlenk tube techniques under dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before used.

The compounds $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**),[10] $[NbCp'_2(\eta^3\text{-}CH_2CHCH_2)]$ (**4**),[7] $[K(\eta^3\text{-}CHRCHCHR')]$ (R = R′ = $SiMe_2$*t*Bu; R = H, R′ = $SiPh_3$)[12] and $[NbCp'_2(\eta^1\text{-}CH_2CH{=}CH_2)(CNC_6H_3Me_2\text{-}2,6)]$ (**13**)[7] were prepared as described earlier. *t*BuNC, *n*BuNC, $CNC_6H_3Me_2$-2,6 were purchased from Aldrich and Fluka and used directly. IR spectra were recorded with a Perkin−Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded with 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.

Preparation of $[NbCp'_2(\eta^3\text{-}t\text{BuMe}_2\text{SiCHCHCHSiMe}_2t\text{Bu})]$ (1): $[K(\eta^3\text{-}t\text{BuMe}_2\text{SiCHCHCHSiMe}_2t\text{Bu})]$ (0.30 g, 1.47 mmol) in THF (50 mL) was added at 0 °C to a solution of $[\{NbCp'_2Cl\}_2]$ (0.20 g, 0.50 mmol) in THF (10 mL). The resulting mixture was warmed to room temperature and stirred for 12 h. Solvent was removed in vacuo and hexane (50 mL) added to the green solid. After filtration, all volatiles were removed, from the filtrate, under reduced pressure to yield a dark green solid of the title complex (0.27 g, 87%). X-ray quality crystals were obtained by recrystallisation from cold hexane. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = -0.05$, 0.34 (2s, each 12 H, 2 × $CHSi\mathit{Me}_2t$Bu), 0.04 (d, $^3J_{H,H} = 11.1$ Hz, 2 H, 2 × $C\mathit{H}SiMe_2t$Bu), 0.23, 0.24 (2s, each 9 H, 2 × $C_5H_4Si\mathit{Me}_3$), 1.17 (s, 18 H, 2 × $CHSiMe_2t$Bu), 3.02 [t, 1 H, $\mathit{H}C(CHSiMe_2t\text{Bu})_2$], 4.28, 4.54, 4.78, 4.89 (4m, each 2 H, 2 × $C_5\mathit{H}_4$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta = -6.1$, -2.4 ($CHSi\mathit{Me}_2t$Bu), 0.5, 0.8

$(C_5H_4Si\mathit{Me}_3)$, 27.3, 33.7 $(CHSiMe_2\mathit{t}Bu)$, 39.9 $[CH(\mathit{C}HSiMe_2\mathit{t}Bu)_2]$, 96.0 $[\mathit{C}H(CHSiMe_2\mathit{t}Bu)_2]$, 85.6, 88.9, 94.3, 94.5, 101.6, 105.2 (C_5H_4) ppm. $C_{31}H_{59}NbSi_4$ (637.1): calcd. C 58.45, H 9.33; found C 58.29, H 9.25.

Preparation of $[NbCp'_2(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (2): The synthesis of **2** was carried out in an identical manner to that described for **1**. From $[K(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (0.31 g, 0.92 mmol) and $[\{NbCp'_2Cl\}_2]$ (0.37 g, 0.46 mmol). Yield 0.47 g, 77%. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = -0.13$ (d, 1 H, $C\mathit{H}SiPh_3$), 0.16, 0.32 (2s, each 9 H, 2 × $C_5H_4Si\mathit{Me}_3$), 1.15 (*anti*), 2.94 (*syn*) (2m, each 1 H, $C\mathit{H}_2CHCHSiPh_3$), 2.81, 3.39, 4.18, 4.38, 4.44, 4.59, 4.82, 5.51 (8m, each 1 H, 2 × $C_5\mathit{H}_4$), 7.27−8.10 (m, 15 H, $Si\mathit{Ph}_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta = 0.1$, 0.5 $(C_5H_4Si\mathit{Me}_3)$ 21.8 $(\mathit{C}H_2CHCHSiPh_3)$, 38.5 $(\mathit{C}HSiPh_3)$, 88.1 $(CH_2\mathit{C}HCHSiPh_3)$, 84.9, 87.0, 90.3, 93.2, 99.2, 100.1, 100.4, 100.7, 104.4, 105.3 (C_5H_4), 126.0−130.0 $(Si\mathit{Ph}_3)$ ppm. $C_{37}H_{45}NbSi_3$ (666.9): calcd. C 66.63, H 6.80; found C 66.45, H 6.70.

