A Synthetic Methodology to Niobium Alkylidenes: Reactivity of a Nb═Nb Double Bond Anchored to a Calix[4]arene Oxo Surface with Ketones, Aldehydes, Imines, and Isocyanides

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Abstract: The active compound leading to the synthesis of niobium alkylidenes and niobium alkylidynes from ketones and aldehydes is a [Nb^{III}═Nb^{III}] dimer, [{*p*-Bu^t-calix[4]-$(O)_4$}$_2$$Nb_2Na_2$] (**3**), supported by the [*p*-Bu^t-calix[4]-$(O)_4$] tetraanion. It was obtained from a stepwise reduction of [{*p*-Bu^t-calix[4]-$(O)_4$}$_2$$Nb_2(Cl)_2$] (**1**) through the intermediate formation of a [Nb−Nb] dimer, [{μ-*p*-Bu^t-calix[4]-$(O)_4$}$_2$$Nb_2$] (**2**). Complex **3** reacted with ketones and aldehydes, RR′CO, via the metathesis of the Nb═Nb bond with the carbonyl functionality, forming an equimolar amount of the niobium alkylidene [{*p*-Bu^t-calix[4]-$(O)_4$}Nb═CRR′)]Na [R = R′ = Ph, **4**; R = Ph, R′ = Me, **5**; R = Cp_2Fe, R′ = Me, **6**; R = Ph, R′ = CH_2Ph, **7**; RR′ = $(CH_2)_4$, **8**; R = Pr^n, R′ = H, **10**; R = Ph, R′ = H, **11**] and of the oxoniobium(V) complex [{*p*-Bu^t-calix[4]-$(O)_4$}Nb═ONa] (**9**). The easy separation of **9** from the niobium alkylidenes makes the reaction of **3** with ketones a useful synthetic methodology to obtain metal alkylidene derivatives. The niobium alkylidene **11** underwent a reversible protonation and deprotonation reaction, leading to the corresponding benzyl derivative [{*p*-Bu^t-calix[4]-$(O)_4$}-Nb−CH_2Ph)] (**12**) and to the bridging alkylidyne [{*p*-Bu^t-calix[4]-$(O)_4$}$_2$$Nb_2$($\mu$-PhC)$_2$$Na_4$] (**13**). A proton transfer from **12** to **13**, assisted by a basic solvent such as pyridine, led to **11**. The latter compound has been obtained as a magnesium salt from a direct alkylation of **1** using 2 equiv of [$Mg(CH_2Ph)_2$]. The significant difference in the reaction rate of **3** with aldehydes or ketones, and the reaction of the niobium alkylidenes with an excess of aldehydes or ketones, leading to the coupling between the alkylidene and the carbonyl functionality, allowed us to carry out the McMurry synthesis of nonsymmetric olefins in a stepwise manner. The four-electron reduction of RNC by complex **3** led to the formation of a dimetalla-imino-alkylidyne, [{*p*-Bu^t-calix[4]-$(O)_4$}Nb(μ-RNC)-Nb{μ-*p*-Bu^t-calix[4]-$(O)_4$}Na_2] [R = Bu^t, **14**; R = 2,6-$Me_2C_6H_3$, **15**], while the reaction with the imine PhCH═NPh led to the η^2-imino complex [{*p*-Bu^t-calix[4]-$(O)_4$}Nb(η^2-PhCH−NPh)Na] (**16**). Both reactions shed some light on the niobium alkylidene formation from ketones and aldehydes. An X-ray structural analysis is given for one of each class of compounds, namely **6**, **9**, **11**, **13**, **15**, and **16**.

Introduction

Although the alkylidene and alkylidyne metal functionalities have a very relevant impact on preparative chemistry and catalysis,[1,2] their access is limited to only a few synthetic methodologies. The present report deals with a direct synthesis of metal alkylidenes and alkylidynes from among the most common organic functionalities, namely ketones and aldehydes. This new entry in the field can open much wider possibilities in the use of such functionalities as synthons in organic synthesis.[3] In addition, this novel synthetic methodology has been applied to niobium,[4] having a limited number of alkylidene[5] and alkylidyne[6,7] derivatives, by the use, as ancillary ligand, of *p*-Bu^t-calix[4]arene tetraanion. The alkoxo groups are, in fact, the ancillary ligands *par excellence* in the field.[1−4] One might wonder what might be the consequence of using the calix[4]-arene as ancillary ligand in metal alkylidene and metal alkylidyne chemistry. The metal bonded to the nearly planar

