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Synthesis and Reactivity of Oxametallacyclic Niobium Compounds by Using α,β-Unsaturated Carbonyl Ligands

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Dedicated to Prof. Dr. W. Herrmann on the occasion of his 60th birthday

Keywords: Niobium / Cyclopentadienyl ligands / Diene ligands / Metallacycles / Acrylate ligands

Reduction of mono(cyclopentadienyl)niobium complexes [NbCp^{R}Cl$_4$] [Cp^R = C_5Me_4H (**1**), $C_5H_4SiMe_2Cl$ (**2**), $C_5H_4SiMe_3$ (**3**)] with Na/Hg in the presence of methyl methacrylate [MMA, CH_2=C(Me)C(O)OMe (**a**)], methyl acrylate [MA, CH_2=CHC(O)OMe (**b**)] and mesityl oxide [MO, CMe_2=CHC(O)Me (**c**)] afforded the corresponding derivatives [NbCp^{R}Cl$_2$(LL)] [Cp^R = C_5Me_4H, LL = MMA (**1a**); Cp^R = $C_5H_4SiMe_2Cl$, LL = MMA (**2a**), MA (**2b**), MO (**2c**); Cp^R = $C_5H_4SiMe_3$, LL = MMA (**3a**), MA (**3b**)] in variable yields depending on both the cyclopentadienyl and the α,β-unsaturated carbonyl compounds. The reactivity of these complexes was studied toward protic and Lewis acids. Addition of triflic acid TfOH (Tf = CF_3SO_2) to **3b** gave the triflate complex [NbCp^{R}Cl$_2${(CH_2)$_2$C(O)OMe}(OTf)] [Cp^R = $C_5H_4SiMe_3$ (**4**)]. The Lewis acids E(C_6F_5)$_3$ (E = B, Al) reacted with complexes **2b** and **3b** to give the three-membered metallacyclic (or η^2-enone) compounds [NbCp^{R}Cl$_2${η^2-CH_2=CHC(OMe){O·E(C_6F_5)$_3$}}] [Cp^R = $C_5H_4SiMe_2Cl$, E = B (**5**), Al (**6**); Cp^R = $C_5H_4SiMe_3$, E = B (**7**), Al (**8**)], which decomposed to the corresponding adducts MA·E(C_6F_5)$_3$. The same reaction with the **2a** and **3a** derivatives only allowed the observation of the corresponding adducts MMA·E(C_6F_5)$_3$. Complexes **2a**,**b** and **3a**,**b** reacted with CO with elimination of the acrylate compounds, MA and MMA, respectively, to give the carbonylniobium(III) compounds [NbCp^{R}Cl$_2$(CO)$_2$]$_2$ [Cp^R = $C_5H_4SiMe_2Cl$ (**9**), $C_5H_4SiMe_3$ (**10**)]. Analogous reactions with CNAr showed the elimination of the free MA and MMA compounds.

Introduction

The bonding interaction of a butadiene ligand with a metal center is clearly dependent on the metal atom and may be formulated as a system containing a dianionic ligand for early high-valent transition metals or as a neutral ligand for low-valent late transition metals. However, the stability of the formal oxidation state of the metal atom and the nature of the ancillary substituents of both the complex and the diene ligand could play an important role in defining this interaction. Hence, complexes with this type of ligand are better represented with contributions from two main canonical forms, σ^2,π-metallacyclic or π^2-butadiene (Figure 1).[1–5]

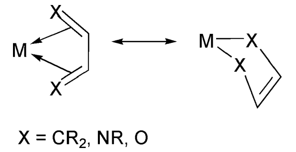

Figure 1. σ^2,π-Metallacyclic or π^2-butadiene form.

Replacement of at least one of the terminal CR_2 moieties by an isolobal fragment such as NR, O, S, etc. induces an important modification on the butadiene ligand.[6–11] Functionalization with one oxygen atom provides an oxametallacyclic system, which consists of a cyclic enolate ligand. The study of enolate derivatives has attracted attention because they have been proposed as the active species for polymerization of polar monomers.[11–16] Another feature of these compounds is that coordination of the asymmetric α,β-unsaturated carbonyl ligands will create two new reactive points in the molecule at the M–C and M–O bonds.

We describe herein the synthesis of mono(cyclopentadienyl)niobium compounds by using different α,β-unsaturated carbonyl ligands and their reactivity with Brönsted

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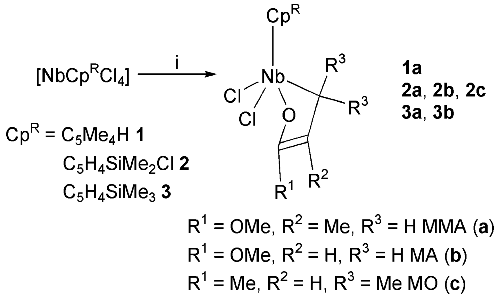
and Lewis acids and with strong π-acceptor ligands such as CO and CNAr.

Results and Discussion

Synthesis of Metallacyclic Compounds

The reduction of the niobium compound [NbCp*Cl$_4$] in toluene with Na/Hg amalgam in the presence of MMA has been reported previously,[7] and we have applied this method using the α,β-unsaturated carbonyl compounds $CH_2{=}C(Me)C(O)OMe$ (MMA), $CH_2{=}CHC(O)OMe$ (MA), and $CMe_2{=}CHC(O)Me$ (MO) to isolate the new derivatives [NbCp^{R}Cl$_2$(LL)] [Cp^R = C_5Me_4H, LL = MMA (**1a**); Cp^R = $C_5H_4SiMe_2Cl$, LL = MMA (**2a**), MA (**2b**), MO (**2c**); Cp^R = $C_5H_4SiMe_3$, LL = MMA (**3a**), MA (**3b**)] (Scheme 1). The whole process can be considered as a reduction of the metal center followed by the oxidative coupling of the α,β-unsaturated carbonyl ligand. These compounds were obtained in good yields for the MMA and MA derivatives, whereas the unique isolated mesityl oxide MO complex was obtained in rather poor yield, probably because of the steric hindrance of the terminal Me_2C group. A similar low yield was reported for the related [TaCp*Cl$_2$(MO)] complex which was obtained from a CO/MO exchange reaction.[17] It is remarkable that reduction proceeded selectively at the niobium atom even in the case of the (chlorosilyl)cyclopentadienyl-functionalized derivatives.



Scheme 1. (i) Na/Hg, toluene, $C(R^3)_2 = C(R^2)C(O)R^1$.