Preparation of $[NbCp'_2(CH_2CH_3)(CN\mathit{t}Bu)]$ (5): To a hexane solution (30 mL) of $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) (0.28 g, 0.71 mmol) an equimolar amount of *tert*-butyl isocyanide (80 µL, 0.71 mmol) was added and the reaction mixture was stirred at room temperature for 16 h. The yellow solution gradually became red, and finally a red oily residue was obtained after removing the solvent. The red oily product was shown to be pure by NMR spectroscopy. At 60 °C the reaction takes place in 6 h. IR (KBr): $\nu_{CN} = 2095\ cm^{-1}$. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.15$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 0.65 (q, $^3J_{H,H} = 7.6$ Hz, 2 H, $C\mathit{H}_2CH_3$), 1.20 [s, 9 H, $CNC(C\mathit{H}_3)_3$], 1.33 (t, 3 H, $CH_2C\mathit{H}_3$), 4.63, 4.72, 5.04, 5.22 (4m, each 2 H, 2 × $C_5\mathit{H}_4$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta = 0.6$ $(C_5H_4Si\mathit{Me}_3)$, 14.8 $(\mathit{C}H_2CH_3)$, 23.6 $(CH_2\mathit{C}H_3)$, 32.0 $[C(\mathit{C}H_3)_3]$, 62.2 $[\mathit{C}(CH_3)_3]$, 91.6, 95.6, 96.3, 102.5, 103.5 (C_5H_4), 270.0 $(\mathit{C}N)$ ppm.

Preparation of $[NbCp'_2(CH_2CH_3)(CNC_6H_3Me_2\text{-}2,6)]$ (6): To a deuterated benzene solution (1 mL) of $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) (0.02 g, 0.05 mmol) in an NMR tube was added an excess of 2,6-dimethylphenyl isocyanide (0.01 g, 0.11 mmol). The reaction mixture was immediately monitored by ^1H NMR spectroscopy and a mixture of three compounds, the starting hydride-olefin compound **3** and the compounds **6** and **9**, in a 1:0.9:0.75 proportion, was identified. **6:** ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.16$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 0.81 (q, $^3J_{H,H} = 7.7$ Hz, 2 H, $C\mathit{H}_2CH_3$), 1.45 (t, 3 H, $CH_2C\mathit{H}_3$), 1.64 (s, 6 H, $CNC_6H_3\mathit{Me}_2$), 3.71, 4.11, 5.13, 5.69 (4m, each 2 H, 2 × $C_5\mathit{H}_4$), 6.39−6.55 (m, 3 H, $CNC_6\mathit{H}_3Me_2$) ppm.

Preparation of $[NbCp'_2(CH_2CH_3)(CN\mathit{n}Bu)]$ (7): The synthesis of **7** was carried out in an identical manner to that described for **6**. From $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) (0.04 g, 0.10 mmol) and *n*-butyl isocyanide (11 µL, 0.10 mmol). A mixture of **3** and **7** in a 2:1 proportion was identified. **7:** ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.16$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 0.75 (m, 3 H, $CNCH_2CH_2CH_2C\mathit{H}_3$), 0.83 (q, $^3J_{H,H} = 7.7$ Hz, 2 H, $C\mathit{H}_2CH_3$), 0.90 (m, 2 H, $CNCH_2CH_2C\mathit{H}_2CH_3$), 1.25 (m, 2 H, $CNCH_2C\mathit{H}_2CH_2CH_3$), 1.45 (t, 3 H, $CH_2C\mathit{H}_3$), 3.35 (m, 2 H, $CNC\mathit{H}_2CH_2CH_2CH_3$), 4.63, 4.69, 4.92, 5.17 (4m, each 2 H, 2 × $C_5\mathit{H}_4$) ppm.