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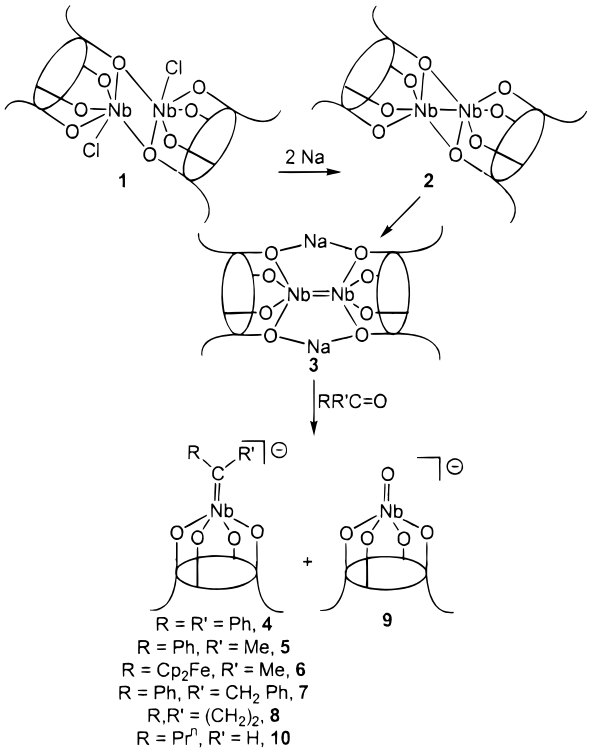
Scheme 1



calix[4]arene skeleton in its cone conformation displays three frontier orbitals, one σ and two π, particularly appropriate for stabilizing the M−C multiple bond functionality.[8] The other unique role of calix[4]arene, which makes comparisons with the heterogeneous metal oxide systems[9] valuable, is the basic surrounding of the metal, where the oxygen donor atoms can assist the protonation−deprotonation of alkylidenes and, in general, their reaction with electrophiles.

The active compound able to manage the chemistry outlined above is a Nb^{III}−calix[4]arene dimer (**3** in Scheme 1), capable of performing the four-electron reduction of the dinitrogen[10] and containing a Nb═Nb double bond.[11] This paper covers, in particular, the genesis of niobium alkylidenes from ketones and aldehydes and their reversible deprotonation−protonation to bridging alkylidynes, along with the use of the [Nb^{III}−calix[4]-arene] dimer in the McMurry[12] synthesis of olefins. The reactions of the [Nb═Nb] functionality with isocyanides and imines shed light on the possible mechanism in the formation of the niobium alkylidenes from ketones and aldehydes.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on a 200-AC or DPX-400 Bruker instrument. IR spectra were recorded with a Perkin-Elmer FT 1600 spectrophotometer. GC−MS analyses were carried out using a Hewlett-Packard 5890A GC system. Elemental analyses were performed using an EA 1110 CHN elemental analyzer from CE Instruments. The synthesis of [*p*-Bu^t-calix[4]-$(OH)_4$] has been performed as reported in the literature.[13]

Synthesis of 1. $NbCl_5$ (18.18 g, 67.30 mmol) was added to a toluene (500 mL) suspension of *p*-Bu^t-calix[4]arene(CH_2Cl_2) (49.39 g, 67.30 mmol), and the resulting red mixture was refluxed for 16 h (note that evolution of HCl took place). The solvent was removed in vacuo, fresh toluene was added (500 mL), stirring was maintained for 20 min, and the solvent was then evaporated to dryness again. **1**·$(C_7H_8)_{2.6}$ was collected from toluene (500 mL) as a red powder (58.65 g, 98%). Anal. Calcd for **1**·$(C_7H_8)_{2.6}$, $C_{106.2}H_{124.8}Cl_2Nb_2O_8$: C, 71.44; H, 7.04. Found: C, 71.00; H, 7.08. ^{1}H NMR (CD_2Cl_2, 298 K, ppm): δ 7.28 (s, 4H, ArH), 7.19 (s, 4H, ArH) overlapping with 7.22−7.12 (m, 13H, toluene), 7.17 (s, 4H, ArH), 7.12 (s, 4H, ArH), 5.07 (d, 4H, J = 12.5 Hz, *endo*-CH_2), 4.62 (d, 4H, J = 13.6 Hz, *endo*-CH_2), 3.51 (d, 4H, J = 12.5 Hz, *exo*-CH_2), 3.36 (d, 4H, J = 13.6 Hz, *exo*-CH_2), 2.34 (s, 8H, toluene), 1.33 (s, 18H, Bu^t), 1.22 (s, 36H, Bu^t), 1.17 (s, 18H, Bu^t). The product is almost insoluble in hydrocarbons and THF, slightly soluble in chlorinated solvents, and thermally stable.

Synthesis of 2. Sodium (1.422 g, 61.85 mmol) and naphthalene (0.396 g, 3.09 mmol) were added to a red THF (500 mL) suspension of **1**·$(C_7H_8)_{2.6}$ (55.40 g, 31.02 mmol), and the reaction mixture was stirred at room temperature. After 3 days, the sodium was consumed, and the resulting brown suspension was extracted with the mother liquors for 48 h. The volume was concentrated to 100 mL, and **2**·4THF was filtered and dried in vacuo as a microcrystalline light brown powder (47.54 g, 87%). Anal. Calcd for **2**·4THF, $C_{104}H_{136}Nb_2O_{12}$: C, 70.81; H, 7.77. Found: C, 70.83; H, 8.10. ^{1}H NMR (CD_2Cl_2, 298 K, ppm): δ 7.32 (s, 4H, ArH), 7.22 (s, 4H, ArH), 7.16 (s, 4H, ArH), 7.07 (s, 4H, ArH), 4.52 (d, 4H, J = 13.1 Hz, *endo*-CH_2), 4.40 (d, 4H, J = 12.0 Hz, *endo*-CH_2), 3.67 (m, 16H, THF), 3.57 (d, 4H, J = 13.1 Hz, *exo*-CH_2), 3.36 (d, 4H, J = 12.0 Hz, *exo*-CH_2), 1.81 (m, 16H, THF), 1.28 (s, 18H, Bu^t), 1.24 (s, 36H, Bu^t), 1.15 (s, 18H, Bu^t). The product is not stable in CD_2Cl_2, yielding in about 1 h to **1**. ^{1}H NMR (DMSO-d_6, 298 K, ppm): δ 7.11 (s, 4H, ArH), 7.02 (s, 4H, ArH), 6.95 (s, 8H, ArH), 4.42 (m, 6H, *endo*-CH_2) overlapping with 4.41 (d, 2H, J = 11.6 Hz, *endo*-CH_2), 3.60 (m, 16H, THF), 3.16 (m, 6H, *exo*-CH_2), 3.01 (d, 2H, J = 11.6 Hz, *exo*-CH_2), 1.75 (m, 16H, THF), 1.16 (s, 18H, Bu^t), 1.13 (s, 36H, Bu^t), 1.12 (s, 18H, Bu^t).