The presence of the enolate ligand endows asymmetry to all of the complexes for which the ^{1}H NMR spectra showed an ABCD spin system for the cyclopentadienyl ring protons and methyl groups. The formation of the metallacyclic compounds **1a**–**3a** and **2b** and **3b** was supported by the low-field signals observed in the ^{1}H NMR spectra for the Nb–CH$_2$ group, shifted to $\delta \approx 1.00$ and 1.70 ppm from δ = 5–6 ppm in the starting free acrylate ligands, and also observed in the ^{13}C NMR spectra shifted to $\delta \approx 70$ ppm with respect to the free acrylate compounds ($\delta \approx 130$ ppm). Moreover, for the MA complexes **2b** and **3b** the signal of the internal C–H proton was observed at $\delta \approx 5.0$ ppm. The coupling constant $^1J_{C,H}$ for the CH$_2$ group of compounds **1a**–**3a** showed a slight decrease consistent with the lower *s* character of this carbon atom ($J \approx 150$ Hz in **1a**–**3a**, J = 159 Hz for free MMA), which was corroborated with the geminal $^2J_{H,H}$ coupling constant of this group ($J \approx 7$ Hz in **1a**–**3a**, J = 2 Hz for free MMA). However, in compounds **2b**–**3b** the $^1J_{C,H}$ coupling constant for the CH$_2$ group remained unchanged, although the increase of $^1J_{C,H}$ for the internal carbon atom suggested higher *s* character ($J \approx 180$ Hz in **2b** and **3b**, J = 162 Hz for free MMA), consistent with the metallacyclic disposition of the MA ligands. The poor yield and the lack of purity of the mesityl oxide compound **2c** made its characterization by NMR and IR spectroscopy difficult, although its molecular structure was determined by X-ray diffraction studies (vide infra) on a single crystal.

The metallacyclic configuration was also supported by the two absorption bands observed in the IR spectrum at about 1515 and 750 cm^{-1} corresponding to ν(C=C) and ν(Nb–O) bands, respectively.

X-ray Structure of 1a, 2a, and 2c

The X-ray structures of complexes **1a**, **2a**, and **2c** (Figure 2, Table 1) were similar to those reported for other related complexes.[7,11,17] The MMA and MO ligands presented a *supine* coordination as expected for the disposition of the five-membered metallacycle folded through the O–C(1) vector, with a dihedral angle of about 103°, as in related oxametallacyclic tantalum compounds.

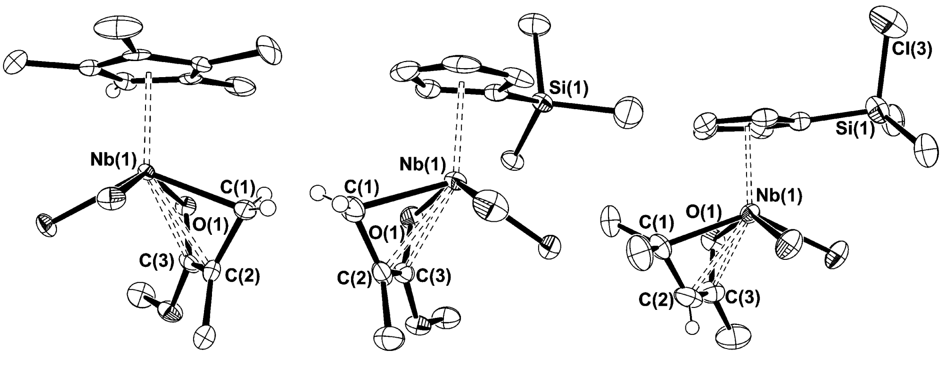


Figure 2. ORTEP diagram of complexes [NbCp^{R}Cl$_2$(LL)] [Cp^R = C_5Me_4H, LL = MMA (**1a**); Cp^R = $C_5H_4SiMe_2Cl$, LL = MMA (**2a**), MO (**2c**)]. Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 50% level.

Table 1. Selected bond lengths [Å] and angles [°] of complexes **1a**, **2a**, and **2c**.

	1a	2a	2c	$R_3CC(R)=C(OR)R$[18]	$R_2C=C(R)C(O)R$[18]
Nb–C(1)	2.194(7)	2.209(4)	2.319(4)		
Nb–O(1)	2.058(5)	2.066(3)	2.005(3)		
Nb–C(2)	2.388(7)	2.364(4)	2.424(5)		
Nb–C(3)	2.421(7)	2.426(4)	2.378(4)		
O(1)–C(3)	1.309(9)	1.310(5)	1.364(5)	1.340	1.222
C(2)–C(3)	1.398(10)	1.406(6)	1.370(7)	1.360	1.475
C(1)–C(2)	1.464(10)	1.446(6)	1.463(3)	1.512	1.340
Nb–O(1)–C(3)	89.1(4)	89.0(2)	87.6(2)		
Nb–C(1)–C(2)	78.7(4)	77.5(2)	76.0(3)		
Nb–LL[a]	103.14	102.21	102.28		

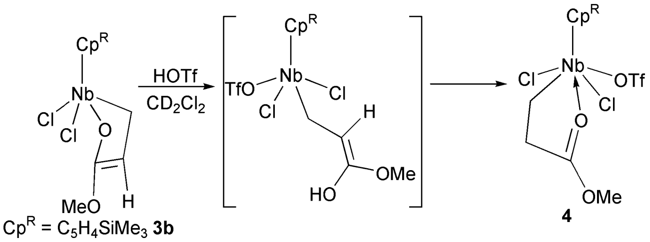
[a] Dihedral angle formed by O(1)–Nb–C(1) and O(1)–C(3)–C(2)–C(1) planes.

A comparison of the O–C and C–C bond lengths of the coordinated MMA and MO ligands in complexes **1a**, **2a**, and **2c** with the corresponding average bond lengths of vinyl ether and α,β-unsaturated carbonyl compounds (Table 1)[18] showed that the O–C and the internal C–C bond values are closer to a vinyl ether disposition (metallacycle), mainly for derivatives **1a** and **2c**, whereas the C(1)–C(2) bond lengths present values intermediate between these two situations. These parameter sets for complexes **1a** and **2c** are very similar to those observed for related compounds [TaCp*Cl_2(MMA)][11] and [TaCpCl_2(MO)].[17]

The Nb–O bonds are longer than those found for (alkoxido)niobium compounds, although they are in the range observed for five-membered alkoxido-metallacyclic derivatives.[19] The distortion due to the formation of the metallacycle makes the Nb–O–C angles (about 88°) clearly more acute than in alkoxido compounds (over 120°) preventing the π-bonding contribution in the oxygen–niobium bond. The Nb–C(terminal) bonds are slightly shorter than in related (butadiene)mono(cyclopentadienyl) complexes[2] for compounds **1a** and **2a** and in the same range for complex **2c**, in which the terminal carbon atom supports two methyl groups. Finally, the Nb–C(internal) bond lengths are also in the range observed for butadiene[2] and diazabutadiene derivatives.[20]

Reaction with Triflic Acid HOTf (Tf = CF_3SO_2)

Complexes **1**–**3** present three nucleophilic centers that can react with protic acids: the Nb–Cl,[21–24] the Nb–C[24], and the oxametallacyclic Nb–O[19] bonds. It would be reasonable to expect that the Nb–C bond should be the most reactive one toward protonolysis due to its lower bond energy, the higher energy of the resulting C–H bond, and the higher nucleophilic character of the niobium-bonded alkyl carbon atom. However, addition of 1 equiv. of HOTf to the acrylate compound **3b** led to the alkyl ester derivative [$NbCp^RCl_2\{(CH_2)_2C(O)OMe\}(OTf)$] [$Cp^R = C_5H_4SiMe_3$ (**4**)] (Scheme 2).



