Synthesis, Structure, and Chemistry of Niobium Cationic Ketenimine Complexes, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}PhRCCNPh\text{-}C,N)(L)]^+$. Molecular Structure of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)][PF_6]$

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Reaction of $NbCp'_2(\eta^2\text{-}PhRCCNPh\text{-}C,N)$ (**2a**, R = Ph; **2b**, R = Me; **2c**, R = Et) (Cp′ = $\eta^5\text{-}C_5H_4SiMe_3$) with 1 equiv of $[Cp_2Fe]^+X^-$ (X = PF_6, BPh_4) in the presence of nitriles or isonitriles produces the cationic ketenimine niobiocene complexes $[NbCp'_2(\eta^2\text{-}PhRCCNPh\text{-}C,N)(L)][X]$ (**3a** R = Ph, L = CH_3CN, X = PF_6^-; **3a′** R = Ph, L = CH_3CN, X = BPh_4^-; **3b** R = Me, L = CH_3CN, X = BPh_4^-; **3c** R = Et, L = CH_3CN, X = BPh_4^-; **3d** R = Ph, L = tBuCN, X = BPh_4^-; **3e** R = Ph, L = PhCN, X = BPh_4^-; **3f** R = Ph, L = tBuNC, X = BPh_4^-; **3g** R = Me, L = tBuNC, X = BPh_4^-; **3h** R = Et, L = tBuNC, X = BPh_4^-) in practically quantitative yields. We have also studied the electrochemical oxidation process of **2a** by means of cyclic voltammetry experiments. The structures of these compounds have been determined by spectroscopic methods. The structure of **3a** was determined by single-crystal diffractometry. Compound **3a** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 9.468(3) Å, b = 10.641(2) Å, c = 19.852(2) Å, α = 86.30(1)°, β = 88.79(1)°, γ = 74.64(2)°, Z = 2, V = 1924.6 Å^3, D_{calcd} = 1.420 g/mL, and R = 0.069, based on 5647 reflections. The molecular structure shows a typical bent-sandwich geometry around the niobium atom with the ketenimine and CH_3CN ligands arrayed in the plane between the two cyclopentadienyl rings. Cationic ketenimine complexes **3** isolated as nitrile adducts are readily converted to the corresponding isonitrile compounds by treatment with an excess of isonitrile. However, the inverse reaction does not occur under the same conditions. Complexes **3a′–c** react with water from wet acetone to produce the hydroxo iminoacyl complexes $[NbCp'_2(OH)(\eta^2\text{-}PhRHCCNPh\text{-}C,N)][BPh_4]$ (**5a**, R = Ph; **5b**, R = Me; **5c**, R = Et), and **3a′** reacts with methanol in the same manner to yield the corresponding methoxide complex $[NbCp'_2(OCH_3)(\eta^2\text{-}Ph_2HCCNPh\text{-}C,N)][BPh_4]$, **6**.

Introduction

The chemistry of electrophilic cationic complexes such as $[Cp_2MR]^+$ (M = Ti, Zr; Cp = C_5H_5) and other related compounds has received much attention in recent years. This is due to the fact that the title complexes have been implicated in a number of important processes, such as alkene polymerization[1] and insertion reactions of unsaturated molecules.[2] In contrast, these aspects of group 4 metallocenes have no parallels in the analogous group 5 metal species because little is known of their electrophilic cationic metallocene complexes.[3]

Recently, as part of our strategy to employ the reactivity of unsaturated organic molecules in the synthesis of niobium organometallic complexes, we have synthesized[4] a family of halo ketenimine complexes $NbCp'_2(X)(\eta^2\text{-}$

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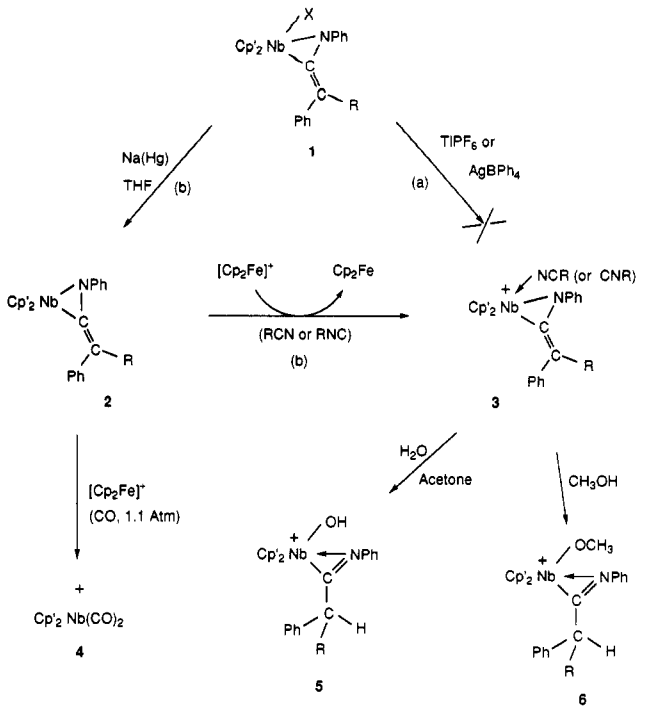
Scheme 1



PhRCCNAr-*C*,*N*), 1 (Cp′ = η^5-$C_5H_4SiMe_3$; X = Cl, Br; R = Ph, Me, Et; Ar = C_6H_5, *p*-BrC_6H_4, *p*-$CH_3C_6H_4$), and the related cationic η^2-iminoacyl compounds[5] [$NbCp'_2(X)(\eta^2$-PhRHCCNAr-*C*,*N*)][BF_4] derived from simple protonation at the free terminus of the complexed ketenimine ligands with HBF_4. However, the reaction of Nb(IV) ketenimine complexes $NbCp'_2(\eta^2$-PhRCCNAr-*C*,*N*), **2**, with 1 equiv HBF_4 goes through an initial oxidation step to give a nonisolated cationic species which then further reacts to yield the fluoro ketenimine complexes $NbCp'_2$-(F)(η^2-PhRCCNAr-*C*,*N*)[5b] via F^- abstraction from the counterion BF_4^-. This last stage of the process is closely related to the halide abstraction observed in titanium and zirconium complexes [Cp_2MR][PF_6].[6]

$$NbCp'_2(\eta^2\text{-PhRCCNAr-}C,N) \xrightarrow[-H_2]{HBF_4} \text{“}[NbCp'_2(\eta^2\text{-PhRCCNAr-}C,N)]^+\text{”} \xrightarrow{F^- \text{ abstraction}} NbCp'_2(F)(\eta^2\text{-PhRCCNAr-}C,N)$$

These results encouraged us to try to develop a synthesis of cationic ketenimine complexes with an available coordination site which could be occupied by basic ligands (CH_3CN, THF, pyridines, etc.) with the aim of further studying insertion processes between the heterocumulene and the basic molecule.[7] In order to explore this chemistry we have decided to essay two possible methods which have been successful in the isolation of titanium and zirconium cationic complexes (Scheme 1): (a) halide abstraction from halo ketenimine complexes **1**, employing Ag^+ or Tl^+ salts ($AgBPh_4$, $TlPF_6$, etc.), in the presence of ligands such as CH_3CN or THF; (b) one-electron oxidation of the Nb(IV) complexes **2** using ferrocenium salts as oxidizing agents in the presence of an appropriate ligand. The first method (a) failed because the starting complexes did not react, while the two stage reaction (b) was successful and allowed the synthesis of a number of cationic complexes, **3**, isolated as nitrile or isonitrile adducts, in very good yields (the oxidation step is nearly quantitative). This paper will focus on the synthesis and structural details of new cationic ketenimine complexes [$NbCp'_2(\eta^2$-PhRCCNPh-*C*,*N*)(L)]-[X], **3** (Cp′ = η^5-$C_5H_4SiMe_3$; R = Ph, Me, Et; L = nitrile or isonitrile; X = PF_6^-, BPh_4^-), and some of their transformations, particularly to hydroxo- and methoxide-iminoacyl complexes (compounds **5** and **6**, respectively). Electrochemical data for compounds **3** are also discussed.