Synthesis of 3. Sodium (0.616 g, 26.79 mmol) was added to a THF (300 mL) suspension of **2**·4THF (23.62 g, 13.39 mmol) under an argon atmosphere. The reaction mixture was stirred for 2 days, the resulting turbid brown solution was filtered, and the solvent was removed in vacuo. *n*-Hexane (100 mL) was added to the residue, and **3**·6THF was collected as a green powder (20.48 g, 78%). Anal. Calcd for **3**·6THF, $C_{112}H_{152}Na_2Nb_2O_{14}$: C, 68.84; H, 7.84. Found: C, 68.92; H, 7.65. ^{1}H NMR (C_4D_8O, 298 K, ppm): δ 7.04 (s, 8H, ArH), 6.97 (s, 8H, ArH), 4.82 (d, 8H, J = 12.0 Hz, *endo*-CH_2), 3.62 (m, 24H, THF), 3.13 (d, 8H, J = 12.0 Hz, *exo*-CH_2), 1.77 (m, 24H, THF), 1.19 (s, 36H, Bu^t), 1.16 (s, 36H, Bu^t). The product is very soluble in THF, soluble in toluene, and slightly soluble in DME, Et_2O, and alkanes. Crystals suitable for X-ray analysis were obtained from a DME/methylcyclohexane-saturated solution under an argon atmosphere as **3**·2DME. **3** is thermally and photochemically stable in THF solutions.

Synthesis of 4. A THF solution of Ph_2CO (0.077 M, 3.49 mmol) was added dropwise to a cold (−25 °C), stirred, green-brown THF (250 mL) solution of **3**·6THF (6.87 g, 3.52 mmol) under an argon atmosphere, giving a fast change in color. Stirring at −25 °C was maintained for 12 h. The argon atmosphere was replaced with N_2, and then white **9**·$Na(THF)_4$ (2.64 g, 70%) was filtered off from the resulting brown suspension. The filtrate was allowed to reach room temperature, volatiles were removed in vacuo, and finally THF (150 mL) was added to the residue. A second crop of **9**·$Na(THF)_4$ (0.94 g, 26%) was filtered off, volatiles were removed in vacuo, the residue was washed with *n*-pentane (125 mL), and **4**·$Na(THF)_3$ was collected as an orange

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powder (2.94 g, 74%). Anal. Calcd for **4**·Na(THF)$_3$, $C_{69}H_{86}NaNbO_7$: C, 72.49; H, 7.58. Found: C, 72.47; H, 7.79. ^{1}H NMR (py-d_5, 298 K, ppm): δ 8.30 (d, 4H, J = 7.6 Hz, ArH(Ph)), 7.47 (t, 4H, J = 7.6 Hz, ArH(Ph)), 7.20 (s, 8H, ArH), 6.93 (t, 2H, J = 7.6 Hz, ArH(Ph)), 5.42 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 3.64 (m, 12H, THF), 3.46 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 12H, THF), 1.17 (s, 36H, Bu^t). ^{13}C NMR (py-d_5, 298 K, ppm): δ 249.17 (*C*Ph$_2$). Crystals suitable for X-ray analysis were grown at −23 °C in a DME/toluene-saturated solution and obtained in the solvated form, **4**·Na(DME)$_3$·C$_7$H$_8$. The product is very soluble in THF and py (about 100 mg/mL) and slightly soluble in hydrocarbons. It is thermally stable as judged from ^{1}H NMR analysis in py-d_5. Solutions are insensitive to solar light.