Scheme 2. Reaction of **3b** with HOTf (Tf = CF_3SO_2).

This compound was formed by protonolysis of the Nb–O bond followed by the keto-enol transformation through proton migration in the generated enol intermediate to give complex **4**. Coordination of the carbonyl group to the Nb atom favors stabilization of complex **4** increasing the electron count and preventing possible side-reactions due to the β-hydrogen atoms of the new alkyl chain.[25–29] This proposal was supported by NMR spectroscopy (see below) and by comparison with the reported analogous tantalum derivative, which was isolated by transmetalation with a zinc enolate compound.[29] Complex **4** was unstable in chlorinated solvents giving a mixture of unidentifiable compounds. A change of solvent from CD_2Cl_2 to $CDCl_3$ accelerated this decomposition process. We were unable to reproduce this reaction on a preparative scale neither in these solvents nor by employing alternative solvents.

The higher nucleophilicity of alkoxido compared with methyl and chlorido ligands may justify the preferential protonolysis of the Nb–O bond. The formation of the five-membered ring may prevent the π-bonding contribution to the Nb–O bond due to the close Nb–O–C angle, which would increase the nucleophilicity of this alkoxido group that is sterically less protected with respect to the more linear M–O–C bond angle in related alkoxido complexes.

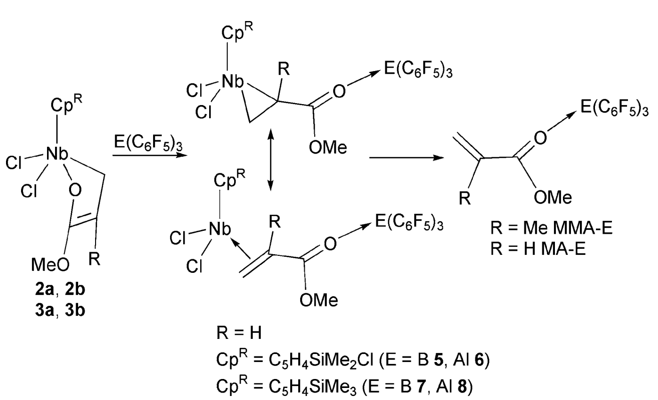
Formation of the C_s-symmetric compound **4** was in agreement with the AA′BB′ pattern observed in the ^1H NMR spectrum for the cyclopentadienyl ligand. The new alkyl chain bonded to the Nb center was confirmed by the ^1H NMR spectrum that shows two multiplets at $\delta = 1.90$ and 3.39 ppm corresponding to the Nb–CH_2 group and the new internal CH_2 group. Also, the generation of this new CH_2 group was supported by a 2-D HSQC-NMR experiment. Finally, the presence of the ester moiety coordinated to the metal atom was confirmed by a resonance observed at $\delta = 194.8$ ppm in the ^{13}C NMR spectrum, which was shifted downfield with respect to this carbon signal in organic esters ($\delta \approx 170$ ppm). This formulation was confirmed by comparison with the related tantalum compound $[TaCp^*Cl_3\{CH_2CH_2C(O)OMe\}]$, for which the X-ray molecular structure has been reported.[29]

The same reaction with compounds **2a**, **2b**, and **3a** and related reactions employing HCl as the Brönsted acid led to decomposition of the starting materials, whereas none of these compounds reacted with the related Lewis acids $[Me_3O][BF_4]$ and $(Me_3Si)OTf$.[30]

Reaction with the Lewis Acids $E(C_6F_5)_3$ (E = B, Al)

The reaction of $B(C_6F_5)_3$ with butadiene compounds has been reported to give betaine derivatives by rupture of the M–C bond.[4,8,31] We have investigated the reactivity of complexes **2a**–**b** and **3a**–**b** with the Lewis acids $E(C_6F_5)_3$ (E = B, Al) with the aim of abstracting the alkyl ligand to generate a cationic enolate compound, considering that early transition-metal derivatives of this type have been used as precursors for the catalytic polymerization of acrylates.[12–16] Although the nucleophilicity of the oxygen atom bonded to the niobium atom could compete with that of the carbon atom, we have previously observed that alkoxido complexes of the type $[Cp^*TaMe_3(OR)]$ reacted with these Lewis acids $E(C_6F_5)_3$ at the Ta–C bond.[32] Furthermore, Mashima and co-workers also reported that reaction of the MMA complex [TaCp*(DAD)(MMA)] [DAD = N(R)CH=CHN(R)] with $AlMe_3$ produced the activation of the Ta–C bond of the coordinated MMA ligand.[11]

Addition of 1 equiv. of $E(C_6F_5)_3$ (E = B, Al) to compounds **2b** and **3b** gave the three-membered metallacyclic compounds $[NbCp^RCl_2\{\eta^2\text{-}CH_2{=}CHC(OMe)\{O\cdot E(C_6F_5)_3\}\}]$ [$Cp^R = C_5H_4SiMe_2Cl$, E = B (**5**), Al (**6**); $Cp^R = C_5H_4SiMe_3$, E = B (**7**), Al (**8**)] (Scheme 3). These complexes evolved slowly at ambient temperature releasing the corresponding adducts $MA\cdot E(C_6F_5)_3$. When the same reaction was carried out with the MMA derivatives **2a** and **3a**, no intermediates were observed, only the formation of the respective adducts $MMA\cdot E(C_6F_5)_3$ was detected. The rate of this transformation was faster for the more oxophilic compound $Al(C_6F_5)_3$. Unfortunately, we could not isolate or characterize the organometallic species in any of these experiments; broad signals were observed in the MeSi region of the NMR spectra. We believe that the metal center was reduced from Nb^V to Nb^{III} as a consequence of the loss of the butadiene ligand and the absence of oxidizing agents. Again, the interaction of the Lewis acids with the Nb–O bond rather than the Nb–C bond could be attributed to the bent Nb–O–C angle.



Scheme 3. Reaction of complexes **2**–**3** [R = Me (**a**), H (**b**)] with $E(C_6F_5)_3$ (E = B, Al).