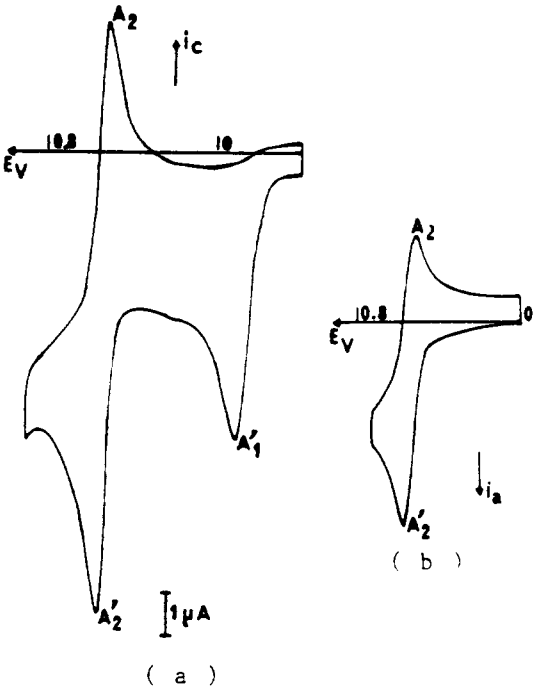


Figure 1. Cyclic voltammogram of complexes **2a** (a) and **3a** (b).

Results and Discussion

First of all we investigated the reaction of complexes $NbClCp'_2(\eta^2$-PhRCCNPh-*C*,*N*), 1 (**1a**, R = Ph; **1b**, R = Me; **1c**, R = Et) (Cp′ = η^5-$C_5H_4SiMe_3$), with silver or thallium salts. The standard reaction procedure involved addition of 1 equiv of $AgBPh_4$ or $TlPF_6$ to solutions of complexes **1** in acetonitrile or THF. After stirring for 12–18 h the starting materials were recovered, with none of the expected cationic species from halide abstraction being observed. In light of these results we have explored an alternative oxidation route. Employing a platinum disk electrode in acetonitrile, with 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, the cyclic voltammogram of **2a** exhibits two oxidation peaks A'_1 and A'_2. On the reverse scan after A'_2 the reduction peak A_2 appears (Figure 1a). After an exhaustive electrolysis of **2a** in CH_3CN at 0.2 V (plateau of wave A'_1) at room temperature, and a consumption of nearly 1 equiv of electrons, the cyclic voltammogram of the electrolyzed solution showns the well-defined reversible system A_2/A'_2. These results can be rationalized if we assume that

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(7) For a selected reference, see: Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456.

the one-electron oxidation of **2a** gives the presumed 16-electron cationic intermediate "$[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N]^+$" which easily adds the CH_3CN ligand to produce the more stable 18-electron species $[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)]^+$. It has also been established that the one-electron reversible system A_2/A'_2 corresponds to this latter species (see Figure 1).

In order to isolate the cationic species by chemical means we have successfully carried out the oxidation processes on the Nb(IV) species **2** using ferrocenium salts as oxidizing agents. In fact, the reaction of $NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)$, **2a**, with $[Cp_2Fe][PF_6]$ proceeds rapidly when an acetonitrile slurry of the reactants is warmed from −20 to +25 °C to yield $[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)][PF_6]$, **3a**, which can be isolated as an air stable orange crystalline solid and purified by recrystallization (acetonitrile–diethyl ether). We have confirmed that the cyclic voltammogram of **3a** shows the reversible system A_2/A'_2 (Figure 1b)). We propose that complex **3a** undergoes, within the time scale of the cyclic voltammetry, a reversible one-electron oxidation to give presumably a dicationic species.

$$[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)]^+ \underset{A_2}{\overset{A'_2}{\rightleftarrows}} [NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)]^{2+}$$

Attempts to chemically prepare the presumed dicationic species from the oxidation of **2a** with 2 equiv of the ferrocenium salt were unsuccessful. While stable as a solid, in solution, **3a** shows a behavior characterized by the electrophilic nature of the niobium center toward the PF_6^- counterion. **3a** liberates acetonitrile when dissolved in THF probably because the PF_6^- anion displaces the acetonitrile, leading to the formation of $NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)F$[5b] formed via F^- abstraction. Attempts to isolate the related THF adduct were unsuccessful even when the oxidiation of **2a** was carried out using THF as solvent. In this case the polymerization of the solvent was observed, the process presumably being initiated by PF_5 resulting from F^- abstraction. Halide abstraction is also observed when **2a** is dissolved in acetonitrile although the decomposition is slower. The use of the counterion BPh_4^- provided a more stable cationic niobocene complex. Thus, treatment of **2a** with $[Cp_2Fe][BPh_4]$ gives the corresponding $[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)][BPh_4]$, **3a'**, which is stable in acetonitrile or THF solutions for several days.

Attempts to prepare the THF adduct by oxidation of **2a** in THF were unsuccessful, although polymerization of the solvent does not occur with BPh_4^- as anion. In this last experiment, we have observed the formation of Cp_2Fe, along with a red oil which is isolated from the reaction mixture after appropriate workup. This oil presumably contains the 16-electron species "$[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)]^+$", which is extremely unstable and therefore difficult to characterize. Its solutions in CD_3CN show very complex ^1H NMR spectra, indicating that decomposition to a mixture of species, one being the complex **3a'**, takes place.[8] **3a** and **3a'** decompose instantaneously in CH_2Cl_2 or $CHCl_3$ solutions to give complicated mixtures of products (experiments monitored by ^1H NMR) from which only $NbCp'_2Cl(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)$, **1**, could be identified.

(8) This experiment was carried out on a preparative scale and quantities of about 10–15% of **3a'** were obtained when CH_3CN was added to the red oil.

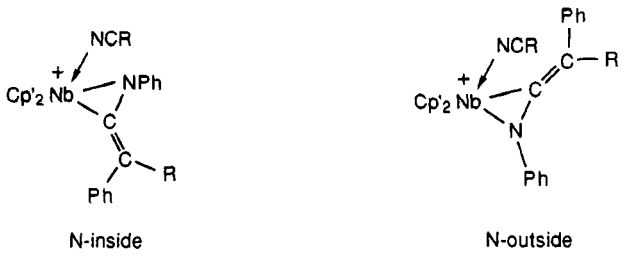

Figure 2.

The synthesis of cationic ketenimine complexes was extended to other ketenimine and nitrile ligands by using the same method: $[NbCp'_2(\eta^2\text{-}PhRCCNPh\text{-}C,N)(L)][BPh_4]$, **3b**, R = Me, L = CH_3CN; **3c**, R = Et, L = CH_3CN; **3d**, R = Ph, L = tBuCN; **3e**, R = Ph, L = PhCN. These products have been isolated as air stable crystalline solids after the corresponding workup. The complexes **3a–e** have been spectroscopically characterized. The shift in the IR (ν_{CN}) bands to 2314 and 2251 cm^{-1} from 2287 and 2251 cm^{-1} for the free CH_3CN indicates the presence of a coordinated CH_3CN ligand (in **3a–c**). In addition, the IR spectra showing the $\nu_{C=C=N}$ bands at ca. 1630 and ca. 1580 cm^{-1} are in agreement with the values reported for $NbCp'_2X(\eta^2\text{-}PhRCCNAr\text{-}C,N)$, 1.[4] The ^1H NMR spectra of **3a–e** in CD_3CN solutions show the resonances of free nitrile (i.e. **3a–c**, δ 1.95, CH_3CN) as well as resonances of Cp', ketenimine, and the BPh_4^- counterion. The signals of the coordinated nitriles measured in freshly dried acetone-d_6 solutions are slightly shifted from those of the free nitrile (i.e. **3a'**, δ 2.94, coordinated CH_3CN) (see Experimental Section). In addition, the ^{13}C NMR spectra of **3a–e** exhibit the characteristic resonances of the ketenimine ligand (δ 146–150, Nb—*C*(NPh)=CRPh; 116–117, Nb—C(NPh)=*C*RPh) and BPh_4^-. On the other hand, both ^1H and ^{13}C NMR data indicate that only the N-inside isomer is obtained with symmetrically substituted ketenimines although the N-inside and N-outside isomers are possible.[4,5] The X-ray crystal structure determination has shown that complex **3a** has the ground-state structure N-inside (vide infra). However, with unsymmetrical ketenimines (R = Me, Et; **3b**, **3c**) isomeric mixtures are observed (via ^1H NMR) due to the *E–Z* isomerism. *E–Z* ratios are in accordance with those found for halo ketenimine complexes **1** (% *E* = 80–95%).[4]

