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# Synthesis, structure, and chemistry of hydrido and alkyl niobocene ketene and ketenimine derivatives. X-ray crystal structure of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CH_3)(\eta^2\text{-}(C,O)O{=}C{=}CPh_2)]$

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**Abstract**

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,Z)\text{–}ZCCRPh)]$ (**1a**, Z = NPh, R = Ph; **1b**, Z = NPh, R = Me; **1c**, Z = NPh, R = Et; **1d**, Z = NPh, R = H; **2**, Z = O, R = Ph) reacts with $Li(BEt_3H)$ and with Grignard ($RMgI$) or dialkyl magnesium ($R_2Mg$) reagents to give the hydride niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(\eta^2\text{-}(C,Z)\text{–}ZCCRPh)]$ (**3a**, Z = NPh, R = Ph; **3b**, Z = NPh, R = Me; **3c**, Z = NPh, R = Et; **3d**, Z = NPh, R = H; **4**, Z = O, R = Ph) and the alkyl niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2R(\eta^2\text{-}(C,Z)\text{–}ZCCR'Ph)]$ (**5a**, Z = NPh, R = Me, R' = Ph; **5b**, Z = NPh, R = R' = Me; **5c**, Z = NPh, R = Me, R' = Et; **5d**, Z = NPh, R = Me, R' = H; **6a**, Z = O, R = Me, R' = Ph; **6b**, Z = O, R = Et, R' = Ph) respectively. The molecular structure of **6a** was determined by single-crystal diffractometry. It shows a typical bent-metallocene geometry around the niobium atom with the $\eta^2(C,O)$ ketene and methyl groups arrayed in the plane between the two cyclopentadienyl rings. Finally, some hydrido and alkyl niobocene ketenimine and ketene complexes were easily protonated with 1 equiv. of $HBF_4 \cdot OEt_2$ giving rise, in one step, to the corresponding $\eta^2$-iminoacyl and $\eta^2$-acyl complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Y(\eta^2\text{-}(C,Z)\text{–}ZCCRHPh)]^+[BF_4^-]$ (**7a**, Y = H, Z = NPh, R = Ph; **7b**, Y = H, Z = NPh, R = Me; **8a**, Y = Me, Z = NPh, R = Ph; **8b**, Y = Me, Z = NPh, R = Et; **9**, Y = Me, Z = O, R = Ph). $^1H$ NMR studies on several unsymmetrical ketenimine-bearing chloro, hydrido and methyl niobocene complexes containing E–Z isomeric mixtures were carried out, and it was found that intermolecular isomerization of the E and Z isomers may govern the different observed E–Z ratios. The structures of the different families of complexes were determined by spectroscopic methods.

*Keywords:* Ketene; Alkyl; Niobocene; Ketenimine; Hydrido

## 1. Introduction

Metal-promoted transformations of ketene, ketenimine and related molecules are important because they can simulate the metal-induced transformations on carbon dioxide, the activation of which is a matter of great interest (see for example Ref. [1]). Furthermore, ketene and ketenimine complexes are used as versatile synthetic building blocks in several processes in fine organic chemistry (see for example Ref. [2]).

In the last few years, as part of our strategy to employ the reactivity of unsaturated organic molecules in the synthesis of niobium organometallic complexes, we synthesized several families of haloketenimine and haloketene complexes [3,4] $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2\text{-}(C,Z)\text{–}ZCCR'R'')]$ (Z = NR, O). The related cationic iminoacyl and acyl complexes [5] $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2\text{-}(C,Z)\text{–}ZCCR'HR'')]^+$ were also prepared by simple protonation at the free terminus of complexed ketenimine or ketene ligands with acids, along with cationic ketenimine complexes [6] $[Nb(\eta^5\text{-}$

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[1] X-ray diffraction studies.


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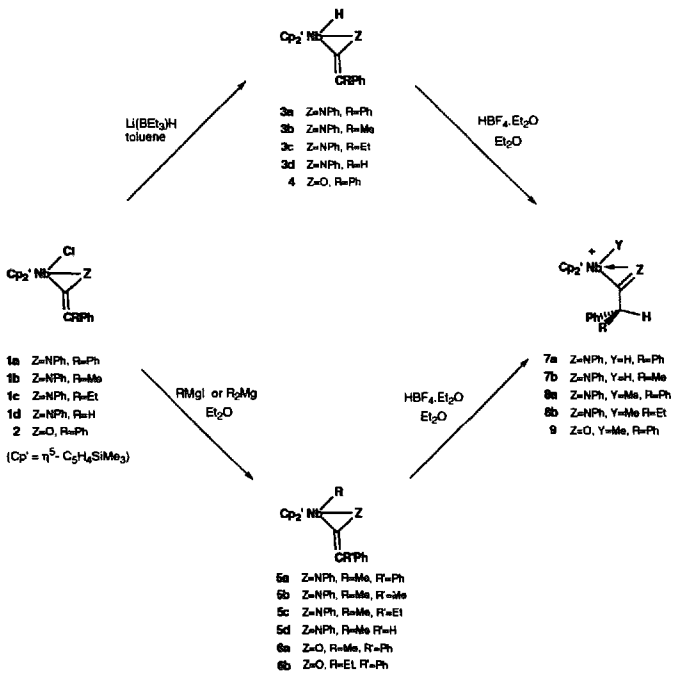
$C_5H_4SiMe_3)_2(\eta^2$-(C,N)–NPhCCPhR)(L)]$^+$, obtained by one-electron oxidation of the corresponding Nb(IV) ketenimine species using ferrocenium salts as oxidizing agents in the presence of an appropriate nitrile or isonitrile ligand.

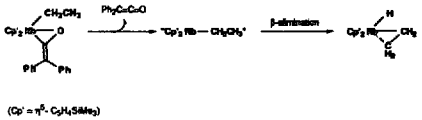
Continuing our research in this field we have decided to explore the preparation of new families of heterocumulene containing niobocene complexes where hydride and alkyl ligands take the place of the halide ancillary ligands. Initial attempts to prepare hydrido derivatives by reducing chloro niobocenes with $LiAlH_4$, NaH, $CaH_2$ or $SnHBu_3$ failed. $Li(BEt_3H)$, however, proved successful and allowed the synthesis of a number of hydrido niobocene complexes. Moreover, alkyl niobocene complexes could be prepared by the reaction of the halo niobocenes with Grignard or dialkylmagnesium reagents but not with the corresponding lithium reagents. This paper will focus on the synthesis and structural details of new ketenimine and ketene complexes [Nb($\eta^5$-$C_5H_4SiMe_3)_2Y(\eta^2$-(C,Z)–ZCCRPh)] (Y = H, R) and their transformation to iminoacyl and acyl complexes [Nb($\eta^5$-$C_5H_4SiMe_3)_2Y(\eta^2$-(C,Z)–ZCCRHPh)]$^+$.