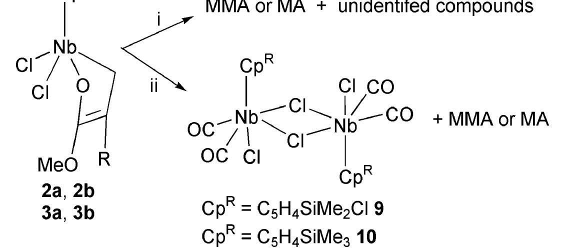
Complexes **5**–**8** are best described in terms of contributions from two canonical forms, as a metallacycle–olefin formulation, consistent with the spectroscopic data that supported a metallacyclic Nb^V complex formulation, whereas their instability toward decomposition releasing the $MMA\cdot E(C_6F_5)_3$ and $MA\cdot E(C_6F_5)_3$ adducts corresponds better with an Nb^{III} metal compound with a coordinated η^2-enone ligand.

This type of η^2-enone complex with the oxygen atom of the carbonyl group coordinated to a Lewis acid has been reported for Pd and Pt, although in the starting compounds the α,β-unsaturated carbonyl ligand was η^2-coordinated through the terminal C–C double bond.[30,33,34]

The most-striking feature of the ^{13}C NMR spectrum is the signal observed at $\delta \approx 185$ ppm for the new carbonyl group. The ^{13}C NMR spectra showed the resonances due to the Nb-bonded carbon atoms shifted to low field, corresponding to the formation of a strained three-membered metallacyclic system,[28,35] with the $^1J_{C,H}$ value observed for these carbon atoms decreased from ca. 180 Hz [C–C(O)] and ca. 160 Hz (CH_2) to ca 160 Hz and ca. 150 Hz, respectively. The ^{19}F NMR spectra were also in agreement with the formation of adducts of the type $R_2CO\cdot E(C_6F_5)_3$. The generation of the carbonyl group was confirmed by the absorption band observed at 1640 cm^{-1} in the IR spectra.

Reaction with CO and CNAr (Ar = 2,6-$Me_2C_6H_3$)

Following on from our study on the chemical behavior of the oxametallacyclic system, we carried out the reaction of the starting compounds **2a**, **2b**, **3a**, and **3b** with CO and CNAr, for which the ability to be inserted into σ-M–C bonds is well documented.[36–40] However, the insertion reaction was not observed, rather displacement of the coordinated MMA and MA ligands (Scheme 4) gave the carbonyl derivatives $[NbCp^RCl_2(CO)_2]_2$ [$Cp^R = C_5H_4SiMe_2Cl$ (**9**), $Cp^R = C_5H_4SiMe_3$ (**10**)] for the reaction with CO, although we could not characterize the corresponding organometallic species resulting from the reaction with CNAr (Scheme 4).



Scheme 4. Reaction of complexes **2**–**3** [R = Me (**a**), H (**b**)] with (i) CNAr (Ar = 2,6-$Me_2C_6H_3$), (ii) CO.

Therefore, the formally Nb^{V} starting compounds **2**–**3** undergo a reductive decoupling to the Nb^{III} derivatives. This process is the reverse of the procedure used for their synthesis. This behavior is a demonstration of the weak Nb–O interaction of the coordinated ligands, highlighting the tendency of Nb to reduce its oxidation state in the presence of strong π-acceptor ligands. This type of complex has been previously synthesized by reduction of $[NbCp^{R}Cl_4]$ in the presence of CO.[41–43]

The IR and NMR spectroscopic data for compounds **9**–**10** were analogous to those reported for related complexes[41–43] and the molecular structure of complex **10** was confirmed by X-ray diffraction studies on an appropriate single crystal (Figure 3).

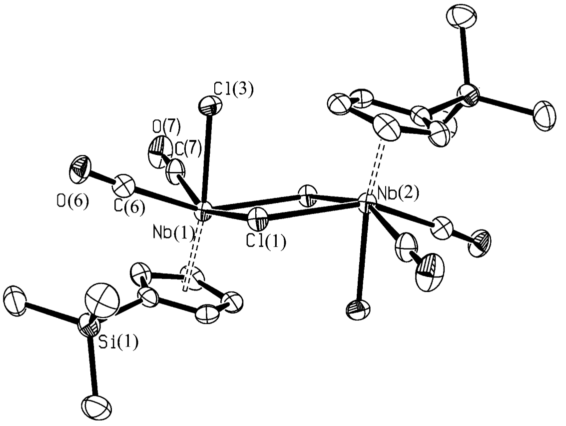


Figure 3. ORTEP diagram of $[NbCp^{R}Cl_2(CO)_2]_2$ [Cp^{R} = $C_5H_4SiMe_2Cl$ (**10**)]. Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 50% level. Selected bond lengths [Å] and angles [°]: Nb(1)–Cl(1) 2.6266(7), Nb(1)–Cl(3) 2.5103(7), Nb(1)–C(7) 2.132(2), C(7)–O(7) 1.141(4); Nb(1)–C(6)–O(6) 176.9(2), Nb(1)–C(7)–O(7) 178.8(2), Nb(1)–Cl(1)–Nb(2) 101.92(2).

The molecular structure of complex **10** corresponds to a dimetallic system with both niobium atoms hexacoordinate, assuming that the cyclopentadienyl ligand occupies only one coordination position. The carbonyl ligands are located in equatorial positions, one chlorido ligand in an apical position *trans* to the cyclopentadienyl group, and the other two positions correspond with two bridging chlorido substituents. The substituents on one metal atom present a *trans* disposition with respect to the substituents on the other niobium atom. The Nb–Cl(bridge) bonds are about 0.1 Å longer than the Nb–Cl(terminal) bonds. The terminal carbonyl ligands are linear with Nb–C–O bond angles of 176.9(2)° and 178.8(2)°. All these bond lengths and angles are similar to those reported in the literature.[41–43]

Conclusions

Compounds of the type $[NbCp^{R}Cl_2(LL)]$ [Cp^{R} = C_5Me_4H, LL = MMA (**1a**); Cp^{R} = $C_5H_4SiMe_2Cl$, LL = MMA (**2a**), MA (**2b**), MO (**2c**); Cp^{R} = $C_5H_4SiMe_3$, LL = MMA (**3a**), MA (**3b**)] were obtained by reactions based on the oxidative addition of the α,β-unsaturated carbonyl ligands LL to the Nb^{III} species generated in situ by reduction of the Nb^{V} halides $[NbCp^{R}Cl_4]$ with Na/Hg. The NMR and crystallographic data supported the formulation of these complexes as alkyl-alkoxido-metallacyclic rather than as butadiene species.