The nitrile ligand in **3a–e** does not undergo substitution by either 4-(*N*,*N*-dimethylamino)pyridine or ethylene (polymerization of this compound has never been observed under our experimental conditions), indicating that substitution by other larger ligands does not occur. We suggest that the substitution process only proceeds with appropriate linear ligands. In fact, the nitrile ligand is displaced by the *tert*-butyl isocyanide molecule to yield the corresponding adducts $[NbCp'_2(\eta^2\text{-}PhRCCNPh\text{-}C,N)(tBuNC)][BPh_4]$ (**3f**, R = Ph; **3g**, R = Me; **3h**, R = Et), isolated as air stable crystalline solids. Alternatively, these complexes may be prepared by oxidation of **2a–c** with $[Cp_2Fe][BPh_4]$ in hexane, in the presence of tBuNC. Displacement of tBuNC by nitriles does not occur and the isonitrile adducts remain stable for days in acetonitrile or THF solutions. On the basis of the ligand characteristics given above, we have also oxidized **2a** with $[Cp_2Fe][BPh_4]$ in the presence of CO (1.2 atm). None of the desirable cationic carbonyl ketenimine niobocene species was found, but rather the unexpected 18-electron dicarbonyl compound $[NbCp'_2(CO)_2][BPh_4]$, **4**, was isolated as a yellow crystalline solid. An analogous species with $\eta^5\text{-}C_5H_5$ was described several years ago[9] which was formed by the treatment of $[NbCp_2$-

$(CO)(THF)]^+$ with CO under drastic reaction conditions (at 200 atm!). Our complex can be envisaged as the result of a reduction process by CO of the presumably generated Nb(V) cationic species, accompanied by ketenimine elimination. In fact, ferrocene and free ketenimine were isolated from the reaction mixture. Complexes **3f–h** and **4** were spectroscopically characterized. IR spectra of **3f–h** show the absorptions of the coordinated tBuNC ligand (ν_{NC} = 2195 cm^{-1}) and the $\nu_{C=C=N}$ bands at ca. 1630 and ca. 1580 cm^{-1}. The IR spectrum of **4** shows two very characteristic absorption bands at 2045 and 1985 cm^{-1} corresponding to ν_{CO}.[9] NMR data for these complexes are similar to those described above for related compounds (see Experimental Section).

Reactions of 3a–c with Water and Methanol. We have found an interesting reactivity when complexes **3a–c** were dissolved in wet acetone. In fact, under these conditions, at room temperature, these complexes give rise to hydroxo iminoacyl complexes derived from both formal protonation at the β-carbon atom of the ketenimine ligand and a hydroxide–acetonitrile exchange.

$$[NbCp'_2(\eta^2\text{-PhRCCNPh-}C,N)(CH_3CN)][BPh_4] \xrightarrow{\text{wet acetone}} [NpCp'_2(OH)(\eta^2\text{-PhRHCCNPh-}C,N)][BPh_4]$$

5a, R = Ph; **5b**, R = Me; **5c**, R = Et

The complexes have been isolated at air stable colorless needles. The reaction does not take place in freshly dried acetone. Following an identical procedure for **3a'** in D_2O–acetone the dideuterated complex $[NbCp'_2(OD)(\eta^2\text{-}Ph_2DCCNPh\text{-}C,N)][BPh_4]$ was obtained. Interchange Nb—OD ⇌ NbOH is also observed when **5a** is dissolved in acetone-d_6 and D_2O is added (monitored by ^1H NMR). In light of these results we might suppose that complexes **5a–c** are either formed by initial protonation at the free terminus of the complexed ketenimine to give an η^2-iminoacyl moiety followed by hydroxide trapping or by the reverse procedure. Support for this proposal is found in published results,[5] where a facile protonation of halo ketenimines is reported, giving rise to niobocene halo iminoacyl species. However, an alternative process, implicating displacement of the acetonitrile ligand by H_2O followed by proton transfer, cannot be excluded. In the reaction of tantalocene methylidene hydride complexes with water, the formation of tantalocene hydroxide intermediates has already been postulated.[10] However, as far as we know, these hydroxide complexes constitute the first characterized niobocene hydroxide species. **5a–c** are characterized by IR, NMR, and MS techniques. IR spectra show the ν_{O-H} and the $\nu_{C=N}$ vibrations at ca. 3640 cm^{-1} and ca. 1670 cm^{-1}, respectively. ^1H NMR spectra show resonances corresponding to the OH, cyclopentadienyl rings and η^2-iminoacyl ligand. The expected low field resonance for the η^2-*C*NPh carbon atom in the ^{13}C NMR spectra was found at ca. 224 ppm, in accordance with previously reported data.[5] Both ^1H and ^{13}C NMR data indicate the presence of one of two (N-inside and N-outside) possible conformations in the isolated complexes.

Finally, the methoxide iminoacyl complex $[NbCp'_2(OMe)(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)][BPh_4]$, **6**, was obtained by a similar reaction of **3a'** with CH_3OH. Key spectroscopic features of this complex include the ν_{CN} absorbance at 1651 cm^{-1} for the η^2-iminoacyl ligand and the low field ^{13}C NMR resonance for the η^2-*C*NPh carbon atom at 227 ppm.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a

Nb–CP1[a]	2.11	CP1–Nb–CP2	129.3
Nb–CP2	2.12	N1–Nb–N2	77.9(5)
Nb–N1	2.15(2)	N1–Nb–C1	35.7(4)
Nb–N2	2.22(2)	C1–Nb–N2	113.4(4)
Nb–C1	2.19(1)	Nb–N1–C1	73.6(8)
N1–C1	1.33(1)	Nb–N1–C31	130.0
C1–C2	1.36(2)	C1–N1–C31	126.1(9)
N1–C31	1.41(2)	Nb–C1–N1	70.7(6)
C2–C41	1.48(2)	Nb–C1–C2	148(1)
C2–C51	1.50(2)	N1–C1–C2	141(1)
N2–C3	1.13(3)	Nb–N2–C3	173(1)

[a] CP are the centroids of the cyclopentadienyl rings.

X-ray Structure of $[NbCp'_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)][PF_6]$, 3a. The crystal structure of **3a** is built of organometallic cations and PF_6^- anions without any particular cation–anion interaction. The molecular structure of the cation (Figure 3, Table 1) is typical of bent metallocenes and is closely related to those reported earlier for η^2-iminoacyl halo complexes of niobium.[5a] It is interesting to note that the Nb–N1 and Nb–C1 distances in a formally metallaazacyclopropane structure of **3a** are the same as the corresponding distances found in metallaazacyclopropene ones (2.15 and 2.18 Å, respectively). The Nb–CP separations and the CP1–Nb–CP2 angle are also very close to the values observed in η^2-iminoacyl halo complexes (≈130°). However, the conformations of the substituted cyclopentadienyl rings are clearly different in **3a** and in the halo compounds. The dihedral angle C11–CP1–CP2/CP1–CP2–C21 is equal to 75.7° in **3a** (supplementary material), while it is equal to 27 and 37° in the fluoride and in chloride compounds, respectively. The Si2 atom lies almost directly over N1. The deviations of the N1 and Si2 atoms from the plane defined by CP1, Nb, and CP2 are equal to 0.77 and 0.42 Å, respectively. These observations may indicate an interaction between the lone pair of the N1 atom and the vacant d orbitals of Si2 atom. However, the Si2–N1 distance is equal to 3.7 Å and should be so considered as noninteracting. Moreover, the geometries around the Si1 and Si2 atoms are essentially the same, indicating that there is no particular perturbation of the Si2 atom. The conformation observed in **3a** may be explained by the fact that the phenyl ring bound to the N1 atom and the $Si2Me_3$ group lie on the opposite sides of the N1, C1, Nb, N2 bisecting plane.