## 2. Results and discussion

First of all we investigated the reaction of chloroketene and chloroketenimine complexes [Nb($\eta^5$-$C_5H_4SiMe_3)_2$(Cl)($\eta^2$-(C,Z)–ZCCRPh)] (Z = O, NPh) with various conventional hydrido transfer reagents, such as $LiAlH_4$, NaH, $CaH_2$, $SnHBu_3$. With the first reagent the only product isolated was [Nb($\eta^5$-$C_5H_4SiMe_3)_2H_3$], together with a considerable amount of intractable products. With the remaining reagents the starting materials were recovered even after refluxing in THF, with none of the expected hydrido niobocenes being observed. The desired product could be obtained however using $Li(BEt_3H)$ in toluene (Scheme 1). The reactions were carried out using a 1:2 molar ratio, as starting material was recovered when a smaller molar ratio was employed. In some preparations variable amounts of the by-product [Nb($\eta^5$-$C_5H_4SiMe_3)_2H_3$] were formed, the extent of which depended on the reaction time. The complexes were isolated as air-stable yellow materials. Several hydrido ketene niobocenes, including **4**, were previously prepared [7] by the treat-




Scheme 1.



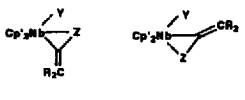
Scheme 2.

ment of chloro complexes with Na/Hg (1:2 molar ratio), through the formation of metallaenolate intermediates which were then protonated and reduced to give the title compounds.

The reaction of complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(\eta^2\text{-}(C,Z)\text{-}ZCCRPh)]$ with alkylating lithium reagents was also considered. The standard procedure which involved the addition of 1 equiv. of MeLi or BuLi to solutions of niobocene complexes failed to yield any of the expected alkyl species after stirring for 48 h, with only starting material being recovered. However, these compounds reacted with MeMgI under the appropiate reaction conditions, to give the corresponding methyl niobocene complexes (Scheme 1). Alternatively, **6a** and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Et)(\eta^2\text{-}(C,O)\text{-}O{=}C{=}CPh_2)]$ **6b** can be obtained by reaction of the corresponding chloroketene derivative with $Me_2Mg$ and $Et_2Mg$ respectively. The reaction with $Et_2Mg$ must be carried out at 0 °C because a considerable amount of the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}(C,C)\text{-}CH_2{=}CH_2)]$ was formed at higher temperature through loss of the ketene ligand and subsequent β-elimination from the ethyl intermediate (Scheme 2). With the exception of **5a** which was crystallized, complexes **5** were isolated as air-stable oily materials while **6a,b** were obtained as air-sensitive crystalline solids.

Unsymmetrical ketene and ketenimine containing hydrido and alkyl niobocenes were isolated as mixtures of E–Z isomers, although the E–Z ratios found by $^1H$ NMR spectroscopy were different to those observed in the starting chloro complexes. The assignment of E–Z isomers was carried out by nuclear Overhauser enhancement (NOE) experiments. With the aid of these data, the isomerization processes for the E and Z isomers, which were previously considered for hydrido ketene niobocenes [7], have been fully analyzed (vide infra).

The new hydrido and alkyl complexes have been spectroscopically characterized. The IR spectra of com-



exo endo

Fig. 1. Possible N(O)-inside and N(O)-outside isomers for unsymmetrical ketene and ketenimine containing hydrido and alkyl niobocenes.

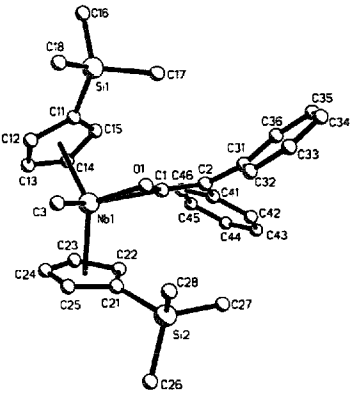


Fig. 2. ORTEP drawing of compound **6a** with the atomic labelling scheme.

plexes **3** show the $\nu$(Nb–H) at ca. 1700 $cm^{-1}$, in agreement with the values reported in other hydrido niobocene complexes [8]; in addition, the IR spectra exhibit the $\nu$(C=C=N) or $\nu$(C=C=O) bands of the ketenimine and ketene ligands in the range 1620 to 1580 $cm^{-1}$ [3,4]. The $^1H$ NMR spectra of complexes **3** exhibit a resonance at ca. 1.45 ppm for the hydride ligand, in

Table 1
Details of the X-ray diffraction study for **6a**

| | |
|---|---|
| Molecular formula | $C_{31}H_{39}NbOSi_2$ |
| Space group | $P2_1/n$ |
| Unit cell volume ($Å^3$) | 3034.8(4) |
| $a$ (Å) | 13.954(1) |
| $b$ (Å) | 15.160(1) |
| $c$ (Å) | 14.352(1) |
| $\beta$ (deg) | 91.67(1) |
| $Z$ | 4 |
| Calculated density ($g\,cm^{-3}$) | 1.262 |
| Crystal dimensions ($mm^3$) | 0.40×0.28×0.25 |
| Absorption coefficient ($cm^{-1}$) | 4.96 |
| $2\theta$ range (deg) | 4–50 |
| Total no. of reflections measured | 5785 |
| Independent reflections | 5318 ($R_{int}$ = 0.002) |
| Observed reflections [$F_o > 4\sigma(F_o)$] | 3728 |
| No. of parameters | 316 |
| Scan type | $\omega$–$2\theta$ |
| $R_1$ | 0.088 |
| $wR_2$ | 0.258 |
| Weighting scheme | calc $w = 1/[\sigma^2(F_o^2) + (0.1454P)^2 + 5.8605]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Final residual ($e\,Å^{-3}$) | 2.07, −2.17 |
| GOF | 1.12 |

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 2
Atomic coordinates ($\times 10^4$) for **6a**