Synthesis of 5. A THF solution of Ph(CH$_3$)CO (0.067 M, 3.34 mmol) was added dropwise to a cold (−40 °C), stirred, green-brown THF (60 mL) solution of **3**·6THF (6.52 g, 3.34 mmol) under argon atmosphere, leading to a fast change in color. It was allowed to stand at −40 °C over 24 h, and then the argon atmosphere was replaced with N$_2$. White **9**·Na(THF)$_4$ (3.3 g, 92%) was filtered off from the resulting reddish suspension and was allowed to reach room temperature. Volatiles were removed in vacuo, the residue was washed with *n*-pentane (30 mL), and **5**·Na·THF·(C$_5$H$_{12}$)$_{0.5}$ was collected as an orange powder (2.0 g, 62%). Anal. Calcd for **5**·Na·THF·(C$_5$H$_{12}$)$_{0.5}$, $C_{58.5}H_{74}NaNbO_5$: C, 72.20; H, 7.67. Found: C, 72.01; H, 7.81. ^{1}H NMR (py-d_5, 298 K, ppm): δ 8.04 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.47 (t, 2H, J = 7.6 Hz, ArH(Ph)), 7.26 (s, 8H, ArH), 6.81 (t, 1H, J = 7.6 Hz, ArH(Ph)), 5.45 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 4.11 (s, 3H, Me), 3.64 (m, 4H, THF), 3.40 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 4H, THF), 1.20 (s, 36H, Bu^t) overlapping with 1.20 (m, 3H, pentane), 0.80 (m, 3H, pentane). ^{13}C NMR (py-d_5, 298 K, ppm): δ 242.16 (*C*(CH$_3$)Ph).

Synthesis of 6. Acetylferrocene (0.43 g,1.89 mmol) was added in one step to a cold (−40 °C), stirred, green-brown THF (100 mL) solution of **3**·6THF (3.70 g, 1.89 mmol) under an argon atmosphere, leading to a fast change in color. The resulting reddish suspension was allowed to reach room temperature overnight, white **9**·Na(THF)$_4$ (1.65 g, 82%) was filtered off, volatiles were removed in vacuo, and THF (100 mL) was added to the residue. A second crop of **9**·Na(THF)$_4$ (0.2 g, 10%) was filtered off, volatiles were removed in vacuo, the reddish residue was washed with *n*-pentane (30 mL), and **6**·Na(THF)$_3$ was collected as a brick-colored powder (1.77 g, 79%). Anal. Calcd for **6**·Na(THF)$_3$, $C_{68}H_{88}FeNaNbO_7$: C, 68.68; H, 7.46. Found: C, 68.84; H, 7.60. ^{1}H NMR (py-d_5, 298 K, ppm): δ 7.26 (s, 8H, ArH), 5.49 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 4.93 (t, 2H, J = 1.6 Hz, Cp), 4.66 (s, 5H, Cp), 4.31 (t, 2H, J = 1.6 Hz, Cp), 4.15 (s, 3H, Me), 3.64 (m, 12H, THF), 3.41 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 12H, THF), 1.20 (s, 36H, Bu^t). ^{13}C NMR (py-d_5, 298 K, ppm): δ 247.62 (*C*(CH$_3$)Cp$_2$Fe). The C_{4v} symmetry of the ^{1}H NMR spectrum remained unchanged at low temperatures (py-d_5, −35 °C). The product reacts with chlorinated solvents and is poorly soluble in toluene. Crystals suitable for X-ray analysis were grown from a THF/toluene solution.

Synthesis of 7. A THF solution of Ph(PhCH$_2$)CO (0.073 M, 2.93 mmol) was added dropwise to a cold (−40 °C), stirred, green-brown THF (80 mL) solution of **3**·6THF (5.72 g, 2.93 mmol) under an argon atmosphere, producing a rapid change in color. The reaction mixture was allowed to reach room temperature overnight, the argon atmosphere was replaced with N$_2$, white **9**·Na(THF)$_4$ (0.15 g, 6%) was filtered off from the resulting reddish suspension, volatiles were removed in vacuo, and THF (70 mL) was added to the residue. A second crop of **9**·Na(THF)$_4$ (2.6 g, 84%) was filtered off, volatiles were removed in vacuo, the reddish residue was washed with diethyl ether (30 mL), and **7**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ was collected as an orange powder (1.35 g, 40%). Anal. Calcd for **7**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$, $C_{70}H_{91}NaNbO_7$: C, 72.46; H, 7.90. Found: C, 72.28; H, 7.48. ^{1}H NMR (py-d_5, 298 K, ppm): δ 8.32 (d, 2H, J = 7.6 Hz, ArH(Ph)), 8.12 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.33 (t, 2H, J = 7.6 Hz, ArH(Ph)), 7.27 (t, 2H, J = 7.6 Hz, ArH(Ph)) overlapping with 7.24 (s, 8H, ArH), 7.05 (t, 1H, J = 7.6 Hz, ArH(Ph)), 6.68 (t, 1H, J = 7.6 Hz, ArH(Ph)), 6.10 (s, 2H, CH$_2$), 5.48 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 3.64 (m, 6H, THF), 3.39 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$) overlapping with 3.35 (m, 6H, Et$_2$O), 1.60 (m, 6H, THF), 1.19 (s, 36H, Bu^t), 1.11 (m, 9H, Et$_2$O). ^{13}C NMR (py-d_5, 298 K, ppm): δ 247.40 (*C*(CH$_2$Ph)Ph).