The different natures of η^2-*N,C* ligands in the structure of **3a** and in those of halo complexes is exhibited by the differences of N1–C1 and C1–C2 bond lengths. The N1–C1 one is equal to 1.33 Å in **3a** and 1.21 Å in the halo derivatives, while the C1–C2 distance is **3a** (1.36 Å) is clearly shorter than in the halo complexes (1.51 Å).

The sum of the bond angles around the N1 atom is close to 360° in the halo compounds, but it is equal to 329.7° in **3a**. This last value is nearly the same as that for an idealized tetrahedron (328.5°), suggesting the pyramidal sp^3 nature of the N1 atom and no or very little conjugation of its lone pair with the π C1–C2 bond. The sums of the bond angles around C1 and C2 are equal to 360°.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere by using standard vacuum line (Schlenk) techniques. Solvents were purified by distil-

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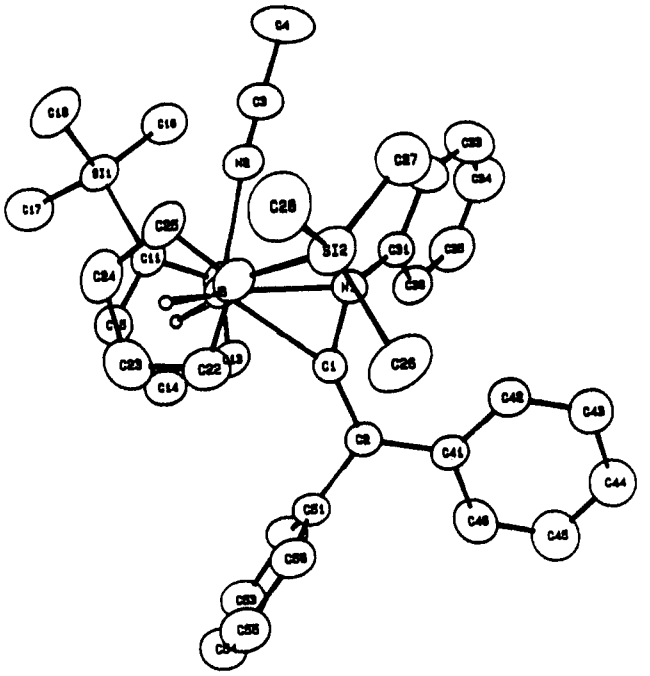

Figure 3. ORTEP plot of **3a**. Hydrogen atoms and labels for four carbon atoms have been omitted for clarity.

lation from appropriate drying agents before use. NMR spectra were obtained on a Varian Unity FT-300 instrument. 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. Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For the voltammetric experiment the working electrode was a platinum disk electrode (surface area = 3.1 mm^2) which was initially polished with alumina of decreasing particle size (down to 0.05 mm). For controlled potential electrolysis, a mercury pool was used as the cathode and a platinum plate as the anode, the latter being separated from the solution by a sintered glass disk. The electrolyte was acetonitrile 0.2 M in tetrabutylammonium hexafluorophosphate. The electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. Mass spectral analyses were performed on a VG autospec spectrometer using the FAB technique; the relative intensities are reported in parentheses. The following compounds were prepared as described earlier: $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}RPhCCNPh\text{-}C,N)$ (**1a**, R = Ph; **1b**, R = Me; **1c**, R = Et) and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}RPhCCNPh\text{-}C,N)$ (**2a**, R = Ph; **2b**, R = Me; **2c**, R = Et).[4] Oxidative reagent Cp_2FeBPh_4 was prepared according to a known procedure.[11] $MBPh_4$ salts (M = Ag, Tl) were made by precipitation of the respective nitrates or acetates with BPh_4^- in aqueous solution. Other reagents were used as purchased.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(CH_3CN)][PF_6]$, 3a. To an equimolar mixture of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)$ (**2a**) (360 mg, 0.56 mmol) and Cp_2FePF_6 (180 mg, 0.56 mmol) was added 30 mL of CH_3CN at −20 °C via vacuum transfer. The solution was stirred and allowed to warm to room temperature for 15 min. The solvent was removed in vacuo and the resulting unpurified red solid was washed with diethyl ether to remove the Cp_2Fe. The crude orange product was recrystallized from a mixture of acetonitrile–diethyl ether to yield **3a** as red crystals (440 mg, 95%). ^1H NR (CD_3CN): δ 0.21 (s, 18H, $SiMe_3$); 5.77 (2H), 5.82 (2H), 6.16 (2H), 6.23 (2H) (m, $C_5H_4SiMe_3$); 1.95 (s, 3H, free CH_3CN); 2.61 (s, 3H, coordinated CH_3CN); 6.67–7.61 (m, 15H, phenyl groups). ^{13}C NMR (CD_3CN): δ −0.34 ($SiMe_3$); 112.26 (C_{ipso} $C_5H_4SiMe_3$); 108.60, 112.00, 116.91, 120.80 ($C_5H_4SiMe_3$); 117.42 (C=C=N); 148.25 (C=C=N); 146.80, 144.08, 142.11 (C_{ipso} of phenyl groups); 123.51, 124.13, 124.60, 127.29, 128.22, 129.27, 129.81, 130.76, 132.22 (C of phenyl groups). IR (Nujol): ν_{CN} 2323, 2295 cm^{-1}; $\nu_{C=C=N}$ 1616, 1578 cm^{-1}. Anal. Calcd for $C_{38}H_{44}F_6N_2NbSi_2P$: C, 55.51; H, 5.40; N, 3.41. Found: C, 55.69; H, 5.60; N, 3.12.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)][BPh_4]$, 3a′. This complex was prepared from the reaction of **2a** (250 mg, 0.40 mmol) with an equimolar amount of Cp_2FeBPh_4 (200 mg, 0.40 mmol) using the procedure described for the preparation of **3a**, yield 370 mg (96%). ^1H NMR (CD_3CN): δ 0.23 (s, 18H, $SiMe_3$); 5.77 (2H), 5.82 (2H), 6.17 (2H), 6.23 (2H) (m, $C_5H_4SiMe_3$); 1.96 (s, 3H, free CH_3CN). ^1H-NMR (CD_3COCD_3): δ 0.30 (s, 18H, $SiMe_3$); 2.94 (s, 3H, coordinated CH_3CN); 6.02 (4H), 6.42 (2H), 6.60 (2H) (m, $C_5H_4SiMe_3$); 6.75 (m, 4H, para H), 6.92 (m, 8H, meta H), 7.34 (m, 8H, ortho H) (BPh_4^- signals); signals of the ketenimine ligand are obscured by BPh_4^- signals. ^{13}C NMR (CD_3CN): δ −0.25 ($SiMe_3$); 107.15, 110.70, 111.00, 115.60, 119.43 ($C_5H_4SiMe_3$); 116.77 (C=C=NPh); 146.91 (=C=NPh); 140.71, 142.72, 145.46 (C_{ipso} phenyl groups of ketenimine ligand); 121.45, 122.15, 122.83, 123.27, 125.21, 126.03, 126.82, 126.92, 127.96, 128.52, 130.98, 135.44 (C of phenyl groups); 163.81 (q, C_{ipso} phenyl groups of BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.45 Hz). IR (Nujol): ν_{CN} 2314, 2283 cm^{-1}; $\nu_{C=C=N}$ 1628, 1582 cm^{-1}. Anal. Calcd for $C_{62}H_{64}N_2NbSi_2B$: C, 73.96; H, 6.48; N, 2.81. Found: C, 73.25; H, 6.54; N, 2.72.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}MePhCCNPh\text{-}C,N)(CH_3CN)][BPh_4]$, 3b. This complex was prepared from the reaction of **2b** (340 mg, 0.50 mmol) with an equimolar amount of Cp_2FeBPh_4 (250 mg, 0.50 mmol) using the procedure described for the preparation of **3a**, yield 440 mg (95%). ^1H NMR (CD_3CN), major isomer (exo-*E*): δ 0.21 (s, 18H, $SiMe_3$); 1.95 (s, 3H, free CH_3CN); 2.33 (s, 3H, C=CPhCH_3); 5.93 (2H), 6.09 (2H), 6.27 (2H), 6.34 (2H) (m, $C_5H_4SiMe_3$); 6.85 (4H, para H), 7.00 (8H, meta H) and 7.28 (8H, ortho H) (phenyl groups of BPh_4^-); signals of the ketenimine ligand are obscured by BPh_4^- signals. ^1H NMR minor isomer (exo-*Z*): δ 0.26 (s, 18H, $SiMe_3$); 1.95 (s, 3H free CH_3CN); 2.38 (s, 3H, C=CPhCH_3); 6.02 (2H), 6.16 (2H), 6.22 (2H), 6.39 (2H) (m, $C_5H_4SiMe_3$). The isomer ratio was measured from the ^1H NMR spectrum, 8:2 (exo-*E*: exo-*Z*). ^{13}C NMR (CD_3CN), major isomer (exo-*E*): δ −0.31 ($SiMe_3$); 20.34 (CH_3CPh); 106.11, 109.68, 114.59, 119.80, 121.87 ($C_5H_4SiMe_3$); 116.40 (C=C=Ph); 146.39 (C=C=N-Ph); 144.25, 140.54 (C_{ipso} phenyl groups ketenimine ligand); 121.41, 122.26, 123.01, 125.25, 125.47, 126.85, 127.76, 129.96, 135.42 (C phenyl groups); 163.47 (q, C_{ipso} phenyl groups BPh_4^-, $J_{^{13}C-^{11}B}$ = 49.40 Hz). IR (Nujol): ν_{CN} 2277, 2304 cm^{-1}; $\nu_{C=C=N}$ 1644, 1585 cm^{-1}. Anal. Calcd for $C_{57}H_{62}N_2NbSi_2B$: C, 71.26, H, 5.70; N, 2.99. Found: C, 71.34; H, 5.38; N, 2.89.