The reactivity of these complexes with Brönsted and Lewis acids is controlled by the higher nucleophilicity of the oxygen atom compared with that of the metallacyclic carbon atom, because of the closely bent Nb–O–C angle, which probably does not allow strong π-bonding of the oxygen atom free pairs with the metal atom and also makes this oxygen atom easily accessible. However, the different nature of both types of acid employed showed two different transformations. Thus, whereas protonation of the Nb–O bond with TfOH gives an enol intermediate which evolves to give an alkyl ester derivative, addition of the Lewis acids $E(C_6F_5)_3$ (E = B, Al) generated a new three-membered metallacyclic system by reforming the α,β-unsaturated carbonyl ligands which remained coordinated by the terminal C=C double bond. This interaction was not stable enough, and their evolution to give the adducts $MMA·E(C_6F_5)_3$ and $MA·E(C_6F_5)_3$ was observed, implying a reduction of the metal center.

Finally, addition of CO and CNAr produced the reductive decoupling and displacement of the coordinated α,β-unsaturated carbonyl ligands to give the Nb^{III} complexes demonstrating the important contribution of the butadiene-like canonical form.

Experimental Section

General Considerations: All manipulations were carried out under argon, and solvents were purified from appropriate drying agents. NMR spectra were recorded at 400.13 (^{1}H), 376.70 (^{19}F), and 100.60 (^{13}C) MHz with a Bruker AV400 spectrometer. Chemical shifts (δ) are given in ppm using C_6D_6 as solvent, unless otherwise stated. ^{1}H and ^{13}C resonances were measured relative to solvent peaks considering δ(TMS) = 0 ppm, whereas ^{19}F resonances were measured relative to external $CFCl_3$. Assignment of resonances was made from HMQC and HMBC NMR experiments. Elemental analyses were performed with a Perkin–Elmer 240C spectrometer. Compounds $C_5Me_4H(SiMe_3)$,[44] $[NbCp^{R}Cl_4]$ (Cp^{R} = $C_5H_4SiMe_2Cl$,[21] $C_5H_4SiMe_3$[23]), $B(C_6F_5)_3$[45], and 0.5(toluene)·$Al(C_6F_5)_3$[46] were prepared according to literature methods. The α,β-unsaturated carbonyl compounds $C(R^3)_2{=}C(R^2)C(O)R^1$ were purchased from Aldrich, dried with CaH_2, distilled under vacuum, and stored under an inert gas prior to use. HOTf (Tf = CF_3SO_2) from Aldrich was used without further purification.

$[Nb(\eta^5\text{-}C_5Me_4H)Cl_4]$ (1): $C_5Me_4H(SiMe_3)$ (2.88 g, 14.80 mmol) in toluene (20 mL) was added to a solution of $[NbCl_5]$ (4.0 g, 14.80 mmol) in toluene/CH_2Cl_2 (100:50 mL). The reaction mixture was further stirred for 6 h, after which the volume was concentrated under vacuum to ca. 30 mL. The solution was cooled to –40 °C overnight yielding **1** as a red solid (2.00 g, 38%). ^{1}H NMR (C_6D_6): δ = 1.80 (s, 6 H, C_5Me_4H), 2.00 (s, 6 H, C_5Me_4H), 5.69 (s, 1 H, C_5Me_4H) ppm. ^{13}C NMR (C_6D_6): δ = 13.9 (C_5Me_4H), 16.7 (C_5Me_4H), 123.8 (CH, C_5Me_4H), 137.1 (CMe, C_5Me_4H), 138.5 (CMe, C_5Me_4H) ppm. $C_9H_{13}Cl_4Nb$ (355.92): calcd. C 30.37, H 3.68; found C 29.95, H 3.30.

[Nb(η^5-C_5Me_4H)Cl_2(LL)] [LL = MMA (1a)]: A solution of [Nb(η^5-C_5Me_4H)Cl_4] (**1**) (1.00 g, 2.81 mmol) and CH_2=C(Me)C(O)OMe (MMA) (0.30 g, 3.0 mmol) in toluene (30 mL) was added to 10% Na/Hg amalgam (0.130 g, 5.62 mmol), and the mixture was stirred overnight. The solution was filtered, concentrated to ca. 15 mL and cooled to –40 °C to yield **1a** as green crystals (0.52 g, 48%). ^{1}H NMR: δ = 0.80 (d, J = 6.3 Hz, 1 H, Nb-CH_2), 1.58 (d, J = 6.3 Hz, 1 H, Nb-CH_2), 1.76 (s, 3 H, C_5Me_4H), 1.80 (s, 3 H, C_5Me_4H), 1.87 (s, 3 H, C_5Me_4H), 2.05 (s, 3 H, C_5Me_4H), 2.40 (s, 3 H, CH_2-CMe), 3.40 (s, 3 H, OMe), 5.79 (s, 1 H, C_5Me_4H) ppm. ^{13}C{^{1}H} NMR: δ = 11.3 (C_5Me_4H), 13.2 (C_5Me_4H), 13.4 (C_5Me_4H), 13.9 (C_5Me_4H), 15.9 (CH_2-CMe), 53.9 (OMe), 72.5 (Nb-CH_2), 86.9 (CH_2-CMe), 116.1 (C_5Me_4H), 122.2 (C_5Me_4H), 122.3 (C_5Me_4H), 123.6 (C_5Me_4H), 125.6 (C_5Me_4H), 160.5 (MeOC) ppm. $C_{14}H_{21}Cl_2NbO_2$ (385.13): calcd. C 43.66, H 5.50; found C 43.45, H 5.25.

[Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_2(LL)] [LL = MMA (2a)]: The same procedure described above for **1a** was applied by using [Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_4] (**2**) (1.00 g, 2.54 mmol) and CH_2=C(Me)C(O)OMe (MMA) (0.27 g, 2.70 mmol) to give **2a** as a brown solid (0.91 g, 85%). ^{1}H NMR: δ = 0.65 (s, 3 H, SiMe_2Cl), 0.71 (s, 3 H, SiMe_2Cl), 1.15 (d, J = 9.9 Hz, 1 H, Nb-CH_2), 1.81 (d, J = 9.9 Hz, 1 H, Nb-CH_2), 2.33 (s, 3 H, CH_2-CMe), 3.28 (s, 3 H, OMe), 5.86 (m, 1 H, C_5H_4), 6.10 (m, 1 H, C_5H_4), 6.53 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = 2.3 (SiMe_2Cl), 2.5 (SiMe_2Cl), 15.8 (CH_2-CMe), 54.4 (OMe), 71.9 (Nb-CH_2), 88.2 (CH_2-CMe), 119.1 (C_5H_4), 120.3 (C_5H_4), 121.0 (C_5H_4), 124.3 (C_5H_4), 125.6 (C_5H_4), 161.4 (MeOC) ppm. $C_{12}H_{18}Cl_3NbO_2Si$ (421.62): calcd. C 34.18, H 4.30; found C 34.05, H 4.25.

[Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_2(LL)] [LL = MA (2b)]: The same procedure described above for **1a** was applied by using [Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_4] (**2**) (1.00 g, 2.54 mmol) and CH_2=C(H)C(O)OMe (MA) (0.23 g, 2.70 mmol) to give **2b** as a brown solid (0.85 g, 82%). ^{1}H NMR: δ = 0.65 (s, 3 H, SiMe_2Cl), 0.70 (s, 3 H, SiMe_2Cl), 1.03 (m, 1 H, Nb-CH_2), 1.88 (m, 1 H, Nb-CH_2), 3.27 (s, 3 H, OMe), 5.00 (m, 1 H, CH_2-CH), 5.83 (m, 1 H, C_5H_4), 6.08 (m, 1 H, C_5H_4), 6.54 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = 1.9 (SiMe_2Cl), 2.1 (SiMe_2Cl), 54.5 (OMe), 62.6 (Nb-CH_2), 76.2 (CH_2-CH), 119.0 (C_5H_4), 121.5 (C_5H_4), 125.4 (C_5H_4), 125.6 (C_5H_4), 137.8 (C_5H_4), 166.0 (MeOC) ppm. $C_{11}H_{16}Cl_3NbO_2Si$ (407.59): calcd. C 32.41, H 3.96; found C 32.50, H 4.00.

[Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_2(LL)] [LL = MO (2c)]: The same procedure described above for **1a** was applied by using [Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_4] (**2**) (1.00 g, 2.54 mmol) and C(Me)$_2$ = C(H)C(O)Me (MO) (0.26 g, 2.70 mmol) to give **2c** as a brown solid (0.17 g, 16%). ^{1}H NMR: δ = 0.73 (s, 3 H, SiMe_2Cl), 0.80 (s, 3 H, SiMe_2Cl), 1.11 (s, 3 H, Nb-CMe_2), 1.76 (s, 3 H, Nb-CMe_2), 2.08 (s, 3 H, MeCO), 5.11 (s, 1 H, CMe_2-CH), 5.66 (m, 1 H, C_5H_4), 5.85 (m, 1 H, C_5H_4), 6.48 (m, 1 H, C_5H_4), 6.67 (m, 1 H, C_5H_4) ppm. $C_{13}H_{20}Cl_3NbOSi$ (419.65): calcd. C 37.21, H 4.80; found C 35.95, H 4.06. Because of the low yield and solubility of this compound, we could not obtain pure samples for an adequate ^{13}C NMR spectrum and elemental analysis, although single crystals appropriate for X-ray diffraction studies were isolated.

[Nb(η^5-$C_5H_4SiMe_3$)Cl_2(LL)] [LL = MMA (3a)]: The same procedure described above for **1a** was applied by using [Nb(η^5-$C_5H_4SiMe_3$)Cl_4] (**3**) (1.00 g, 2.69 mmol) and CH_2=C(Me)C(O)OMe (MMA) (0.28 g, 2.80 mmol) to give **3a** as a brown solid (0.89 g, 83%). ^{1}H NMR: δ = 0.26 (s, 9 H, SiMe_3), 1.21 (d, J = 6.6 Hz, 1 H, Nb-CH_2), 1.88 (d, J = 6.6 Hz, 1 H, Nb-CH_2), 2.36 (s, 3 H, CH_2-CMe), 3.36 (s, 3 H, OMe), 5.80 (m, 1 H, C_5H_4), 6.31 (m, 1 H, C_5H_4), 6.54 (m, 1 H, C_5H_4), 6.71 (m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = –0.7 (SiMe_3), 15.2 (CH_2-CMe), 54.7 (OMe), 72.0 (Nb-CH_2), 88.3 (CH_2-CMe), 118.5 (C_5H_4), 122.1 (C_5H_4), 122.2 (C_5H_4), 124.1 (C_5H_4), 127.9 (C_5H_4), 160.8 (MeOC) ppm. $C_{13}H_{21}Cl_2NbO_2Si$ (401.20): calcd. C 38.92, H 5.28; found C 38.72, H 5.20.

[Nb(η^5-$C_5H_4SiMe_3$)Cl_2(LL)] [LL = MA (3b)]: The same procedure described above for **1a** was applied by using [Nb(η^5-$C_5H_4SiMe_3$)Cl_4] (**3**) (1.00 g, 2.69 mmol) and CH_2=C(H)C(O)OMe (MA) (0.24 g, 2.80 mmol) to give **3b** as a brown solid (0.89 g, 86%). ^{1}H NMR: δ = 0.26 (s, 9 H, SiMe_3), 1.09 (m, 1 H, Nb-CH_2), 1.97 (m, 1 H, Nb-CH_2), 3.35 (s, 3 H, OMe), 5.05 (m, 1 H, CH_2-CH), 5.80 (m, 1 H, C_5H_4), 6.27 (m, 1 H, C_5H_4), 6.55 (m, 1 H, C_5H_4), 6.70 (m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = –0.5 (SiMe_3), 54.7 (OMe), 68.3 (Nb-CH_2), 76.2 (CH_2-CH), 119.3 (C_5H_4), 121.5 (C_5H_4), 125.3 (C_5H_4), 125.6 (C_5H_4), 127.9 (C_5H_4), 166.0 (MeOC) ppm. $C_{12}H_{19}Cl_2NbO_2Si$ (387.18): calcd. C 37.23, H 4.95; found C 37.20, H 5.00.

Reaction of 3b with Triflic Acid HOTf (Tf = CF_3SO_2): A teflon-valved NMR tube was charged with a solution of [Nb(η^5-$C_5H_4SiMe_3$)Cl_2(LL)] [LL = MA (**3b**)] (0.015 g, 0.039 mmol) in CD_2Cl_2, and HOTf was added (3.43 µL, 0.039 mmol). The reaction was monitored by NMR spectroscopy, and the formation of [NbCp^RCl_2{$(CH_2)_2$C(O)OMe}(OTf)] [Cp^R = $C_5H_4SiMe_3$ (**4**)] was observed as the only product. After 24 h at room temperature, NMR spectroscopy showed decomposition of **4**. ^{1}H NMR (CD_2Cl_2): δ = 0.38 (s, 9 H, SiMe_3), 1.90 (m, 2 H, Nb-CH_2), 3.39 (m, 2 H, CH_2CO), 4.21 (s, 3 H, OMe), 6.97 (m, 2 H, C_5H_4), 7.18 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = –0.3 (SiMe_3), 40.2 (CH_2CO), 57.3 (OMe), 65.6 (Nb-CH_2), 117.3 (C_5H_4), 121.4 (C_5H_4), 125.5 (C_5H_4), 194.8 (MeOCO) ppm.