| Atom | x | y | z |
|---|---|---|---|
| Nb(1) | 1302(1) | 1672(1) | 3163(1) |
| Si(1) | −118(2) | 3907(3) | 3508(2) |
| Si(2) | 2821(2) | 319(2) | 5070(2) |
| O(1) | 1581(3) | 2349(3) | 4409(3) |
| C(1) | 2339(4) | 2474(4) | 3909(4) |
| C(2) | 3142(4) | 2952(4) | 4094(4) |
| C(3) | 51(7) | 1343(8) | 4072(8) |
| C(11) | 379(7) | 3018(7) | 2752(7) |
| C(12) | −109(9) | 2288(9) | 2359(9) |
| C(13) | 434(12) | 1913(8) | 1694(9) |
| C(14) | 1313(9) | 2360(7) | 1639(6) |
| C(15) | 1275(7) | 3067(6) | 2294(6) |
| C(16) | −432(10) | 4840(9) | 2777(10) |
| C(17) | 766(11) | 4257(12) | 4383(12) |
| C(18) | −1179(13) | 3560(13) | 4070(17) |
| C(21) | 2301(7) | 450(5) | 3873(6) |
| C(22) | 2744(8) | 784(6) | 3086(7) |
| C(23) | 2131(11) | 585(8) | 2266(7) |
| C(24) | 1351(14) | 166(7) | 2596(9) |
| C(25) | 1420(9) | 68(6) | 3525(8) |
| C(26) | 3003(10) | −885(6) | 5230(8) |
| C(27) | 3967(7) | 947(7) | 5166(7) |
| C(28) | 1973(7) | 711(7) | 5948(6) |
| C(31) | 3231(4) | 3515(4) | 4930(4) |
| C(32) | 2774(5) | 3314(5) | 5766(5) |
| C(33) | 2816(5) | 3900(6) | 6518(5) |
| C(34) | 3322(6) | 4688(6) | 6454(6) |
| C(35) | 3767(6) | 4892(6) | 5656(6) |
| C(36) | 3744(5) | 4312(5) | 4918(5) |
| C(41) | 3965(5) | 2894(4) | 3459(5) |
| C(42) | 4899(5) | 2855(5) | 3832(7) |
| C(43) | 5683(8) | 2746(6) | 3264(10) |
| C(44) | 5536(10) | 2678(7) | 2313(11) |
| C(45) | 4655(12) | 2740(7) | 1949(8) |
| C(46) | 3845(7) | 2847(6) | 2492(6) |

accordance with the chemical shift value previously found in hydrido niobium(V) complexes [9], while a resonance at ca. 0.75 ppm corresponding to the methyl ligand is observed for complexes **5** [10]. $^1H$ and $^{13}C$

Table 3
Selected bond lengths (Å) and angles (°) for **6a**

| | | | |
|---|---|---|---|
| Nb(1)–O(1) | 2.088(4) | Nb(1)–C(3) | 2.265(10) |
| Nb(1)–C(1) | 2.151(6) | O(1)–C(1) | 1.308(7) |
| C(1)–C(2) | 1.355(9) | C(2)–C(31) | 1.474(9) |
| C(2)–C(41) | 1.490(8) | Nb(1)–Cp(1) | 2.132 |
| Nb(1)–Cp(2) | 2.145 | | |
| O(1)–Nb(1)–C(3) | 75.1(3) | O(1)–Nb(1)–C(1) | 35.9(2) |
| C(1)–Nb(1)–C(3) | 110.9(3) | Nb(1)–O(1)–C(3) | 74.7(3) |
| Nb(1)–C(1)–O(1) | 69.4(3) | Nb(1)–C(1)–C(2) | 160.2(5) |
| O(1)–C(1)–C(2) | 130.3(6) | C(1)–C(2)–C(31) | 121.2(5) |
| C(1)–C(2)–C(41) | 119.8(6) | C(31)–C(2)–C(41) | 119.0(6) |
| Cp(1)–Nb(1)–C(3) | 102.2 | Cp(1)–Nb(1)–C(1) | 105.0 |
| Cp(1)–Nb(1)–O(1) | 110.5 | Cp(1)–Nb(1)–Cp(2) | 132.9 |
| Cp(2)–Nb(1)–C(3) | 101.2 | Cp(2)–Nb(1)–C(1) | 103.9 |
| Cp(2)–Nb(1)–O(1) | 114.8 | | |

Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings.

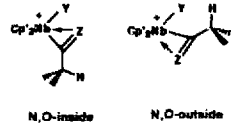



Fig. 3. Possible N(O)-inside and N(O)-outside conformations in the iminoacyl and acyl complexes.

NMR spectra indicate that only one of the two possible N(O)-inside or N(O)-outside isomers is present (Fig. 1), and based on data previously described for haloketene and haloketenimine derivatives [3,4,6] and on the X-ray crystal structure of **6a**, the *exo* isomer is proposed to be present in all complexes

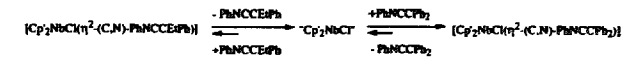
The structure of **6a** is depicted in Fig. 2, together with the atomic numbering scheme. Tables 1 and 2 summarize the crystal and structural data, while selected bond lengths and angles appear in Table 3. The compound crystallized in the space group $P2_1/n$ with four molecules of **6a** per unit cell. There was no intermolecular contact distance which could be considered to imply a bonding interaction. The ketene ligand is complexed through the C=O bond, Nb(1)–O(1) 2.088(4) Å and Nb(1)–C(1) 2.151(6) Å, and Nb(1), O(1) and C(3) atoms and constitute the equatorial plane in the bent metallocene, the Cp centroids are at 1.94 and 1.98 Å from this plane and the C(1) atom is 0.113 Å below it. The ketene ligand adopts the above mentioned O-inside (*exo*) configuration as can be observed in Fig. 2, with structural features similar to those found for the compound $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Br)(\eta^2\text{-}(C,O)\text{-}OOCPh_2)]$ [4]. The distance from the niobium atom to the methyl C(3), 2.265(10) Å, is in the range observed for Nb–C($sp^3$) bonds in niobocene alkyls [11].

Previously it was found that ketene and ketenimine containing niobocenes were easily protonated at the free terminus of the coordinated cumulene to give acyl and iminoacyl cationic derivatives respectively [4,5,12]. Thus, in order to test this reactivity in the new hydrido

Table 4
Data on the equilibrium ratios for E–Z isomers in complexes with unsymmetrically sustituted ketenimines ($C_6D_6$ at 20°C; assignation of E–Z isomers was carried out by NOE experiments)

| Complex | X | R | E:Z |
|---|---|---|---|
| **1b** | Cl | Me | 73:27 |
| **1c** | Cl | Et | 70:30 |
| **1d** | Cl | H | 73:27 |
| **3b** | H | Me | 50:50 |
| **3c** | H | Et | 50:50 |
| **3d** | H | H | > 95:5 [a] |
| **5b** | Me | Me | 35:65 |
| **5c** | Me | Et | 60:40 |
| **5d** | Me | H | 63:37 |

[a] Z isomer was not observed.




Scheme 3.

and alkyl niobocenes, some of them were treated with tetrafluoroboric acid. The standard reaction procedure involved the addition of 1 equiv. of $HBF_4 \cdot OEt_2$ to ethereal solutions of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Y(\eta^2\text{-}(C,Z)\text{-}Z{=}C{=}CRPh)]$ (Y = hydride or methyl, Scheme 1). The complexes were isolated, after appropriate work-up, as air-stable white solids, with the exception of **7b** which was obtained as a yellow oil. It is noteworthy that the electrophilic proton attack takes place exclusively on the β-carbon of the ketene and ketenimine ligands but not on the Nb–H or Nb–alkyl bonds. Several examples of electrophilic attack on Nb–H bonds of hydrido niobocenes are known [13], and protonolysis of metal–carbon bonds has been described in alkyl zirconocenes (see for example Ref. [14]); for our complexes both processes would be expected to give the corresponding cationic cumulene niobocenes [6], but such compounds were not observed in any case.