Synthesis of 8. A THF solution of cyclopentanone (0.071 M, 2.14 mmol) was added dropwise to a cold (−40 °C), stirred, green-brown THF (100 mL) solution of **3**·6THF (4.28 g, 2.19 mmol) under an argon atmosphere, producing a rapid color change. Stirring at −40 °C was maintained over 12 h, the argon atmosphere was replaced with N$_2$, white **9**·Na(THF)$_4$ (2.0 g, 87.7%) was filtered off from the resulting amber suspension, the filtrate was allowed to reach room temperature, volatiles were removed in vacuo, and THF (60 mL) was added to the residue. A second crop of **9**·Na(THF)$_4$ (0.2 g, 8.8%) was filtered off, volatiles were removed in vacuo, the residue was washed with *n*-pentane (30 mL), and **8**·Na(THF)$_{1.5}$ was collected as a rose-colored powder (1.59 g, 79%). Anal. Calcd for **8**·Na(THF)$_{1.5}$, $C_{55}H_{72}NaNbO_{5.5}$: C, 70.50; H, 7.75. Found: C, 70.52; H, 7.77. ^{1}H NMR (py-d_5, 298 K, ppm): δ 7.23 (s, 8H, ArH),5.43 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 4.91 (m, 4H, CH$_2$), 3.64 (m, 6H, THF), 3.37 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 6H, THF), 1.50 (m, 4H, CH$_2$), 1.19 (s, 36H, Bu^t). ^{13}C NMR (py-d_5, 298 K, ppm): δ 262.24 (*C*(CH$_2$)$_4$).

Synthesis of 9. A THF (100 mL) solution of **3**·6THF (5.77 g, 5.91 mmol), prepared under an argon atmosphere in a 250-mL flask, was saturated with dry O$_2$, yielding immediately a yellow suspension. O$_2$ was replaced with N$_2$, and the solvent was evaporated to 50 mL. A yellowish powder was collected and washed with THF (3 × 10 mL), yielding white **9**·Na(THF)$_4$ (3.22 g, 51%). Anal. Calcd for **9**·Na(THF)$_4$, $C_{60}H_{84}NaNbO_9$: C, 67.65; H, 7.95. Found: C, 67.69; H, 8.32. ^{1}H NMR (C$_6$D$_6$, 298 K, ppm): δ 7.10 (s, 8H, ArH), 5.05 (d, J = 12.2 Hz, 4H, *endo*-CH$_2$), 3.66 (m, 16H, THF), 3.38 (d, J = 12.2 Hz, 4H, *exo*-CH$_2$), 1.38 (m, 16H, THF), 1.11 (s, 36H, Bu^t). ^{1}H NMR (py-d_5, 298 K, ppm): δ 7.27 (s, 8H, ArH), 5.25 (d, J = 11.7 Hz, 4H, *endo*-CH$_2$), 3.64 (m, 16H, THF), 3.38 (d, J = 11.7 Hz, 4H, *exo*-CH$_2$), 1.59 (m, 16H, THF), 1.20 (s, 36H, Bu^t). Crystals suitable for X-ray analysis were grown in a room-temperature supersaturated THF solution.

Synthesis of 10. A THF solution of butyraldehyde (0.070 M, 2.11 mmol) was added dropwise to a cold (−20 °C), stirred, green-brown THF (100 mL) solution of **3**·6THF (4.21 g, 2.16 mmol) under an argon atmosphere. The reaction mixture was allowed to reach room temperature while it was being stirred overnight. The argon atmosphere was replaced with N$_2$, a brownish mixture (0.5 g) of **9**·Na(THF)$_4$ and **10**·Na(THF)$_3$ in a 1:1 ratio (^{1}H NMR analysis (py-d_5)) was filtered off from the resulting amber suspension, volatiles were removed in vacuo, and THF (60 mL) was added to the residue. A few milligrams of a brownish solid were filtered off, volatiles were removed in vacuo, the residue was washed with *n*-pentane (30 mL), and a mechanic mixture of **10**·Na(THF)$_3$ and **9**·Na(THF)$_4$ was collected as a brownish powder (1.89 g). ^{1}H NMR of **10**·Na(THF)$_3$ (py-d_5, 298 K, ppm): δ 10.95 (t, 1H, J = 7.1 Hz, C*H*), 7.23 (s, 8H, ArH), 5.38 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 3.79 (q, 2H, J = 7.1 Hz, C*H*$_2$), 3.64 (m, 12H, THF), 3.35 (d, 4.5H, J = 11.6 Hz, *exo*-CH$_2$), 1.96 (sextet, 2H, J = 7.1 Hz, CH$_2$), 1.60 (m, 12H, THF), 1.18 (s, 40.5H, Bu^t), 0.80 (t, 3H, J = 7.1 Hz, C*H*$_3$). ^{13}C NMR (py-d_5, 298 K, ppm): δ 239.00 (*C*H). Any attempt to separate **9**·Na(THF)$_4$ from **10** by crystallization failed.