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[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-EtPhCCNPh-*C,N*)(CH_3CN)][BPh_4], 3c. This compound was obtained in the same manner as **3a**, but using in this case an equimolar mixture of **2c** (600 mg, 1.01 mmol) and Cp_2FeBPh_4 (500 mg, 1.01 mmol). Recrystallization from acetonitrile–diethyl ether yielded **3c** as red crystals (920 mg, 96%). ^{1}H NMR, major isomer (exo-*E*): δ 0.19 (s, 18H, $SiMe_3$); 1.19 (t, 3H, CH_3CH_2); 2.70 (q, 2H, CH_3CH_2); 5.88 (2H), 6.18 (2H), 6.21 (2H), 6.26 (2H) (m, $C_5H_4SiMe_3$); 6.83 (4H, para H), 6.97 (8H, meta H), 7.25 (8H, ortho H) (m, phenyl groups BPh_4^-); signals of ketenimine ligand are obscured by BPh_4^- signals. ^{13}C NMR (CD_3CN), major isomer (exo-*E*): δ −0.34 ($SiMe_3$); 14.61 (CH_3CH_2); 28.62 (CH_3CH_2); 108.04, 111.36, 115.47, 121.08, 123.32 ($C_5H_4SiMe_3$); 117.31 (*C*=C=N); 147.67 (C=*C*=N); 122.77, 123.43, 124.64, 126.59, 128.03, 128.30, 128.93, 136.79 (C phenyl groups); 143.65, 140.92 (C_{ipso} phenyl groups ketenimine ligand); 164.85 (C_{ipso} BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.50 Hz). IR (Nujol): ν_{CN} 2278, 2305 cm^{-1}; $\nu_{C=C=N}$ 1641, 1586 cm^{-1}. Anal. Calcd for $C_{58}H_{64}N_2NbSi_2B$: C, 73.39; H, 6.81; N, 2.95. Found: C, 73.03; H, 6.75; N, 2.85.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CCNPh-*C,N*)(tBuCN)][BPh_4], 3d. Method A. To a slurry of **2a** (300 mg, 0.47 mmol) and Cp_2FeBPh_4 in hexane, was added tBuCN (52.27 μL, 0.47 mmol). The solution was stirred for 12 h, yielding an orange precipitate which was isolated by filtration. This crude product was recrystallized from a mixture of acetonitrile–diethyl ether to yield **3d** as red crystals (460 mg, 96%).

Method B. The complex, **3d**, can be alternatively prepared by using this experimental procedure: excess tBuCN (0.11 mL, 1.02 mmol) was directly added to complex **3a′** (170 mg, 0.17 mmol). The resulting red solution was stirred for 12 h at room temperature. Excess tBuCN was removed under vacuum and the resulting impure red solid was recrystallized from a mixture of acetonitrile–diethyl ether to give **3d** as red crystals (171 mg, 97%). ^{1}H NMR (CD_3COCD_3): δ 0.35 (s, 18H, $SiMe_3$); 1.63 (s, 9H, $(CH_3)_3CCN$); 5.94 (2H), 6.37 (2H), 6.60 (2H) (m, $C_5H_4SiMe_3$, the signal of the remaining 2H is obscured by the signals of phenyl groups); 6.75 (m, 4H, para H), 6.92 (m, 8H, meta H), 7.35 (m, 8H, ortho H) (phenyl groups of BPh_4^-); signals of ketenimine ligand are obscured by BPh_4^- signals. ^{13}C NMR (CD_3COCD_3): δ −0.22 ($SiMe_3$); 29.70 ($C(CH_3)_3$); 63.56 ($C(CH_3)_3$); 111.55 (C_{ipso} $C_5H_4SiMe_3$), 108.00, 109.40, 117.96, 123.75 ($C_5H_4SiMe_3$); 116.73 (*C*=C=N); 148.79 (C=*C*=N); 140.57, 142.33, 144.20 (C_{ipso} phenyl groups of ketenimine ligand); 122.74, 125.00, 125.65, 126.56, 128.35, 129.32, 129.55, 130.00, 130.22, 130.68, 132.45, 136.73 (C phenyl groups); 164.72 (q, C_{ipso} BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.92 Hz). IR (Nujol): ν_{CN} 2256 cm^{-1}; $\nu_{C=C=N}$ 1626, 1581 cm^{-1}. Anal. Calcd for $C_{65}H_{70}N_2NbSi_2B$: C, 73.12; H, 6.80; N, 2.70. Found: C, 73.24; H, 6.70; N, 2.60.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CCNPh-*C,N*)(PhCN)][BPh_4], 3e. Method A. This complex was prepared from the reaction of **2a** (470 mg, 0.70 mmol) with an equimolar amount of Cp_2FeBPh_4 (360 mg, 0.70 mmol) in 10 mL of PhCN. The solution was stirred for 15 min. Then, it was concentrated and diethyl ether was added to the point of precipitation. The compound **3e** was obtained as red crystals (700 mg, 94%).