Preparation of $[NbCp'_2(\eta^1\text{-}CH_2CH{=}CHSiPh_3)(CNC_6H_3Me_2\text{-}2,6)]$ (8): The synthesis of **8** was carried out in an identical manner to that described for **6**. From $[NbCp'_2(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (**2**) (0.02 g, 0.03 mmol) and $CNC_6H_3Me_2$-2,6 (0.01 g, 0.09 mmol). ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.04$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 2.08 (s, 6 H, $CNC_6H_3\mathit{Me}_2$), 1.65 (d, 2 H, $C\mathit{H}_2CH{=}CHSiPh_3$), 4.70 (m, 2 H, $CH_2CH{=}C\mathit{H}SiPh_3$), 5.50 (m, 2 H, $CH_2C\mathit{H}{=}CHSiPh_3$), 4.60, 4.61, 4.89, 5.11, (4m, each 2 H, 2 × $C_5\mathit{H}_4$), 7.20−7.76 (m, 15 H, $SiPh_3$) ppm.

Preparation of $[NbCp'_2\{\eta^1\text{-}C({=}NC_6H_3Me_2\text{-}2,6)(CH_2CH_3)\}(CNC_6H_3Me_2\text{-}2,6)]$ (9): The synthesis of **9** was carried out in an identical manner to that described for **5**. From $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) (0.15 g, 0.39 mmol) and 2,6-dimethylphenyl isocyanide (0.10 g, 0.78 mmol). Yield 0.23 g, 90%. IR (KBr/Nujol): $\tilde{\nu} = 1657$ ($\nu_{C=N}$, iminoacyl), 2021 (ν_{CN}, isocyanide) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.09$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 0.90 (t, $^3J_{H,H} = 7.6$ Hz, 3 H, $CH_2C\mathit{H}_3$), 2.15 (s, 6 H, $CNC_6H_3\mathit{Me}_2$), 2.17 (s, 6 H, $\eta^1\text{-}C\{NC_6H_3\mathit{Me}_2\}$), 2.35 (q, 2 H, $C\mathit{H}_2CH_3$), 4.93, 5.25, 5.28, 5.49 (4m, each 2 H, 2 × $C_5\mathit{H}_4$), 6.39−6.55 (m, 6 H, 2 × $CNC_6\mathit{H}_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta =$ 0.4 $(Si\mathit{Me}_3)$, 11.2 $(\mathit{C}H_2CH_3)$, 19.1 $(CNC_6H_3\mathit{Me}_2)$, 19.9 $(\eta^1\text{-}C\{NC_6H_3\mathit{Me}_2\})$, 44.7 $(CH_2\mathit{C}H_3)$, 91.8, 96.0, 98.2, 98.5, 105.0 (C_5H_4), 120.5−128.9 ($\eta^1\text{-}C\{N\mathit{C}_6H_3Me_2\}$ and $CN\mathit{C}_6H_3Me_2$), 153.6 $(\eta^1\text{-}\mathit{C}\{NC_6H_3Me_2\})$, 218.2 $(\mathit{C}NC_6H_3Me_2)$ ppm. $C_{36}H_{49}N_2NbSi_2$ (658.9): calcd. C 65.63, H 7.50, N 4.25; found C 65.50, H 7.42, N 4.25.