The IR and NMR spectra of these complexes prove that they contain $\eta^2$-acyl and $\eta^2$-iminoacyl moieties. The IR $\nu$(C–O) and $\nu$(C–N) absorptions appear at ca. 1594 and 1670 $cm^{-1}$ respectively, and the hydrido derivatives exhibit a band at ca. 1750 $cm^{-1}$ which corresponds to $\nu$(Nb–H). In the $^{13}C$ NMR the most notable characteristic is the position of the resonance for the acyl and iminoacyl carbon atoms, which were found to resonate at ca. 292.4 and 218.0 ppm respectively in accordance with data previously reported for $\eta^2$-acyl [15] and $\eta^2$-iminoacyl (see for example Ref. [16]) complexes of early transition metals. Both the $^1H$ and $^{13}C$ NMR data indicated the presence of only one of the two possible (N,O-inside and N,O-outside) (Fig. 3) conformations in these complexes, and on the basis of the behavior previously found in other analogous complexes [4,5] we propose the structure to be the O- or N-inside isomer.

In order to gain more insight into the E–Z isomerism, $^1H$ NMR studies were carried out on some complexes bearing unsymmetrical ketenimines. Data on the equilibrium ratios for E–Z isomers are shown in Table 4. The E–Z ratio for all these complexes was found to be the same regardless of whether the complex was derived from coordination of the free ketenimine with the $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]_2$, or from deprotonation of the corresponding iminoacyl complex [5]. From the data in Table 4 we can establish that the E isomer is the major, more stable isomer, probably because of the smaller steric volume of the R group located near the $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$ moiety, and thus, in the case of **3d**, the E isomer is the only one present. However, this must be interpreted with care because complex **5b** contains the E isomer as the minor product. We think that in addition to the steric element other factors must be considered responsible for the equilibrium ratios. In order to confirm the existence of an equilibrium between isomers and establish the variations in the E–Z ratio, a $^1H$ NMR variable temperature study (from 20 to 80 °C) on **5b** was carried out. The value for the E–Z ratio changed from 35:65 (20 °C) to 48:52 (80 °C). When the solution was cooled the initial E–Z ratio was re-established. We thus demonstrated the existence of the proposed equilibrium, although the observed variations are small and do not allow numerical calculations. We propose that the equilibrium could take place through labilization of the ligand, and in order to lend support to this proposal the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{-}PhNCCEtPh)]$ **1c** was treated with free PhN=C=CPh$_2$. After 48 h stirring at room temperature (experiment monitored by $^1H$ NMR) an appreciable amount of the complex **1a** $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{-}PhNCCPh_2)]$ (80:20) was detected, and after 4 days the mixture contained the two compounds in the ratio 45:55 together with free PhN=C=CEtPh. This result agrees with the substitution process of Scheme 3.

In addition, complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{-}PhNCCPh_2)]$ **1a** was treated with free PhN=C=CEtPh but after stirring for several days complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{-}PhCCEtPh)]$ **1c** was not detected in accordance with the greater stability of the former complex. We can conclude that the ketenimine niobocene complexes undergo a facile E–Z isomerization to give an equilibrium ratio which is dependent in each case on the relative stability of the isomers, and although a mechanism through the labilization of the ketenimine ligand could be proposed, an alternative internal mechanism cannot definitively be excluded. Thus, the hydride and alkyl niobocenes were isolated in E–Z ratios which differed from the parent chloro complexes. Although a thermodynamic control must be considered in the E–Z isomerization process, nevertheless the presence of a kinetic control prior to this process cannot be ruled out.

## 3. Experimental section

### 3.1. General procedures

All operations were performed under an inert atmosphere using standard vacuum line (Schlenk) techniques. Solvents were purified by distillation from ap-

propriate drying agents before use. NMR spectra were obtained on Varian Unity FT-300 and FT-500.PLUS instruments. IR spectra were recorded as Nujol mulls between CsI plates (in the region between 4000 and 200 $cm^{-1}$) on a Perkin–Elmer PE 883 IR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240B microanalyzer. Mass spectral analyses were performed on a Hewlett–Packard 5890, $m/z$ 50–1000 using chemical ionization techniques. The following compounds were prepared as described earlier: $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\}_2]$ [17,18], $Ph_2CCO$ [19], $PhNCC(R)(Ph)$ (R = Ph, Me, Et, H) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(\eta^2\text{-}(C,N)\text{–}PhN)(R)(Ph)]$ (R = Ph, Me, Et) [3], $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(\eta^2\text{-}(C,O)\text{–}OC\text{-}CPh_2)]$ [7] and other reagents were used as purchased.

### 3.2. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{–}PhNCC(H)(Ph))]$ 1d

To a brown solution of $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\}_2]$ (0.92 g, 0.57 mmol) in 50 ml of hexane was added a solution of $PhNCC(H)(Ph)$. The mixture was stirred for 12 h at room temperature whereon the solution became an increasingly deeper red colour. It was then concentrated to ca. 5 ml, and after cooling a brown precipitate was obtained which was filtered off and identified as impurities. The filtrate was concentrated to give a red oil which on freezing gave a microcrystalline solid that was identified as $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{–}PhNCC(H)(Ph))]$ **1d**; yield 0.84 g (61%).

IR (Nujol) $\nu$(N=C=C) 1641, 1586 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): 0.13 (s, 18H, $SiMe_3$); 5.31 (2H), 5.69 (2H), 5.79 (2H), 6.36 (2H) (m, $C_5H_4SiMe_3$); 7.14–7.81 (m, 10H, $C_6H_5$). (Z isomer): 0.14 (s, 18H, $SiMe_3$); 5.17 (2H), 5.39 (2H), 5.59 (2H), 5.89 (2H) (m, $C_5H_4SiMe_3$); 7.14–7.81 (m, 10H, $C_6H_5$).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): −0.2 ($SiMe_3$); 96.0, 104.2, 107.5, 117.0, 121.5 ($C_5H_4SiMe_3$); 116.2 ($C$=$C$=N); 151.5 (C=$C$=N); 147.7, 142.5 ($C_{ipso}$ of phenyl groups). (Z isomer): 0.1 ($SiMe_3$); 97.5, 105.0, 109.2, 117.5, 122.2 ($C_5H_4SiMe_3$); 116.5 ($C$=C=N); 152.5 (C=$C$=N); 145.7, 140.5 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 60.93; H, 6.10; N, 2.39. $C_{30}H_{37}ClNNbSi_2$ Calc.: C, 60.43; H, 6.27; N, 2.35%.