Method B. This complex, **3e**, can be alternatively prepared in the same manner as **3d** (method B), but using in this case an excess of PhCN (15 mL) and **3a′** (200 mg, 0.20 mmol), yield (201 mg, 95%). ^{1}H NMR (CD_3COCD_3): δ 0.28 (s, 18H, $SiMe_3$); 6.06 (2H), 6.14 (2H), 6.56 (2H) (m, $C_5H_4SiMe_3$, the signal of the remaining 2H is obscured by signals of the phenyl groups); 6.75 (m, 4H, para H), 6.92 (m, 8H, meta H), 7.35 (m, 8H, ortho H) (phenyl groups of BPh_4^-); signals of ketenimine ligand are obscured by BPh_4^- signals; 7.81–8.13 (m, 5H, phenyl group of PhCN). ^{13}C NMR (CD_3CN): δ −0.26 ($SiMe_3$); 108.67, 112.07, 112.36, 116.76, 120.90 ($C_5H_4SiMe_3$); 116.77 (*C*=C=NPh); 148.12 (=*C*=NPh); 142.18, 144.14, 146.88 (C_{ipso} phenyl groups of ketenimine ligand); 164.55 (q, C_{ipso} BPh_4^-). IR (Nujol): ν_{CN} 2256 cm^{-1}; $\nu_{C=C=N}$ 1631, 1583 cm^{-1}. Anal. Calcd for $C_{67}H_{66}N_2NbSi_2B$: C, 75.96; H, 6.29; N, 2.64. Found: C, 75.95; H, 6.54; N, 2.66.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CCNPh-*C,N*)(tBuNC)][BPh_4], 3f. Method A. This complex was obtained from the reaction of **2a** (250 mg, 0.40 mmol) with Cp_2FeBPh_4 (200 mg, 0.40 mmol) and tBuNC (45 μL, 0.40 mmol) by using the procedure described for the preparation of **3d** (method A), yield 390 mg (95%).

Method B. 3f can be alternatively prepared in the same manner as **3d** (method B) but using in this case an excess of tBuNC (0.12 mL, 1.02 mmol) and **3a′** (170 mg, 0.17 mmol). Yield: (155 mg, 93%). ^{1}H NMR (CD_3CN): δ 0.24 (s, 18H, $SiMe_3$); 1.65 (s, 9H, tBu); 5.58 (2H), 6.05 (2H), 6.25 (2H), 6.46 (2H) (m, $C_5H_4SiMe_3$); 6.82 (m, 4H, para H), 6.99 (m, 8H, meta H), 7.28 (m, 8H, ortho H) (phenyl groups BPh_4^-); signals of phenyl groups of ketenimine ligand are obscured by signals of BPh_4^-. ^{13}C NMR (CD_3CN): δ −0.20 ($SiMe_3$); 29.60 ($C(CH_3)_3$); 66.30 ($C(CH_3)_3$); 111.35 (C_{ipso} $C_5H_4SiMe_3$); 107.93, 109.19, 117.96, 123.55 ($C_5H_4SiMe_3$); 117.53 (*C*=C=N); 149.29 (C=*C*=N); 140.67, 142.63, 144.10 (C_{ipso} phenyl groups of ketenimine ligand); 122.74, 124.00, 125.15, 126.56, 128.25, 129.12, 129.35, 129.70, 130.24, 130.48, 132.25, 136.73 (C phenyl groups); 164.82 (q, C_{ipso} BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.91 Hz). IR (Nujol): ν_{NC} 2188 cm^{-1}; $\nu_{C=C=N}$ 1629, 1582 cm^{-1}. Anal. Calcd for $C_{65}H_{70}N_2NbSi_2B$: C, 73.12; H, 6.80; N, 2.70. Found: C, 73.69; H, 6.72; N, 2.35.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-MePhCCNPh-*C,N*)(tBuNC)][BPh_4], 3g. Method A. This complex was obtained from the reaction of **2b** (425 mg, 0.74 mmol) with Cp_2FeBPh_4 (370 mg, 0.74 mmol) and tBuNC (84 μL, 0.74 mmol) by using the procedure described for the preparation of **3d** (method A), yield 665 mg (92%).

Method B. 3g can be alternatively prepared in the same manner as **3d** (method B) but using in this case excess of tBuNC (0.14 mL, 1.26 mmol) and **3b** (200 mg, 0.21 mmol). Yield: 160 mg (80%). ^{1}H NMR (CD_3CN), major isomer (exo-*E*): δ 0.25 (s, 18H, $SiMe_3$); 1.72 (s, 9H, tBu); 2.44 (s, 3H, CH_3); 5.44 (2H), 6.12 (2H), 6.39 (4H) (m, $C_5H_4SiMe_3$); 6.83 (m, 4H, para H), 6.98 (m, 8H, meta H), 7.28 (m, 8H, ortho H) (phenyl groups BPh_4^-); signals of phenyl groups of ketenimine ligand are obscured by signals of BPh_4^-. ^{13}C NMR (CD_3CN), major isomer (exo-*E*): δ −0.33 ($SiMe_3$); 22.13 (CH_3CPh); 29.71 ($C(CH_3)_3$); 66.26 ($C(CH_3)_3$); 106.12, 107.94, 110.38, 117.96, 123.10 ($C_5H_4SiMe_3$); 115.41 (*C*=C=N); 149.86 (C=*C*=N); 141.55, 138.66 (C_{ipso} phenyl groups of ketenimine ligand); 122.74, 123.49, 124.42, 126.21, 126.53, 126.92, 128.17, 129.16, 136.76 (C phenyl groups); 164.79 (C_{ipso} phenyl groups BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.45 Hz). IR (Nujol): ν_{NC} 2193 cm^{-1}; $\nu_{C=C=N}$ 1660, 1587 cm^{-1}. Anal. Calcd for $C_{60}H_{68}N_2NbSi_2B$: C, 73.74; H, 7.02; N, 2.86. Found: C, 73.53; H, 7.36; N, 2.60.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-EtPhCCNPh-*C,N*)(tBuNC)][BPh_4], 3h. Method A. This complex was obtained from the reaction of **2c** (350 mg, 0.59 mmol) with Cp_2FeBPh_4 (300 mg, 0.59 mmol) and tBuNC (67 μL, 0.59 mmol) by

using the procedure described for the prepartion of **3d** (method A), yield 533 mg (91%).

Method B. **3h** can be alternatively prepared in the same manner as **3d** (method B) but using in this case excess of tBuNC (0.16 mL, 1.44 mmol) and **3c** (230 mg, 0.24 mmol). Yield: 197 mg (82%). ^{1}H NMR (CD_3CN), major isomer (exo-*E*): δ 0.25 (s, 18H, $SiMe_3$); 1.67 (s, 9H, tBu); 1.23 (t, 3H, CH_3CH_2); 2.85 (q, 2H, CH_3CH_2); 5.49 (2H), 6.09 (2H), 6.37 (2H0, 6.41 (2H) (m, $C_5H_4SiMe_3$); 6.82 (m, 4H, para H), 6.97 (m, 8H, meta H), 7.25 (8H, ortho H) (phenyl groups BPh_4^-); signals of phenyl groups of ketenimine ligand are obscured by signals of BPh_4^-, ^{13}C NMR (CD_3CN), major isomer (exo-*E*): δ −0.40 ($SiMe_3$); 12.21 (CH_3CH_2—C—Ph); 28.93 (CH_3CH_2—C—Ph); 29.62 ($C(CH_3)_3$); 66.25 ($C(CH_3)_3$); 106.44, 108.25, 110.35, 117.42, 123.11 ($C_5H_4SiMe_3$); 115.78 (C=C=N); 149.84 (C=C=N); 141.22, 138.97 (C_{ipso} phenyl groups of ketenimine ligand); 122.73, 124.60, 125.00, 126.53, 128.00, 128.22, 128.93, 130.26, 136.73 (C phenyl groups); 164.77 (C_{ipso} phenyl groups BPh_4^-; $J_{^{13}C-^{11}B}$ = 48.53 Hz). IR (Nujol): ν_{NC} 2195 cm^{-1}; $\nu_{C=C=N}$ 1645, 1586 cm^{-1}. Anal. Calcd for $C_{61}H_{70}N_2NbSi_2B$: C, 73.91; H, 7.13; N, 2.82. Found: C, 73.73; H, 7.22; N, 2.64.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(CO)$_2$][BPh$_4$], 4. To an equimolar mixture of **2a** (400 mg, 0.62 mmol) and Cp_2FeBPh_4 (320 mg, 0.62 mmol) was added 50 mL of hexane. The brown solution was stirred for 48 h under CO atmosphere (1.2 atm). The solution turned red, and a yellow solid formed. The crude product was isolated by filtration, washed with hexane, and recrystallized from a mixture of acetonitrile–diethyl ether to give **4** as yellow crystals (390 mg, 85%). ^{1}H NMR (CD_3CN): δ 0.24 (s, 18H, $SiMe_3$); 5.75 (4H), 5.82 (4H) (m, $C_5H_4SiMe_3$); 6.83 (m, 4H, para H), 7.00 (m, 8H, meta H), 7.26 (m, ortho H) (phenyl groups of BPh_4^-). IR (Nujol): ν_{CO} 2045, 1985 cm^{-1}; ν_{Ph} 1578 cm^{-1}. Anal. Calcd for $C_{42}H_{46}NbO_2Si_2B$: C, 67.91; H, 6.25. Found: C, 67.28; H, 6.21. MS: *m/e* 423 (100) [base peak, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(CO)$_2$]$^+$], 395 (35) [[Nb(η^5-$C_5H_4SiMe_3$)$_2$(CO)]$^+$], 367 (65) [Nb(η^5-$C_5H_4SiMe_3$)$_2$].