Reaction of Compounds 2a and 3a with E(C_6F_5)$_3$ (E = B, Al): Teflon-valved NMR tubes were charged with C_6D_6 solutions of [NbCp^RCl_2(MMA)] [Cp^R = $C_5H_4SiMe_2Cl$ (**2a**), 0.015 g, 0.037 mmol; Cp^R = $C_5H_4SiMe_3$ (**3a**), 0.015 g, 0.039 mmol] and E(C_6F_5)$_3$ (0.037 mmol for **2a**, 0.039 mmol for **3a**). The reactions were monitored by NMR spectroscopy which indicated formation of compounds MMA·E(C_6F_5)$_3$[15] as the only characterizable compounds.

Reaction of Compounds 2b and 3b with E(C_6F_5)$_3$ (E = B, Al): Teflon-valved NMR tubes were charged with C_6D_6 solutions of [NbCp^RCl_2(MA)] [Cp^R = $C_5H_4SiMe_2Cl$ (**2b**), 0.015 g, 0.036 mmol; Cp^R = $C_5H_4SiMe_3$ (**3b**), 0.015 g, 0.038 mmol) and E(C_6F_5)$_3$ (0.036 mmol for **2b**, 0.038 mmol for **3b**). The reactions were monitored by NMR spectroscopy showing the formation of compounds [NbCp^RCl_2{η^2-CH_2=CHC(OMe){O·E(C_6F_5)$_3$}}] [Cp^R = $C_5H_4SiMe_2Cl$, E = B (**5**), Al (**6**); Cp^R = $C_5H_4SiMe_3$, E = B (**7**), Al (**8**)]. After several hours, decomposition of **5**–**8** and formation of the adducts MA·E(C_6F_5)$_3$ as the only characterizable compound were observed. **5:** ^{1}H NMR: δ = 0.33 (s, 3 H, SiMe_2Cl), 0.35 (s, 3 H, SiMe_2Cl), 2.29 (m, 1 H, CH_2-CH), 2.49 (m, 1 H, Nb-CH_2), 2.95 (m, 1 H, Nb-CH_2), 3.49 (s, 3 H, OMe), 4.51 (m, 1 H, C_5H_4), 4.75 (m, 1 H, C_5H_4), 5.32 (m, 1 H, C_5H_4), 5.56 (m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = 2.0 (SiMe_2Cl), 2.1 (SiMe_2Cl), 55.4 (OMe), 55.9 (CH_2-CH), 67.6 (Nb-CH_2), 119.5 (C_5H_4), 119.8 (C_5H_4), 122.1 (C_5H_4), 122.4 (C_5H_4), C_{ipso} of C_5H_4 not observed, 134.9 (C_6F_5), 138.8 (C_6F_5), 146.4 (C_6F_5), 149.6 (C_6F_5), 185.2 (MeOCO) ppm. ^{19}F NMR: δ = –131.3 (m, 6 F, o-C_6F_5), –156.4 (m, 3 F, p-C_6F_5), –162.7 (m, 6 F, m-C_6F_5) ppm. IR (C_6D_6): ṽ = 1638 [ν(CO)] cm^{-1}. **6:** ^{1}H NMR: δ = 0.30 (s, 3 H, SiMe_2Cl), 0.35 (s, 3 H, SiMe_2Cl), 2.35 (m, 1 H, CH_2-CH), 2.60 (m, 1 H, Nb-CH_2), 2.86 (m, 1 H, Nb-CH_2), 3.49 (s, 3 H, OMe), 4.61 (m, 1 H, C_5H_4), 5.10 (m, 1 H, C_5H_4), 5.34 (m, 1 H, C_5H_4), 5.53 (m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR: δ = 2.1 (SiMe_2Cl), 2.2 (SiMe_2Cl), 56.2 (OMe), 57.0 (CH_2-CH), 65.2 (Nb-

CH$_2$), 119.2 (C_5H$_4$), 119.5 (C_5H$_4$), 121.4 (C_5H$_4$), 125.7 (C_5H$_4$), C_{ipso} of C$_5$H$_4$ not observed, 135.5 (C_6F$_5$), 138.8 (C_6F$_5$), 148.9 (C_6F$_5$), 152.1 (C_6F$_5$), 184.2 (MeOCO) ppm. ^{19}F NMR: δ = –123.8 (m, 6 F, *o*-C$_6\mathit{F}_5$), –153.1 (m, 3 F, *p*-C$_6\mathit{F}_5$), –161.7 (m, 6 F, *m*-C$_6\mathit{F}_5$) ppm. IR (C$_6$D$_6$): $\tilde{\nu}$ = 1638 [ν(CO)] cm^{-1}. **7:** ^{1}H NMR: δ = 0.02 (s, 9 H, SiMe_3), 2.45 (m, 1 H, Nb-CH_2), 2.62 (m, 1 H, Nb-CH_2), 3.09 (m, 1 H, CH$_2$-CH), 3.51 (s, 3 H, OMe), 4.66 (m, 1 H, C$_5\mathit{H}_4$), 4.77 (m, 1 H, C$_5\mathit{H}_4$), 5.43 (m, 1 H, C$_5\mathit{H}_4$), 5.48 (m, 1 H, C$_5\mathit{H}_4$) ppm. ^{13}C{^{1}H} NMR: δ = –1.1 (SiMe_3), 55.1 (OMe), 56.0 (CH$_2$-CH), 67.1 (Nb-CH$_2$), 116.5 (C_5H$_4$), 117.1 (C_5H$_4$), 118.6 (C_5H$_4$), 119.5 (C_5H$_4$), C_{ipso} of C$_5$H$_4$ not observed, 135.7 (C_6F$_5$), 139.1 (C_6F$_5$), 146.7 (C_6F$_5$), 149.9 (C_6F$_5$), 186.4 (MeOCO) ppm. ^{19}F NMR: δ = –132.3 (m, 6 F, *o*-C$_6\mathit{F}_5$), –156.7 (m, 3 F, *p*-C$_6\mathit{F}_5$), –164.1 (m, 6 F, *m*-C$_6\mathit{F}_5$) ppm. IR (C$_6$D$_6$): $\tilde{\nu}$ = 1640 [ν(CO)] cm^{-1}. **8:** ^{1}H NMR: δ = 0.01 (s, 9 H, SiMe_3), 2.45 (m, 1 H, CH$_2$-CH), 2.64 (m, 1 H, Nb-CH_2), 2.88 (m, 1 H, Nb-CH_2), 3.51 (s, 3 H, OMe), 4.75 (m, 1 H, C$_5\mathit{H}_4$), 5.10 (m, 1 H, C$_5\mathit{H}_4$), 5.42 (m, 2 H, C$_5\mathit{H}_4$) ppm. ^{13}C{^{1}H} NMR: δ = –1.2 (SiMe_3), 56.0 (OMe), 57.3 (CH$_2$-CH), 65.4 (Nb-CH$_2$), 117.2 (C_5H$_4$), 117.4 (C_5H$_4$), 118.7 (C_5H$_4$), 119.5 (C_5H$_4$), C_{ipso} of C$_5$H$_4$ not observed, 135.7 (C_6F$_5$), 138.9 (C_6F$_5$), 148.9 (C_6F$_5$), 152.0 (C_6F$_5$), 184.9 (MeOCO) ppm. ^{19}F NMR: δ = –120.5 (m, 6 F, *o*-C$_6\mathit{F}_5$), –153.0 (m, 3 F, *p*-C$_6\mathit{F}_5$), –161.5 (m, 6 F, *m*-C$_6\mathit{F}_5$) ppm. IR (C$_6$D$_6$): $\tilde{\nu}$ = 1647 [ν(CO)] cm^{-1}.