Preparation of $[NbCp'_2\{\eta^1\text{-}C({=}N\mathit{n}Bu)(CH_2CH_3)\}(CN\mathit{n}Bu)]$ (10): The synthesis of **10** was carried out in an identical manner to that described for **6**. From $[NbCp'_2H(\eta^2\text{-}CH_2{=}CH_2)]$ (**3**) (0.04 g, 0.10 mmol) and *n*-butyl isocyanide (22 µL, 0.20 mmol). IR (KBr/Nujol): $\tilde{\nu} = 1690$ ($\nu_{C=N}$, iminoacyl), 2046 (ν_{CN}, isocyanide) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.26$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 0.96 (t, $^3J_{H,H} = 7.7$ Hz, 3 H, $CH_2C\mathit{H}_3$), 0.81, 0.84 (2m, each 3 H, 2 × $CNCH_2CH_2CH_2C\mathit{H}_3$), 0.93, 0.97 (2m, each 2 H, 2 × $CNCH_2CH_2C\mathit{H}_2CH_3$), 1.30, 1.36 (2m, each 2 H, 2 × $CNCH_2C\mathit{H}_2CH_2CH_3$), 2.03 (q, 2 H, $C\mathit{H}_2CH_3$), 3.25, 3.30 (2m, each 2 H, 2 × $CNC\mathit{H}_2CH_2CH_2CH_3$), 3.38, 3.53, 5.06, 5.43 (4m, each 2 H, 2 × $C_5\mathit{H}_4$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta = 1.3$ $(C_5H_4Si\mathit{Me}_3)$, 11.4 $(CH_2\mathit{C}H_3)$, 13.5, 16.4, 25.3, 27.2, 34.2, 35.9, 60.4, 62.7 (*n*Bu), 49.5 $(\mathit{C}H_2CH_3)$, 82.5, 93.6, 93.7, 94.7, 97.4 (C_5H_4), 162.6 $(\eta^1\text{-}\mathit{C}\{N\mathit{n}Bu\})$, 222.0 $(\mathit{C}N\mathit{n}Bu)$ ppm. $C_{28}H_{49}N_2NbSi_2$ (562.8): calcd. C 59.76, H 8.78, N 4.98; found C 59.44, H 8.69, N 4.96.

Preparation of $[NbCp'_2\{\eta^1\text{-}C(NC_6H_3Me_2\text{-}2,6)(CH_2CH{=}CHSiPh_3)\}(CNC_6H_3Me_2\text{-}2,6)]$ (11): The synthesis of **11** was carried out in an identical manner to that described for **5**. From $[NbCp'_2(\eta^3\text{-}CH_2CHCHSiPh_3)]$ (**2**) (0.11 g, 0.17 mmol) and 2,6-dimethylphenyl isocyanide (0.04 g, 0.34 mmol). Yield 0.13 g, 85%. IR (KBr/Nujol): $\tilde{\nu} = 1659$ ($\nu_{C=N}$, iminoacyl), 2019 (ν_{CN}, isocyanide) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.08$ (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 2.06, 2.07 (2s, each 6 H, 2 × $CNC_6H_3\mathit{Me}_2$), 3.54 (d, 2 H, $C\mathit{H}_2CH{=}CHSiPh_3$), 4.61 (m, 1 H, $CH_2CH{=}C\mathit{H}SiPh_3$), 5.70 (m, 1 H, $CH_2C\mathit{H}{=}CHSiPh_3$), 4.82, 5.22, 5.28, 5.52 (4m, each 2 H, 2 × $C_5\mathit{H}_4$), 6.50−7.00 (m, 15 H, $SiPh_3$), 7.20−7.90 (m, 6 H, 2 × $CNC_6\mathit{H}_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta =$ 0.4 $(C_5H_4Si\mathit{Me}_3)$, 19.1 $(CNC_6H_3\mathit{Me}_2)$, 20.0 $(\eta^1\text{-}C\{NC_6H_3\mathit{Me}_2\})$, 61.9 $(\mathit{C}H_2CH{=}CHSiPh_3)$, 91.8, 95.3, 97.7, 98.0, 105.6 (C_5H_4), 120.8 $(CH_2CH{=}\mathit{C}HSiPh_3)$, 121.6−129.8 ($\eta^1\text{-}C\{N\mathit{C}_6H_3Me_2\}$, $CN\mathit{C}_6H_3Me_2$ and $Si\mathit{Ph}_3$), 150.1 $(CH_2\mathit{C}H{=}CHSiPh_3)$, 171.1 $(\eta^1\text{-}\mathit{C}\{NC_6H_3\mathit{Me}_2\})$, 228.0 $(CNC_6H_3\mathit{Me}_2)$ ppm. $C_{55}H_{63}N_2NbSi_3$ (929.3): calcd. C 71.09, H 6.83, N 3.01; found C 70.89, H 6.74, N 3.04.