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CHCNPh-*C,N*)(OH)][BPh$_4$], 5a. Compound **3a′** (250 mg, 0.25 mmol) was dissolved at room temperature in 25 mL of wet acetone and stirred for 3 h. The color changed from red to yellow. The solvent was removed in vacuo and the resulting impure yellow solid was washed with hexane, giving a white solid. This crude product was crystallized from a mixture of acetone–diethyl ether to yield **5a** as colorless needles (194 mg, 80%). ^{1}H NMR (CD_3COCD_3): δ 0.21 (s, 18H, $SiMe_3$); 1.00 (s, 1H, O*H*); 6.05 (2H), 6.46 (2H), 6.57 (2H), 6.80 (2H) (m, $C_5H_4SiMe_3$); 6.76 (s, 1H, −C*H*Ph$_2$); 6.82 (m, 4H, para H), 6.94 (m, 8H, meta H), 7.38 (m, 8H, ortho H) (phenyl groups BPh_4^-); 7.40–7.49 (signals of phenyl groups of iminoacyl ligand). ^{13}C NMR (CD_3COCD_3): δ −0.84 ($SiMe_3$); 59.96 (*C*HPh$_2$); 109.95, 111.69, 113.33, 121.11, 125.03 ($C_5H_4SiMe_3$); 122.13, 125.91, 128.98, 129.55, 130.23, 130.33, 136.98, 137.00, 137.63 (C phenyl groups); 138.43, 138.88 (C_{ipso} phenyl groups of iminoacyl ligand); 164.93 (q, C_{ipso} phenyl groups BPh_4^-; $J_{^{13}C-^{11}B}$ = 49.60 Hz); 223.48 (*C*=N). IR (Nujol): ν_{OH} 3639 cm^{-1}; $\nu_{C=N}$ 1668, ν_{Ph} 1586 cm^{-1}. Anal. Calcd for $C_{60}H_633NNbOSi_2B$: C, 73.97; H, 6.53; N, 1.43. Found: C, 73.72; H, 6.66; N, 1.34.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-MePhCHCNPh-*C,N*)(OH)][BPh$_4$], 5b. This complex was prepared in the same manner as **5a**, but using in this case **3b** (150 mg, 0.16 mmol) in 20 mL of wet acetone. Yield: 120 mg (82%). ^{1}H NMR (CD_3COCD_3): δ 0.14 (s, 9H, $SiMe_3$); 0.18 (s, 9H, $SiMe_3$); 1.02 (s, 1H, Nb—O*H*); 1.96 (d, 3H, Ph—CH—CH_3); 5.31 (q, 1H, Ph—C*H*-CH_3); 5.81, 6.30, 6.49, 6.55, 6.76, 6.83 (m, signals of $C_5H_4SiMe_3$, each one integrating for 1:1:2:1:2:1, respectively); 6.78 (m, 4H, para H); 6.92 (m, 8H, meta H), 7.35 (m, 8H, ortho H) (phenyl groups BPh_4^-); 7.40–7.59 (phenyl groups of iminoacyl ligand). ^{13}C NMR (CD_3COCD_3): δ −0.86 ($SiMe_3$), −0.82 ($SiMe_3$) (different signal for each Cp′); 19.49 (CH_3—CH—Ph); 48.75 (CH_3—*C*H—Ph); 108.65, 110.61, 111.09, 111.57, 113.79, 114.58, 120.10, 121.01, 121.32 ($C_5H_4SiMe_3$, different signals for each diastereotopic Cp′); 122.14, 125.91, 129.04, 129.20, 129.35, 129.60, 130.14, 130.42, 136.95 (C phenyl groups); 138.83, 140.31 (C_{ipso} phenyl groups of iminoacyl ligand); 164.84 (q, C_{ipso} phenyl groups BPh_4^-); 225.69 (*C*=N). IR (Nujol): ν_{OH} 3642 cm^{-1}; $\nu_{C=N}$ 1678 cm^{-1}, ν_{Ph} 1582 cm^{-1}. Anal. Calcd for $C_{55}H_{61}NNbOSi_2B$: C, 72.34; H, 6.85; N, 1.56. Found: C, 72.12; H, 6.80; N, 1.58. MS: *m/e* 592 (100) [base peak, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-MePhCHC=NPh-*C,N*)(OH)]$^+$], 454 (10) [base peak, ($C_5H_4SiMe_3$)], 384 (38) [Cp′$_2$NbOH].

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-EtPhCHCNPh-*C,N*)(OH)][BPh$_4$], 5c. This complex was prepared in the same manner as **5a**, but using in this case **3c** (350 mg, 0.37 mmol) in 30 mL of wet acetone. Yield: 280 mg (82%). ^{1}H NMR (CD_3COCD_3): δ 0.15 (s, 9H, $SiMe_3$); 0.16 (s, 9H, $SiMe_3$); 1.00 (s, 1H, Nb—O*H*); 0.97 (t, 3H, Ph—CH—CH_2-CH_3); 2.39 (m, 2H, CH—CH_AH_BCH$_3$); 5.01 (dd, 1H, Ph—C*H*—CH_2CH_3); 5.72, 6.23, 6.47, 6.74 (m, C_5H_4, each one integrating for 1:1:4:2 H, respectively); 6.80 (m, 4H, para H); 6.93 (m, 8H, meta H); 7.35 (m, 8H, ortho H) (phenyl groups BPh_4^-); 7.41–7.62 (phenyl groups of iminoacyl ligand). ^{13}C NMR (CD_3COCD_3): δ −0.88 ($SiMe_3$), −0.91 ($SiMe_3$); 12.31 (CH_3CH_2—CH); 26.96 (CH_3CH_2—CH); 56.34 (Et*C*HPh); 108.82, 110.75, 110.79, 111.32, 112.76, 114.97, 120.82, 120.95, 121.19 ($C_5H_4SiMe_3$, different signals for each diastereotopic Cp′); 122.09, 125.86, 129.09, 129.53, 130.01, 130.14, 130.40, 136.89 (C phenyl groups); 137.76, 138.12 (C_{ipso} phenyl groups iminoacyl ligand); 164.75 (C_{ipso} BPh_4^-); 224.94 (*C*=N), IR (Nujol): ν_{OH} 3643 cm^{-1}; $\nu_{C=N}$ 1666 cm^{-1}, ν_{Ph} 1580 cm^{-1}. Anal. Calcd for $C_{56}H_{63}NNbOSi_2B$: C, 72.60; H, 6.87; N, 1.53. Found: C, 72.10; H, 6.82; N, 1.54. MS: *m/e* 606 (100) [base peak, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-EtPhCHC=NPh-*C,N*)(OH)]$^+$], 468 (20) [base peak, ($C_5H_4SiMe_3$)], 384 (45) [Cp′$_2$NbOH].