Synthesis of 11. A THF solution of PhCHO (0.126 M, 5.02 mmol) was added dropwise to a cold (−40 °C), stirred, green-brown THF (100 mL) solution of **3**·6THF (9.79 g, 5.01 mmol) under an argon atmosphere, producing a rapid color change. Stirring at −40 °C was maintained over 12 h, and then the argon atmosphere was replaced with N$_2$. White **9**·Na(THF)$_4$ (2.5 g, 46%) was filtered off from the resulting amber suspension, the filtrate was allowed to reach room temperature, volatiles were removed in vacuo, and THF (100 mL) was added to the residue. A second crop of **9**·Na(THF)$_4$ (1.9 g, 36%) was filtered off, volatiles were removed in vacuo, the residue was washed with diethyl ether (50 mL), and **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ was collected as a light brown powder (2.60 g, 49%). Anal. Calcd for **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$, $C_{63}H_{85}NaNbO_7$: C, 70.70; H, 8.01. Found: C, 70.53; H, 7.81. ^{1}H NMR (py-d_5, 298 K, ppm): δ 11.51 (s, 1H, C*H*), 7.69 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.28 (t, 2H, J = 7.6 Hz, ArH(Ph)) overlapping with 7.26 (s, 8H, ArH), 6.76 (t, 1H, J = 7.6 Hz, ArH(Ph)), 5.41 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 3.64 (m, 6H, THF), 3.39 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$) overlapping with 3.34 (m, 6H, Et$_2$O), 1.60 (m, 6H, THF), 1.19 (s, 36H, Bu^t), 1.11 (m, 9H, Et$_2$O). ^{13}C NMR (py-d_5, 298 K, ppm): δ 228.85 (J = 126 Hz, *C*HPh). The C_{4v} symmetry of the ^{1}H NMR spectrum remained unchanged at low temperatures (py-d_5, −35 °C).

The product reacts with chlorinated solvents and is poorly soluble in toluene. The product is very soluble in pyridine and THF and poorly soluble in hydrocarbons, Et_2O, and DME. Crystals suitable for X-ray analysis were obtained from a THF/diglyme solution at −23 °C and isolated as **11**·Na(Digly)$_2$·THF. The product is thermally stable, as judged by ^{1}H NMR analysis (py-d_5); solutions are stable to solar light.

Protonation of 11. PyHCl (0.18 g, 1.81 mmol) was added in one step to a stirred THF (100 mL) solution of **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ (1.94 g, 1.81 mmol). The resulting reddish suspension was extracted with mother liquors, volatiles were removed in vacuo, the light yellow residue was washed with diethyl ether (30 mL), and **12** 0.5THF·1.5Et$_2$O was collected as a yellow powder (1.31 g, 74%). Anal. Calcd for **12** 0.5THF·1.5Et$_2$O, $C_{59}H_{78}NbO_6$: C, 72.27; H, 7.66. Found: C, 72.41; H, 7.79. ^{1}H NMR (C_6D_6, 298 K, ppm): δ 7.50 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.22 (t, 2H, J = 7.6 Hz, ArH(Ph)), 7.04 (s, 8H, ArH), 6.95 (t, 1H, J = 7.6 Hz, ArH(Ph)), 4.94 (d, 4H, J = 12.0 Hz, *endo*-CH$_2$), 3.86 (s, 2H, C*H*$_2$), 3.55 (m, 2H, THF), 3.28 (d, 4H, J = 12.0 Hz, *exo*-CH$_2$) overlapping with 3.26 (m, 6H, Et$_2$O), 1.39 (m, 2H, THF), 1.11 (m, 9H, Et$_2$O) overlapping with 1.09 (s, 36H, Bu^t).

Synthesis of 12 from 1. A THF solution of [Mg(CH$_2$Ph)$_2$] (0.51 M, 6.12 mmol) was added dropwise to a benzene (200 mL) solution of **1**·2.6C$_7$H$_8$ (10.88 g, 6.09 mmol). The resulting red suspension was refluxed for 3 h, yielding a turbid brownish solution. To this was added dioxane (1 mL), volatiles were removed in vacuo, and the residue was extracted with benzene (150 mL) overnight. Volatiles were removed in vacuo, the residue was washed with diethyl ether (60 mL), and **12**·(Et$_2$O)$_{1.5}$ was collected as a scarlet microcrystalline powder (6.09 g, 53%). Anal. Calcd for **12**·(Et$_2$O)$_{1.5}$, $C_{57}H_{74}NbO_{5.5}$: C, 72.82; H, 7.93. Found: C, 72.79; H, 7.69. ^{1}H NMR (C_6D_6, 298 K, ppm): δ 7.51 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.22 (t, 2H, J = 7.6 Hz, ArH(Ph)), 7.05 (s, 8H, ArH), 6.96 (t, 2H, J = 7.6 Hz, ArH(Ph)), 4.94 (d, 4H, J = 12.0 Hz, *endo*-CH$_2$), 3.86 (s, 2H, C*H*$_2$), 3.28 (d, 4H, J = 12.0 Hz, *exo*-CH$_2$) overlapping with 3.26 (m, 6H, Et$_2$O), 1.11 (m, 9H, Et$_2$O) overlapping with 1.10 (s, 36H, Bu^t). The product is thermally stable in solution, as judged by ^{1}H NMR (C_6D_6) analysis.