### 3.3. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(\eta^2\text{-}(C,Z)\text{–}ZCCRPh)]$ (Z = NPh, R = Ph, 3a; Z = NPh, R = Me, 3b; Z = NPh, R = Et, 3c; Z = NPh, R = H, 3d; Z = O, R = Ph, 4)

To a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,Z)\text{–}ZCCRPh)]$ in toluene was added $Li(BEt_3)H$ (1 M solution in THF) in a 1:2 ratio and the mixture was stirred for 12 h at room temperature. The solvent was then removed under vacuum to give a yellow–green oil. The addition of hexane precipitated a solid which after recrystallization from hexane was identified as the hydrido-ketenimine or -ketene product **3a–4**.

**3a**. From 0.5 g (0.74 mmol) of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{–}PhNCCPh_2)]$ **1a** and 1.48 ml (1.48 mmol) of $Li(BEt_3)H$ (1 M solution), 0.32 g of **3a** was obtained (yield 68%).

IR (Nujol) $\nu$(Nb–H) 1718; $\nu$(N=C=C) 1633, 1565 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.18 (s, 18H, $SiMe_3$); 1.45 (s, 1H, Nb–$H$); 4.51 (2H), 4.54 (2H), 4.83 (2H), 5.79 (2H) (m, $C_5H_4SiMe_3$); 6.63–7.77 (m, 15H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: 0.1 ($SiMe_3$); 110.0 ($C_{ipso}$ $C_5H_4SiMe_3$); 98.7, 100.5, 102.6, 110.8 ($C_5H_4SiMe_3$); 150.4 (C=$C$=N); 110.5 ($C$=C=N); 144.4, 146.1, 147.8 ($C_{ipso}$ of phenyl groups); 119.9, 122.5, 123.8, 124.2, 127.8, 128.1, 129.8 (C of phenyl groups).

Anal. Found: C, 67.78; H, 6.55; N, 2.57. $C_{36}H_{42}NNbSi_2$ Calc.: C, 67.87; H, 6.41; N, 2.61%.

M/S: $m/e$ (relative intensity): 638 (100) [base peak, $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(\eta^2\text{-}C,N)Ph_2C$=C=NPh$\}$]; 367 (10) $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H\}]$; 270 (69) $[Ph_2C$=C=NPh$]$.

**3b**. From 0.5 g (0.80 mmol) of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{–}PhNCCMePh)]$ **1b** and 1.60 ml (1.60 mmol) of $Li(BEt_3)H$ (1 M solution), 0.29 g of **3b** was obtained (as a 50:50 mixture of E–Z isomers) (yield 62%).

IR (Nujol) $\nu$(Nb–H) 1737; $\nu$(N=C=C) 1612, 1576 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.11 (18H), 0.21 (18H) (s, $SiMe_3$); 1.15 (1H), 1.29 (1H) (s, Nb–$H$); 2.29 (s, 3H, C=CPhC$H_3$ Z isomer); 2.64 (s, 3H, C=CPhC$H_3$ E isomer); 4.27 (2H), 4.62 (2H), 4.67 (2H), 4.77 (2H), 4.88 (2H), 4.99 (2H), 5.79 (2H), 5.91 (2H) (m, $C_5H_4SiMe_3$); 6.69–7.96 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.2, 0.1 ($SiMe_3$); 22.7, 23.1 ($CH_3$PhC=C=N); 96.3, 97.6, 98.3, 99.9, 100.3, 102.5, 102.8, 108.7, 109.6, 109.8 ($C_5H_4SiMe_3$); 111.6 ($C$=C=N); 151.6, 155.5 (C=$C$=N); 142.8, 143.2, 145.6 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 64.56; H, 6.98; N, 2.48. $C_{31}H_{40}NNbSi_2$ Calc.: C, 64.66; H, 7.01; N, 2.43%.

**3c**. From 0.4 g (0.65 mmol) of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{–}PhNCCEtPh)]$ **1c** and 1.30 ml (1.30 mmol) of $Li(BEt_3)H$ (1 M solution), 0.22 g of **3c** was obtained (as a 50:50 mixture of E–Z isomers) (yield 59%).

IR (Nujol) $\nu$(Nb–H) 1735; $\nu$(N=C=C) 1616, 1575 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.18 (18H), 0.11 (18H) (s, $SiMe_3$); 1.38 (1H), 1.17 (1H) (s, Nb–$H$); 1.48 (t, 3H, C=CPhCH$_2$C$H_3$ E isomer); 1.18 (t, 3H, C=CPhCH$_2$C$H_3$ Z isomer); 3.06 (2H), 2.81 (2H) (q, 2H, C=CPhC$H_2$CH$_3$); 4.33 (2H), 4.53 (2H), 4.64 (2H),

4.76 (2H), 4.82 (2H), 4.86 (2H), 5.84 (2H), 5.97 (2H) (m, $C_5H_4SiMe_3$); 6.52–7.84 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.1, 0.1 ($SiMe_3$); 13.6, 15.5 ($C{=}CPhCH_2CH_3$); 28.1, 29.9 ($C{=}CPhCH_2CH_3$); 97.3, 98.2, 98.4, 99.6, 101.7, 103.1, 106.5, 108.9, 109.4, 110.2 ($C_5H_4SiMe_3$); 113.6, 114.1 ($C{=}C{=}NPh$); 151.6, 155.6 ($C{=}C{=}NPh$); 141.7, 141.9, 142.2, 144.6 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 65.66; H, 7.08; N, 2.32. $C_{32}H_{42}NNbSi_2$ Calc.: C, 65.72; H, 7.19; N, 2.37%.

**3d**. From 0.23 g (0.38 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,N)–PhNCCHPh)] **1d** and 0.77 ml (0.77 mmol) of Li($BEt_3$)H (1 M solution), 0.11 g of **3d** was obtained (yield 52%).

IR (Nujol) $\nu$(Nb–H) 1718; $\nu$(N=C=C) 1628, 1575 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.05 (s, 18H, $SiMe_3$); 1.37 (s, 1H, Nb–*H*); 4.80 (2H), 4.92 (2H), 5.00 (2H), 5.75 (2H) (m, $C_5H_4SiMe_3$); 7.00–7.80 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.2 ($SiMe_3$); 97.2, 100.5, 103.0, 108.0, 113.1 ($C_5H_4SiMe_3$); 111.4 ($C{=}C{=}NPh$); 148.6 ($C{=}C{=}NPh$); 145.0, 145.2 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 63.56; H, 7.45; N, 2.45. $C_{30}H_{38}NNbSi_2$ Calc.: C, 63.69; H, 7.48; N, 2.47%.

**4**. From 0.22 g (0.37 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,O)–O=C=$CPh_2$)] **2** and 0.74 ml (0.74 mmol) of Li($BEt_3$)H (1 M solution), 0.15 g of **4** was obtained (yield 68%).