Preparation of $[NbCp'_2\{\eta^1\text{-}C(N\text{-}Me_2C_6H_3\text{-}2,6)(CH_2CH{=}CH_2)\}(CNC_6H_3Me_2\text{-}2,6)]$ (12): The synthesis of **12** was carried out in an identical manner to that described for **5**. From $[NbCp'_2(\eta^3\text{-}CH_2CHCH_2)]$ (**4**) (0.27 g, 0.66 mmol) and 2,6-dimethylphenyl isocyanide (0.17 g, 1.32 mmol). Yield 0.40 g, 90%. IR (KBr/Nujol): $\tilde{\nu} = 1677$ ($\nu_{C=N}$, iminoacyl), 2029 (ν_{CN}, isocyanide) cm^{-1}. ^1H

NMR (200 MHz, C_6D_6, 25 °C): δ = 0.09 (s, 18 H, 2 × $C_5H_4Si\mathit{Me}_3$), 2.15, 2.18 (2s, each 6 H, 2 × $CNC_6H_3\mathit{Me}_2$), 3.26 (d, 2 H, $C\mathit{H}_2CH{=}CH_2$), 4.73 (m, 2 H, $CH_2CH{=}C\mathit{H}_2$), 6.10 (m, 2 H, $CH_2C\mathit{H}{=}CH_2$), 4.95, 5.27, 5.29, 5.56 (4m, each 2 H, 2 × $C_5\mathit{H}_4$), 6.60−7.90 (m, 6 H, 2 × $CNC_6\mathit{H}_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ = 0.4 ($C_5H_4Si\mathit{Me}_3$), 19.2, 19.3 ($CNC_6H_3\mathit{Me}_2$), 58.0 ($\mathit{C}H_2CH{=}CH_2$), 92.5, 96.4, 99.0, 99.3, 105.6 (C_5H_4), 110.6 ($CH_2CH{=}\mathit{C}H_2$), 153.6 ($CH_2\mathit{C}H{=}CH_2$), 115.3−129.9 (η^1-C{N$\mathit{C}_6H_3Me_2$} and CN$\mathit{C}_6H_3Me_2$), 170.0 (η^1-C\{$NC_6H_3Me_2$\}), 225.0 ($\mathit{C}NC_6H_3Me_2$) ppm. $C_{37}H_{49}N_2NbSi_2$ (670.9): calcd. C 66.24, H 7.36, N 4.18; found C 66.03, H 7.31, N 4.13.

X-ray Crystal Structure Determination of [$NbCp'_2(\eta^3$-tBuMe$_2$Si-CHCHCHSiMe$_2t$Bu)] (1): The crystallographic data and experimental details are given in Table 2. Crystallographic reflections were collected at 230 K on a Nonius-Mach3 diffractometer equipped with graphite-monochromated radiation (λ = 0.71073 Å). Unit cell dimensions were obtained by least-squares fit of the 2θ values of 25 high-order reflections by using the Mach3 centring routines. The intensities of 8372 reflections were collected ($2 < \theta < 28$); of these only 5489 reflections obeyed the condition $I > 2\sigma(I)$. Data were corrected in the usual fashion for Lorentz and polarisation effects and absorption correction was not necessary. The structure was solved by direct methods (SIR92)[22] and refinement on F^2 was carried out by full-matrix least-squares analysis (SHELXL-97).[23] A number of cycles of refinement with isotropic thermal parameters, followed by difference synthesis, enabled location of all the non-hydrogen atoms. For the final cycles of refinement all non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in calculated positions but non refined. CCDC-201888 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(internat.) +44−1223/336−033; Email: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinement for **1**

Empirical formula	$C_{31}H_{59}NbSi_4$
Molecular mass	637.05
Temperature	230(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 11.875(3) Å b = 25.236(3) Å, β = 107.57(2)° c = 12.701(2) Å
Volume	3628.6(12) Å^3
Z, calculated density	4, 1.166 g/cm^3
Absorption coefficient	4.81 cm^{-1}
F(000)	1368
Crystal size	0.3 × 0.2 × 0.2 mm
Limiting indices	$0 \le h \le 15$, $0 \le k \le 33$, $-14 \le l \le 14$
Reflections collected / unique	8372/8372 [R(int) = 0.0000]
Data/restraints/parameters	8372/0/337
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0424, $wR2$ = 0.1039
R indices (all data)	$R1$ = 0.0828, $wR2$ = 0.1734
Largest diff. peak and hole	0.551 and −0.741 e·Å^{-3}

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