Reaction of Compounds 2–3 with CO: Teflon-valved NMR tubes were charged with C$_6$D$_6$ solutions of [NbCp^{R}Cl$_2$(LL)] [Cp^R = C$_5$H$_4$SiMe$_2$Cl, LL = MMA (**2a**), 0.015 g, 0.037 mmol; LL = MA (**2b**), 0.015 g, 0.036 mmol; Cp^R = C$_5$H$_4$SiMe$_3$, LL = MMA (**3a**), 0.015 g, 0.039 mmol; LL = MA (**3b**), 0.015 g, 0.038 mmol] and then filled with CO. The reaction was monitored by NMR spectroscopy showing the immediate formation of compounds [NbCp^{R}Cl$_2$(CO)$_2$]$_2$ [Cp^R = C$_5$H$_4$SiMe$_2$Cl (**9**), C$_5$H$_4$SiMe$_3$ (**10**)] and free MMA or MA. The C$_6$D$_6$ solution was layered with hexane (1 mL) to afford crystals of complex **9** or **10**. **9:** ^{1}H NMR: δ = 0.00 (s, 12 H, SiMe_2Cl), 5.05 (m, 4 H, C$_5\mathit{H}_4$), 5.81 (m, 4 H, C$_5\mathit{H}_4$) ppm. ^{13}C{^{1}H} NMR: δ = –0.7 (SiMe_2Cl), 102.7 (C_5H$_4$), 108.8 (C_5H$_4$), C_{ipso} of C$_5$H$_4$ not observed, 184.4 (CO) ppm. IR (nujol): $\tilde{\nu}$ = 2035, 1960 [ν(CO)] cm^{-1}. C$_{18}$H$_{24}$Cl$_6$Nb$_2$O$_4$Si$_2$ (759.08): calcd. C 28.48, H 3.19; found C 29.48, H 3.00. **10:** ^{1}H NMR: δ = 0.01 (s, 18 H, SiMe_3), 5.04 (m, 4 H, C$_5\mathit{H}_4$), 5.80 (m, 4 H, C$_5\mathit{H}_4$) ppm. ^{13}C{^{1}H} NMR: δ = –0.7 (SiMe_3), 102.6 (C_5H$_4$), 108.7 (C_5H$_4$), C_{ipso} of C$_5$H$_4$ not observed, 185.0 (CO) ppm. IR (nujol): $\tilde{\nu}$ = 2030, 1953 [ν(CO)] cm^{-1}. C$_{20}$H$_{26}$Cl$_4$Nb$_2$O$_4$Si$_2$ (714.22): calcd. C 33.66, H 3.67; found C 33.99, H 3.57.

Single-Crystal X-ray Structure Determination of Compounds 1a, 2a, 2c, and 10: Suitable yellow single crystals of **1a**, **2a**, **2c**, and **10** for the X-ray diffraction study were selected (Table 2). The crystals were placed on the top of a glass fiber using perfluoropolyether oil and cooled to 150 K (**1a** and **2a**) or 200 K (**2c** and **10**). The crystals were mounted on a Bruker–Nonius Kappa CCD single-crystal diffractometer and the data collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Multiscan[47] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[48] by direct methods (SHELXS-97)[49] and refined by using full-matrix least squares against F^2 (SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the hydrogen atom on C(2) in compound **2c**. For **1c** two independent molecules were observed in the asymmetric unit. The crystal measured for **2c** showed some twinning and some positional disorder between the chlorine atom Cl(3) and one of the methyl groups [C(18)] bonded to the silicon atom. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density maps showed no remarkable features. CCDC-674114 (**1a**), -674115 (**2a**), -674116 (**2c**), and -674117 (**10**) contain the supplementary

Table 2. Crystallographic data for **1a**, **2a**, **2c**, and **10**.[a]

	1a	**2a**	**2c**	**10**
Empirical formula	$C_{14}H_{21}Cl_2NbO_2$	$C_{12}H_{18}Cl_3NbO_2Si$	$C_{13}H_{20}Cl_3NbOSi$	$C_{20}H_{26}Cl_4Nb_2O_4Si_2$
Formula mass	385.12	421.61	419.64	714.20
Color/habit	green/prism	green/prism	dark green/prism	dark orange/prism
Crystal size [mm]	0.31 × 0.27 × 0.25	0.12 × 0.12 × 0.05	0.36 × 0.20 × 0.16	0.31 × 0.20 × 0.17
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a [Å]	34.914(4)	6.6776(10)	7.1060(12)	6.9633(8)
b [Å]	8.3580(5)	22.523(2)	11.471(2)	9.8648(13)
c [Å]	27.070(3)	10.8035(11)	22.148(3)	10.6684(17)
α [°]	90	90	90	80.031(11)
β [°]	127.220(8)	90.055(8)	98.3030(13)	81.956(12)
γ [°]	90	90	90	79.204(8)
V [Å^3]	6290.4(11)	1624.9(3)	1786.4(5)	704.60(17)
Z	16	4	4	1
T [K]	150(2)	150(2)	200(2)	200(2)
$D_{\text{calcd.}}$ [g cm^{-3}]	1.627	1.723	1.560	1.683
μ [mm^{-1}]	1.100	1.302	1.180	1.301
F(000)	3136	848	848	356
θ range [°]	3.01–27.50	3.59–27.50	3.55–27.54	3.10–27.50
No. of reflections collected	71593	19644	29896	13916
No. of independent reflections (R_{int})	7206/0.1301	3671/0.0761	4107/0.1047	3218/0.0260
No. of observed reflections [$I > 2\sigma(I)$]	4507	3102	2613	2721
No. of data/restraints/parameters	7206/0/355	3671/0/177	4107/0/176	3218/0/145
$R1/wR2$ [$I > 2\sigma(I)$][a]	0.0722/0.1222	0.0376/0.0700	0.0479/0.0962	0.0295/0.0739
$R1/wR2$ (all data)[a]	0.1305/0.1338	0.0528/0.0743	0.0991/0.1076	0.0384/0.0770
GOF (on F^2)[a]	1.161	1.023	0.987	1.052
Largest difference peak/hole [e Å^{-3}]	+0.818/–0.864	+0.568/–0.529	0.563/–0.807	+0.7021/–0.938

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected NMR spectra.

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