### 3.4. [Nb($\eta^5$-$C_5H_4SiMe_3)_2(CH_3)(\eta^2$-(C,N)–PhNC-CRPh)] (R = Ph, 5a; R = Me, 5b; R = Et, 5c; R = H, 5d)

To a solution of the corresponding chloroketenimine complex in diethyl ether a solution of $CH_3MgI$ (1.44 M in diethyl ether) was added in an equimolar proportion at 0 °C and the mixture was stirred for ca. 1.5 h. The solvent was then removed under vacuum and the residue extracted with hexane. The filtrate was concentrated under vacuum to give an orange–red product that was identified as the corresponding **5a–5d** compound.

**5a**. From 0.45 g (0.67 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,N)–PhNCCPh$_2$)] **1a** and 0.46 ml (0.67 mmol) of $CH_3MgI$, 0.27 g of **5a** was obtained (yield 63%).

IR (Nujol) $\nu$(C=C=N) 1600 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.25 (s, 18H, $SiMe_3$); 0.85 (s, 3H, Nb–$CH_3$); 5.05 (2H), 5.25 (2H), 5.55 (4H) (m, $C_5H_4SiMe_3$); 6.65–7.70 (m, 15H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.2 ($SiMe_3$); 11.6 (Nb–$CH_3$); 102.6, 104.8, 112.1, 117.2, 123.0 ($C_5H_4SiMe_3$); 113.6 ($C{=}C{=}N$); 121.1, 123.6, 124.2, 127.5, 129.5, 129.7 (C of phenyl groups); 143.3, 147.1, 147.8 ($C_{ipso}$ of phenyl groups); 150.6 ($C{=}C{=}N$).

Anal. Found: C, 68.52; H, 6.68; N, 2.17. $C_{37}H_{44}NNbSi_2$ Calc.: C, 68.21; H, 6.75; N, 2.15%.

**5b**. From 0.20 g (0.33 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,N)–PhNCCMePh)] **1b** and 0.27 ml (0.33 mmol) of $CH_3MgI$, 0.12 g of **5b** was obtained (as a 35:65 mixture of E–Z isomers) (yield 63%).

IR (Nujol) $\nu$(C=C=N) 1610 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm (Z isomer): 0.03 (s, 18H, $SiMe_3$); 0.67 (s, 3H, Nb–$CH_3$); 2.20 (s, 3H, $CH_3PhC{=}C{=}N$); 4.83 (2H), 5.46 (2H), 5.61 (2H), 5.65 (2H) (m, $C_5H_4SiMe_3$); 6.65–7.80 (m, 10H, phenyl groups). (E isomer): 0.07 (s, 18H, $SiMe_3$); 0.77 (s, 3H, Nb–$CH_3$); 2.51 (s, 3H, $CH_3PhC{=}C{=}N$); 4.75 (2H), 5.22 (2H), 5.46 (2H), 5.51 (2H) (m, $C_5H_4SiMe_3$); 6.65–7.80 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm (Z isomer): −0.6 ($SiMe_3$); 11.4 (Nb–$CH_3$); 22.1 ($CH_3PhC{=}C{=}N$); 101.4, 104.4, 111.6, 118.0, 122.9 ($C_5H_4SiMe_3$); 113.3 ($C{=}C{=}N$); 141.9, 145.0 ($C_{ipso}$ of phenyl groups); 150.4 ($C{=}C{=}N$). (E isomer): −0.2 ($SiMe_3$); 10.4 (Nb–$CH_3$); 22.9 ($CH_3PhC{=}C{=}N$); 104.3, 110.8, 117.1, 120.9, 122.1 ($C_5H_4SiMe_3$); 112.2 ($C{=}C{=}N$); 150.1 ($C{=}C{=}N$); 147.8, 148.2 ($C_{ipso}$ phenyl groups).

Anal. Found: C, 65.22; H, 7.33; N, 2.29. $C_{32}H_{42}NNbSi_2$ Calc.: C, 65.15; H, 7.19; N, 2.38%.

**5c**. From 0.30 g (0.48 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,N)–PhNCCEtPh)] **1c** and 0.33 ml (0.48 mmol) of $CH_3MgI$, 0.17 g of **5c** was obtained (as a 60:40 mixture of E–Z isomers) (yield 59%).

IR (Nujol) $\nu$(C=C=N) 1620 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): 0.09 (s, 18H, $SiMe_3$); 0.76 (s, 3H, Nb–$CH_3$); 1.49 (t, 3H, $CH_3CH_2$); 2.95 (q, 2H, $CH_3CH_2$); 4.78 (2H), 5.24 (2H), 5.51 (2H), 5.56 (2H) (m, $C_5H_4SiMe_3$); 6.65–7.80 (m, 10H, phenyl groups). (Z isomer): 0.04 (s, 18H, $SiMe_3$); 0.65 (s, 3H, Nb–$CH_3$); 1.21 (t, 3H, $CH_3CH_2$); 2.73 (q, 2H, $CH_3CH_2$); 4.88 (2H), 5.40 (2H), 5.56 (2H), 5.64 (2H) (m, $C_5H_4SiMe_3$); 6.65–7.80 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): −0.1 ($SiMe_3$); 10.5 (Nb–$CH_3$); 15.0 ($CH_3CH_2$); 29.3 ($CH_3CH_2$); 101.6, 104.7, 110.8, 116.2, 120.6 ($C_5H_4SiMe_3$); 112.1 ($C{=}C{=}N$); 147.9 ($C{=}C{=}N$); 123.1, 123.7, 127.2, 127.4, 127.5 (C of phenyl groups); 140.8, 146.6 ($C_{ipso}$ of phenyl groups). (Z isomer): −0.5 ($SiMe_3$); 11.5 (Nb–$CH_3$); 13.2 ($CH_3CH_2$); 27.3 ($CH_3CH_2$); 101.7, 104.4, 111.4, 117.8, 121.1 ($C_5H_4SiMe_3$); 113.3 ($C{=}C{=}N$); 150.7 ($C{=}C{=}N$); 122.7, 125.1, 127.8, 128.1, 128.2 (C of phenyl groups); 144.4, 148.8 ($C_{ipso}$ phenyl groups).

Anal. Found: C, 65.32; H, 7.39; N, 2.35. $C_{33}H_{44}NNbSi_2$ Calc.: C, 65.63; H, 7.36; N, 2.32%.

**5d**. From 0.24 g (0.40 mmol) of [Nb($\eta^5$-$C_5H_4SiMe_3)_2Cl(\eta^2$-(C,N)–PhNCCHPh)] **1d** and 0.28 ml (0.40 mmol) of $CH_3MgI$, 0.13 g of **5d** was

obtained (as a 63:37 mixture of E–Z isomers) (yield 55%).