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CHCNPh-*C,N*)(OMe)][BPh$_4$], 6. A solution of **3a′** (200 mg, 0.20 mmol) in 20 mL of methanol was stirred for 12 h. A white precipitate formed which was isolated by filtration and then washed with diethyl ether. Due to the high insolubility of **6** recrystallization was not possible. Yield: 120 mg (65%). ^{1}H NMR (CD_3CN): δ 0.23 (s, 18H, $SiMe_3$); 3.38 (s, 3H, OCH_3); 5.90 (2H), 6.20 (2H), 6.39 (2H), 6.44 (2H) (m, $C_5H_4SiMe_3$); 6.26 (s, 1H, PhC*H*Ph); 6.82 (m, 4H, para H), 7.01 (m, 8H, meta H), 7.24–7.28 (m, 8H, ortho H) (phenyl groups of BPh_4^-); 7.40–7.65 (phenyl groups of iminoacyl ligand). ^{13}C NMR (CD_3COCD_3): δ −0.68 ($SiMe_3$); 60.32 (Ph*C*HPh); 64.10 (OCH_3); 112.73 (C_{ipso}, $C_5H_4SiMe_3$); 110.63, 111.94, 123.72, 124.53 ($C_5H_4SiMe_3$); 122.14, 125.91, 128.41, 128.54, 129.05, 130.04, 130.16, 130.28, 137.01 (C phenyl groups);

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Table 2. Crystallographic Data for 3a

chem formula	$C_{38}H_{44}N_2NbSi_2PF_6$
fw	822.83
color	red
cryst size (mm)	0.5 × 0.4 × 0.2
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.468(3)
b, Å	10.641(2)
c, Å	19.852(2)
α, deg	86.30(1)
β, deg	88.70(1)
γ, deg	74.64(2)
V, Å^3	1924.6
Z	2
D_{calc}, g/cm^3	1.420
$F(000)$	848
μ(Mo Kα), cm^{-1}	4.573
λ(Mo Kα radiation) Å	0.710 73
temp, K	298
scan type	ω–2θ
scan range, deg in ω	1.10 + 0.34 tan θ
hkl	
lower limit	−11,−13,0
upper limit	11,13,24
θ range, deg	3–26
linear decay, %	−6.4 (corrected)
tot. no. of reflcns	7242
no. of unique reflcns, $I > 3\sigma(I)$	5647
no. variables	421
abs corr, Ψ scan,	64.297–99.962
R	0.069 (unit weights)
GOF	2.490
resid density (max, min), e/Å^3	+1.0, −0.6[a]

[a] Located in the PF_6 region.

135.53, 138.01 (C_{ipso} phenyl groups of iminoacyl ligand); 164.94 (q, $C_{ipso}BPh_4^-$; $J_{^{13}C-^{11}B}$ = 49.45 Hz); 227.73 (*C*=N). IR (Nujol): $\nu_{C=N}$ 1651 cm^{-1}; ν_{Ph} 1583 cm^{-1}. Anal. Calcd for $C_{61}H_{65}NNbOSi_2B$: C, 74.10; H, 6.64; N, 1.41. Found: C, 74.35; H, 6.38; N, 1.32.

Crystal Structure Analysis of 3a. A red crystal having the approximate dimensions 0.5 × 0.4 × 0.2 mm was sealed in a capillary and mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained by use of the CAD4 automatic routines. Intensities were recorded for Lorentz and polarization effects, and an empirical absorption correction (Ψ scan) was applied. The Enraf-Nonius SDP library[12] was used for data reduction, and the solution and refinement of the structure were performed with SHELX76 programs.[13] Neutral atom scattering factors and anomalous dispersion corrections were those given by Cromer and Waber.[14] The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms in the cation and the phosphorus atom in the anion were refined with anisotropic temperature factors, but the isotropic ones were applied to the fluorine atoms in the PF_6^- anion. All hydrogen atoms were placed in calculated positions riding on the carbon atoms bearing them and included in the final calculations with B_{iso} fixed at the values equal to $1.3B_{eq}$ for the corresponding carbon atoms. The crystal data and data collection parameters are summarized in Table 2.

Table 3. Atomic Coordinates (10^4) for $C_{38}H_{44}N_2NbSi_2PF_6$

atom	x/a	y/b	z/c	B, Å^2
Nb	3319(1)	1910(1)	7673(0)	2.42(2)
Si1	3755(3)	2601(2)	9587(1)	3.55(6)
Si2	250(3)	3233(2)	6261(1)	3.62(6)
N1	2273(6)	465(5)	7376(3)	2.67(15)
N2	1405(7)	2205(6)	8365(3)	3.40(18)
C1	3528(7)	270(6)	7031(4)	2.57(18)
C2	4338(8)	−525(7)	6576(4)	2.86(19)
C3	465(9)	2219(8)	8725(5)	3.96(24)
C4	−755(11)	2216(12)	9203(6)	6.40(35)
C11	4407(8)	1787(7)	8780(4)	3.03(19)
C12	4373(9)	490(7)	8621(4)	3.40(21)
C13	5343(8)	92(7)	8083(4)	3.53(21)
C14	5941(8)	1129(8)	7870(4)	3.69(23)
C15	5389(8)	2154(8)	8312(4)	3.40(21)
C16	2870(11)	1502(9)	10108(5)	4.85(29)
C17	5460(11)	2720(11)	10001(5)	5.64(34)
C18	2467(13)	4279(9)	9422(5)	5.83(33)
C21	1834(8)	3346(7)	6775(4)	3.11(20)
C22	3353(9)	2974(8)	6569(4)	3.79(23)
C23	4176(10)	3499(9)	6984(5)	4.47(27)
C24	3222(10)	4206(7)	7473(5)	4.14(25)
C25	1808(9)	4121(7)	7344(4)	3.57(22)
C26	1042(13)	2215(10)	5531(5)	5.68(34)
C27	−1119(11)	2548(10)	6738(5)	5.17(31)
C28	−675(12)	4970(9)	5948(6)	5.77(33)
C31	1787(8)	−488(7)	7772(4)	2.84(19)
C32	311(9)	−208(8)	7972(5)	3.91(24)
C33	−184(11)	−1130(10)	8357(5)	5.13(31)
C34	757(13)	−2315(10)	8577(6)	5.78(35)
C35	2201(11)	−2588(8)	8365(5)	4.89(29)
C36	2710(9)	−1702(7)	7965(4)	3.61(22)
C41	3886(8)	−1606(7)	6293(4)	2.91(19)
C42	2463(9)	−1715(8)	6307(4)	3.58(22)
C43	2067(10)	−2746(8)	6043(5)	4.25(26)
C44	3148(10)	−3721(9)	5741(5)	5.01(30)
C45	4539(11)	−3621(9)	5709(6)	5.76(33)
C46	4936(9)	−2598(9)	5988(5)	4.89(28)
C51	5793(7)	−342(7)	6346(4)	2.84(19)
C52	7070(8)	−1027(8)	6668(4)	3.51(22)
C53	8425(9)	−903(9)	6434(5)	4.41(27)
C54	8511(10)	−133(10)	5871(5)	4.59(29)
C55	7260(11)	548(9)	5542(5)	4.69(29)
C56	5903(9)	427(8)	5770(4)	3.66(23)
P	7184(3)	5608(2)	8226(1)	4.41(7)
F1	7741(9)	4095(8)	8079(4)	9.54(21)
F2	6578(10)	7062(9)	8387(5)	10.53(24)
F3	6190(12)	5129(11)	8752(6)	12.89(30)
F4	8315(13)	5416(11)	8802(6)	13.35(32)
F5	8204(12)	5994(11)	7694(6)	12.83(30)
F6	6045(14)	5790(12)	7665(6)	14.48(36)
CP1[a]	5091	1130	8333	
CP2	2878	3629	7029	

[a] CP are the gravity centers of the C11–C15 and C21–C25 rings.

Final positional parameters of non-hydrogen atoms are given in Table 3.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances and angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

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