Synthesis of 11 from 1. A THF solution of [Mg(CH$_2$Ph)$_2$] (0.48 M, 3.6 mmol) was added dropwise to a red THF (100 mL) suspension of **1**·2.6(C$_7$H$_8$) (3.2 g, 1.8 mmol). The reaction mixture was refluxed for 4 h, yielding a turbid brownish suspension, and to it was added dioxane (1 mL). Volatiles were removed in vacuo, and the residue was extracted with THF (125 mL) overnight. Volatiles were removed in vacuo, the residue was washed with *n*-pentane (40 mL), and **11**·(Mg)$_{0.5}$(THF)$_{1.5}$ was collected as a brownish powder (1.2 g, 35%). Anal. Calcd for **11**·(Mg)$_{0.5}$(THF)$_{1.5}$, $C_{57}H_{70}Mg_{0.5}NbO_{5.5}$: C, 72.20; H, 7.44. Found: C, 72.40; H, 7.63. ^{1}H NMR (py-d_5, 298 K, ppm): δ 11.36 (s, 1H, C*H*), 7.65 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.28 (t, 2H, J = 7.6 Hz, ArH(Ph)) overlapping with 7.26 (s, 8H, ArH), 6.69 (t, 1H, J = 7.6 Hz, ArH(Ph)), 5.41 (d, 4H, J = 11.6 Hz, *endo*-CH$_2$), 3.64 (m, 6H, THF), 3.39 (d, 4H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 6H, THF), 1.19 (s, 36H, Bu^t). ^{13}C NMR (py-d_5, 298 K, ppm): δ 228.41 (*C*HPh).

Deprotonation of 12 to 11. A THF solution of sodium naphthalenide (0.40 M, 2.32 mmol) was added dropwise to a cold (−40 °C), stirred THF (100 mL) solution of **12**·(Et$_2$O)$_{1.5}$ (2.17 g, 2.31 mmol). The reaction mixture was allowed to reach room temperature while being stirred overnight, the resulting turbid reddish solution was filtered, volatiles were removed, the product was dried in vacuo at 40 °C for 4 h, the residue was washed with diethyl ether (30 mL), and **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ was collected as a light brown powder (0.51 g, 21%). Anal. Calcd for **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ $C_{63}H_{85}NaNbO_7$: C, 70.70; H, 8.01. Found: C, 69.27; H, 7.22. The ^{1}H NMR spectrum was identical to that reported for the synthesis of **11**.

Synthesis of 13. A THF solution of sodium naphthalenide (0.31 M, 3.60 mmol) was added dropwise to a cold (−40 °C), stirred THF (100 mL) solution of **11**·Na(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ (3.85 g, 3.60 mmol). The reaction mixture was allowed to reach room temperature while being stirred overnight, the resulting turbid reddish solution was filtered, volatiles were removed, the product was dried in vacuo at 40 °C for 4 h, the residue was washed with *n*-pentane (30 mL), and **13**·Na$_4$(THF)$_3$·C$_5$H$_{12}$ was collected as a light brown powder (1.73 g, 47%). Anal. Calcd for **13**·Na(THF)$_3$·C$_5$H$_{12}$ $C_{119}H_{150}Na_4Nb_2O_{11}$: C, 70.26; H, 7.42. Found: C, 70.30; H, 7.02. ^{1}H NMR (py-d_5, 298 K, ppm): δ 7.13 (s, 16H, ArH), 7.09 (d, 4H, J = 7.2 Hz, ArH(Ph)), 6.66 (t, 4H, J = 7.2 Hz, ArH(Ph)), 6.42 (t, 2H, J = 7.2 Hz, ArH(Ph)), 5.34 (d, 8H, J = 11.6 Hz, *endo*-CH$_2$), 3.64 (m, 12H, THF), 3.16 (d, 8H, J = 11.6 Hz, *exo*-CH$_2$), 1.60 (m, 12H, THF), 1.20 (s, 36H, Bu^t) overlapping with 1.20 (m, 6H, pentane), 0.80 (m, 6H, pentane). ^{13}C NMR (py-d_5, 298 K, ppm): δ 241.22 (*C*HPh). The C_{4v} symmetry of the ^{1}H NMR spectrum remained unchanged at low temperatures (py-d_5, −35 °C). The product reacts with chlorinated solvents and is poorly soluble in toluene. The product is thermally stable, as judged by ^{1}H NMR analysis (py-d_5); solutions are stable to solar light. It is extremely soluble in THF (about 200 mg/mL), soluble in pyridine, and slightly soluble in hydrocarbons and Et_2O. Crystals suitable for X-ray analysis were grown in a supersaturated Et_2O solution at room temperature and obtained as **13**·Na$_4$(Et$_2$O)$_4$.

Protonation of 13 to 11. PyHCl (0.117 g, 1.15 mmol) was added to a stirred THF (100 mL) solution of **13**·Na$_4$(THF)$_3$·C$_5$H$_{12}$ (1.15 g, 0.57 mmol). The resulting reddish suspension was filtered, volatiles were removed in vacuo, the light brown residue was washed with diethyl ether (30 mL), and **11**·Na$_4$(THF)$_{1.5}$(Et$_2$O)$_{1.5}$ was collected as an orange powder (0.55 g, 45%). Anal. Calcd for **11**·Na$_4$(THF)$_{1.5}$(Et$_2$O)$_{1.5}$, $C_{63}H_{85}NaNbO_7$: C, 70.70; H, 8.01. Found: C, 70.20; H, 7.78. The ^{1}H NMR spectrum was identical to that reported in the synthesis of **11**.