IR (Nujol) $\nu$(C=C=N) 1610 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): −0.01 (s, 18H, $SiMe_3$); 0.86 (s, 3H, Nb–$CH_3$); 4.96 (2H), 5.62 (2H), 5.63 (2H), 5.84 (2H) (m, $C_5H_4SiMe_3$); 6.80–7.60 (m, 11H, phenyl groups and C*H*Ph) (Z isomer); 0.17 (s, 18H, $SiMe_3$); 0.86 (s, 3H, Nb–$CH_3$); 5.08 (2H), 5.62 (2H), 6.15 (2H), 6.76 (2H) (m, $C_5H_4SiMe_3$); 6.80–7.60 (m, 11H, phenyl groups and C*H*Ph).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm (E isomer): −0.5 ($SiMe_3$); 8.5 (Nb–$CH_3$); 97.6, 101.8, 104.2, 113.6, 117.2 ($C_5H_4SiMe_3$); 112.7 (*C*=C=N); 151.5 (C=*C*=N). (Z isomer): −0.1 ($SiMe_3$); 8.5 (Nb–$CH_3$); 95.2, 103.0, 106.1, 118.8, 121.2 ($C_5H_4SiMe_3$); 112.3 (*C*=C=N); 149.4 (C=*C*=N).

Anal. Found: C, 64.82; H, 6.93; N, 2.45. $C_{31}H_{40}NNbSi_2$ Calc.: C, 64.93; H, 6.98; N, 2.44%.

### *3.5. [Nb(η⁵-C₅H₄SiMe₃)₂R(η²-(C,O)O=C=CPh₂)] (R = Me, 6a; R = Et, 6b)*

To a solution of the corresponding chloroketene complex in diethyl ether, a solution of $R_2Mg$ (0.15 M in diethyl ether) was added in an equimolar proportion at 0 °C and the mixture was stirred for ca. 30 min. The solvent was then removed under vacuum and the residue extracted with hexane. The filtrate was concentrated under vacuum to give a yellow product that was identified as the corresponding **6a** or **6b** compound.

**6a**. From 0.2 g (0.33 mmol) of [Nb(η⁵-$C_5H_4SiMe_3)_2$(Cl)(η²-(C,O)–OCCPh₂)] **2** and 2.20 ml (0.33 mmol) of $(CH_3)_2Mg$, 0.13 g of **6a** was obtained (69%).

Alternatively, **6a** was obtained from 0.3 g (0.50 mmol) of [Nb(η⁵-$C_5H_4SiMe_3)_2$(Cl)(η²-(C,O)–OCCPh₂)] **2** in 20 ml of diethyl ether and 0.35 ml (0.50 mmol) of $CH_3MgI$ (1.43 M solution in diethyl ether) at 0 °C. The mixture was stirred for ca. 3 h, followed by concentration of the solvent under vacuum to give a yellow residue which was recrystallized from pentane, yielding 0.20 g of **6a** (69%).

IR (Nujol) $\nu$(C=C=O) 1581 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.08 (s, 18H, $SiMe_3$); 0.85 (s, 3H, Nb–$CH_3$); 4.62 (2H), 4.75 (2H), 5.50 (2H), 6.10 (2H) (m, $C_5H_4SiMe_3$); 7.00–8.10 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.6 ($SiMe_3$); 11.7 (Nb–$CH_3$); 99.0, 99.7, 113.0, 115.8, 118.6 ($C_5H_4SiMe_3$); 106.5 (*C*=C=O); 176.4 (C=*C*=O); 123.4, 124.6, 127.4, 128.2, 128.5, 129.9 (C of phenyl groups); 143.1, 144.8 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 64.77; H, 6.79. $C_{31}H_{39}ONbSi_2$ Calc.: C, 64.32; H, 6.81%.

**6b**. From 0.2 g (0.33 mmol) of [Nb(η⁵-$C_5H_4SiMe_3)_2$(Cl)(η²-(C,O)–OCCPh₂)] **2** and 2.20 ml (0.33 mmol) of $(CH_3CH_2)_2Mg$, 0.17 g of **6b** was obtained (86%).

IR (Nujol) $\nu$(C=C=O) 1579 $cm^{-1}$.

$^1H$ NMR ($C_6D_6$) $\delta$ ppm: 0.02 (s, 18H, $SiMe_3$); 1.62 (t, 3H, Nb–$CH_2$–$CH_3$); 1.83 (q, 2H, Nb–$CH_2$–$CH_3$); 4.55 (2H), 4.81 (2H), 5.83 (2H), 6.23 (2H) (m, $C_5H_4SiMe_3$); 6.95–8.00 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ ppm: −0.8 ($SiMe_3$); 19.7 (Nb–$CH_2$–$CH_3$); 23.1 (Nb–$CH_2$–$CH_3$); 97.8, 99.1, 111.5, 117.9, 119.6 ($C_5H_4SiMe_3$); 106.9 (*C*=C=O); 176.9 (C=*C*=O); 123.5, 124.5, 127.6, 128.1, 128.5, 129.5 (C of phenyl groups); 143.2, 144.6 ($C_{ipso}$ of phenyl groups).

Anal. Found: C, 66.50; H, 6.99. $C_{32}H_{41}ONbSi_2$ Calc.: C, 66.40; H, 6.96%.

### *3.6. [Nb(η⁵-C₅H₄SiMe₃)₂Y(η²-(C,Z)–Z=CCRHPh)]⁺[BF₄⁻] (7a, Y = H, Z = NPh, R = Ph; 7b, Y = H, Z = NPh, R = Me; 8a, Y = Me, Z = NPh, R = Ph; 8b, Y = Me, Z = NPh, R = Et; 9, Y = Me, Z = O, R = Ph)*

To a solution of [Nb(η⁵-$C_5H_4SiMe_3)_2$Y(η²-(C,Z)–ZCCRPh)] (Y = H, Z = NPh, R = Ph, **3a**; Y = H, Z = NPh, R = Me, **3b**; Y = Me, Z = NPh, R = Ph, **5a**; Y = Me, Z = NPh, R = Et, **5c**; Y = Me, Z = O, R = Ph, **6a**) in diethyl ether a diethyl ether solution containing 1 equiv. of $HBF_4 \cdot OEt_2$ was added dropwise at 0 °C until the corresponding iminoacyl or acyl compound was completely precipitated as a white product.

**7a**. From 0.1 g (0.16 mmol) of **3a**, 0.11 g of **7a** was obtained (100%).

IR (Nujol) $\nu$(Nb–H) 1759; $\nu$(C=N) 1664 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) $\delta$ ppm: 0.18 (s, 18H, $SiMe_3$); 1.72 (s, 1H, Nb–H); 4.47 (2H), 5.24 (2H), 5.94 (2H), 6.04 (2H) (m, $C_5H_4SiMe_3$); 6.31 (s, 1H, C*H*Ph$_2$); 7.23–7.44 (m, 15H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ ppm: −0.1 ($SiMe_3$); 57.3 (*C*HPh$_2$); 101.3, 103.4, 104.4, 108.6, 114.7 ($C_5H_4SiMe_3$); 124.0, 128.4, 128.5, 129.5, 129.6 (C of phenyl groups); 137.3, 140.5 ($C_{ipso}$ of phenyl groups); 217.1 (*C*=N).

Anal. Found: C, 59.78; H, 5.65; N, 1.91. $C_{36}H_{43}BF_4NNbSi_2$ Calc.: C, 59.58; H, 5.98; N, 1.93%.

**7b**. From 0.25 g (0.43 mmol) of **3b**, 0.28 g of **7b** was obtained as a yellow oil (100%).

IR (Nujol) $\nu$(Nb–H) 1730; $\nu$(C=N) 1669 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) $\delta$ ppm: 0.10 (s, 9H, $SiMe_3$); 0.18 (s, 9H, $SiMe_3$); 1.19 (s, 1H, Nb–H); 1.88 (d, 3H, C$H_3$CHPh); 4.92 (q, 1H, $CH_3$C*H*Ph); 4.32 (1H), 4.63 (1H), 5.19 (1H), 5.24 (1H), 5.39 (1H), 5.99 (1H), 6.16 (1H), 6.79 (1H) (m, $C_5H_4SiMe_3$); 7.11–7.50 (m, 10H, phenyl groups).

Anal. Found: C, 56.30; H, 6.09; N, 2.09. $C_{31}H_{41}BF_4NNbSi_2$ Calc.: C, 56.11; H, 6.23; N, 2.11%.

**8a**. From 0.1 g (0.15 mmol) of **5a**, 0.12 g of **8a** was obtained (100%).

IR (Nujol) $\nu$(C=N) 1687 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) $\delta$ ppm: 0.18 (s, 18H, $SiMe_3$); 0.71 (s, 3H, Nb–C$H_3$); 5.52 (2H), 5.74 (2H), 5.89 (2H), 6.03 (2H) (m, $C_5H_4SiMe_3$); 6.47 (s, 1H, C$H$Ph$_2$); 6.64–7.37 (m, 15H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ ppm: −0.2 ($SiMe_3$); 9.6 (Nb–$CH_3$); 58.5 ($CHPh_2$); 105.3, 110.2, 117.6, 118.4, 122.5 ($C_5H_4SiMe_3$); 127.9, 128.4, 129.4, 129.5, 129.6 (C of phenyl groups); 136.3, 137.6 ($C_{ipso}$ of phenyl groups); 218.0 ($C$=N).

Anal. Found: C, 60.23; H, 6.12; N, 1.91. $C_{37}H_{45}BF_4NNbSi_2$ Calc.: C, 60.07; H, 6.04; N, 1.89%.

**8b**. From 0.30 g (0.5 mmol) of **5c**, 0.35 g of **8b** was obtained (100%).

IR (Nujol) $\nu$(C=N) 1680 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) $\delta$ ppm: 0.22 (s, 9H, $SiMe_3$); 0.23 (s, 9H, $SiMe_3$); 0.68 (s, 3H, Nb–C$H_3$); 0.92 (t, 3H, C$H_3$CH$_2$); 2.16 (1H), 2.18 (1H) (m, –CH$_A$–CH$_B$–CH$_3$); 4.77 (dd, 1H, CH$_3$–CH$_A$–CH$_B$–C$H$Ph, $J$ = 4.40 Hz, $J$ = 10.62 Hz); 5.40 (1H), 5.61 (1H), 5.68 (1H), 5.80 (1H), 5.91 (1H), 5.98 (1H), 6.15 (1H) (m, $C_5H_4SiMe_3$); 6.80–7.45 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ ppm: −0.5 ($SiMe_3$); 11.6 (Nb–$CH_3$); 14.9 ($CH_3$–CH$_2$–CHPh); 26.5 (CH$_3$–$CH_2$–CHPh); 55.0 (CH$_3$–CH$_2$–$CH$Ph); 104.3, 105.2, 109.4, 109.6, 110.1, 110.8, 116.9, 117.3, 122.0 ($C_5H_4SiMe_3$); 127.7, 128.1, 128.7, 129.2, 129.3 (C of phenyl groups); 134.3, 135.9 ($C_{ipso}$ of phenyl groups); 219.2 ($C$=N).

Anal. Found: C, 57.01; H, 6.62; N, 2.09. $C_{33}H_{45}BF_4NNbSi_2$ Calc.: C, 57.22; H, 6.57; N, 2.02%.

**9**. From 0.1 g (0.17 mmol) of **6a**, 0.11 g of **9** was obtained (100%).

IR (Nujol) $\nu$(C=O) 1594 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) $\delta$ ppm: 0.10 (s, 18H, $SiMe_3$); 0.99 (s, 3H, Nb–C$H_3$); 5.80 (2H), 5.97 (2H), 6.07 (2H), 6.13 (2H) (m, $C_5H_4SiMe_3$); 7.56 (s, 1H, C$H$Ph$_2$); 7.20–7.80 (m, 10H, phenyl groups).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ ppm: −0.9 ($SiMe_3$); 13.1 (Nb–$CH_3$); 64.7 ($CHPh_2$); 103.4, 107.4, 117.2 (2C), 118.9 ($C_5H_4SiMe_3$); 128.7, 128.9, 129.6 (C of phenyl groups); 135.9 ($C_{ipso}$ of phenyl groups); 292.4 ($C$=O).

Anal. Found: C, 55.23; H, 6.11. $C_{31}H_{40}BF_4ONbSi_2$ Calc.: C, 55.93; H, 6.01%.

### 3.7. X-ray structure determination of 6a

Data collection was performed at 20 °C using an Enraf–Nonius CAD4 diffractometer. The structure was solved by a combination of direct methods and Fourier synthesis, and refined using full-matrix least-squares techniques against all unique data on $F_o^2$. Calculations were carried out on a PC486 computer using the SHELXS-86 [20] and SHELXL-93 [21] programs. Large $U_{eq}$ for aromatic ring atoms and Si(1), C(16)–C(18) were found, but all attempts to resolve the possible disorder were unsuccessful. However, the core atom positions were well-determined and serve to confirm the proposed structure. All the non-hydrogen atoms were refined anisotropically and at the later stage of refinement H-atoms were included in calculated positions with fixed thermal parameters using a riding model. A weighting scheme, which gave satisfactory agreement analyses, was introduced in the final cycles of refinement. The final converged agreement factors were $R_1$ = 0.088 and $wR_2$ = 0.258 for 3738 reflections with $F_o > 4\sigma(F_o)$, and GOF = 1.125. Although a semi-empirical absorption correction, Ψ-scan, was carried out, a maximum of 2.07 e Å$^{-3}$ was found at 0.88 Å from Nb(1) and it could not be dismissed. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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