Synthesis of 11 from the Reaction of 13 with 12. 13·Na$_4$(THF)$_3$·C$_5$H$_{12}$ (0.57 g, 0.28 mmol) was added in one step to a pyridine (60 mL) solution of **12**·(Et$_2$O)$_{1.5}$ (0.53 g, 0.56 mmol), and the resulting turbid reddish solution was maintained under stirring overnight. Volatiles were removed in vacuo, and the residue was washed with *n*-pentane (30 mL). **11**·(py)$_{1.5}$ was isolated as a light brown powder (0.55 g, 51%). Anal. Calcd for **11**·(py)$_{1.5}$, $C_{58.5}H_{65.5}N_{1.5}NaNbO_4$: C, 72.47; H, 6.81; N, 2.17. Found: C, 72.03; H, 6.89; N, 2.44. The ^{1}H NMR spectrum was identical to that reported for the synthesis of **11**.

Reaction of 4 with PhCHO. PhCHO (0.074 g, 0.702 mmol) was added to a THF (100 mL) solution of **4**·Na(THF)$_3$ (0.803 g, 0.702 mmol). Stirring was maintained over 12 h, yielding a yellow suspension. Volatiles were removed in vacuo, the whitish residue was washed with *n*-pentane (30 mL), and **9**·Na(THF)$_4$ was collected as a yellow powder (0.69 g, 92%). GC−MS analysis of mother liquors revealed triphenylethylene as the major organic product present in solution.

Reaction of 3 with PhCHO, Followed by Ph$_2$CO. A THF solution of PhCHO (0.030 M, 1.48 mmol) was added dropwise to a cold (−40 °C), stirred THF (80 mL) solution of **3**·6THF (2.81 g, 2.88 mmol) under an argon atmosphere. The solution was allowed to reach room temperature overnight, Ph_2CO (0.262 g, 1.44 mmol) was added, and stirring was maintained over 3 h, yielding a yellow suspension. Volatiles were removed in vacuo, the whitish residue was washed with *n*-pentane (30 mL), and **9**·Na(THF)$_4$ was collected as a yellow powder (2.75 g, 92%). GC−MS analysis of mother liquors revealed triphenylethylene as the major organic product present in solution.

Synthesis of 14. A THF solution of Bu^{t}NC (0.048 M, 1.93 mmol) was added dropwise to a cold (−25 °C), stirred THF (70 mL) solution of **3**·6THF (3.77 g, 1.93 mmol) under an argon atmosphere. The resulting blue-violet suspension was maintained under stirring at −25 °C over 12 h. It was filtered, the argon atmosphere was replaced with N_2, and the suspension was allowed to reach room temperature. Volatiles were removed in vacuo, the violet residue was washed with *n*-pentane (40 mL), and **14**·Na$_2$(THF)$_6$·C$_5$H$_{12}$ was collected as a blue-velvet powder (2.39 g, 59%). Anal. Calcd for **14**·Na$_2$(THF)$_6$,·C$_5$H$_{12}$ $C_{122}H_{173}NNa_2Nb_2O_{14}$: C, 69.46; H, 8.27; N; 0.66. Found: C, 69.67; H, 8.02; N, 0.61. The product is slightly soluble in Et_2O and quite soluble in THF, DME, and toluene. Crystals were grown in a DME solution at 6 °C. Solutions of **14** in C_6D_6, py-d_5, CD_2Cl_2, and toluene-d_8 gave ^{1}H NMR spectra with extremely broad signals, even at low temperatures. IR spectra showed no absorption between 3000 and 1700 cm^{-1}.

Synthesis of 15. 2,6-Dimethylphenyl isocyanide (0.21 g, 1.60 mmol) was added in one step to a THF (100 mL) solution of **3**·6THF (3.12 g, 1.60 mmol) under an argon atmosphere. The resulting violet solution was maintained under stirring over 12 h, the argon atmosphere was replaced with N_2, the solution was filtered, volatiles were removed in vacuo, and the brown residue was treated with *n*-hexane (40 mL) and

Table 1. Crystal Data and Details of the Structure Determination for **6**, **9**, **11**, **13**, **15**, and **16**

	6	**9**	**11**	**13**	**15**	**16**
formula	$C_{68}H_{88}FeNaNbO_7 \cdot 0.5C_7H_8$	$C_{60}H_{84}NaNbO_9$	$C_{51}H_{58}NbO_4 \cdot C_{12}H_{28}NaO_6 \cdot C_4H_8O$	$C_{118}H_{154}Na_4Nb_2O_{12}$	$C_{105}H_{133}NNa_2Nb_2O_{12} \cdot 3C_7H_8$	$C_{63}H_{79}N_3NaNbO_4 \cdot 3C_7H_8$
a, Å	21.358(7)	12.837(2)	12.284(4)	11.7635(9)	19.643(4)	12.6102(8)
b, Å	22.496(3)	12.837(2)	12.877(4)	13.7937(7)	18.881(4)	13.8468(11)
c, Å	26.613(10)	19.373(3)	21.036(3)	18.3594(13)	32.665(7)	23.0656(18)
α, deg	90	90	103.74(2)	106.675(5)	90	102.801(7)
β, deg	90	90	93.82(2)	92.169(6)	102.62(3)	102.485(6)
γ, deg	90	90	90.23(2)	91.520(5)	90	97.101(6)
V, Å^3	12787(7)	3192.4(9)	3224.3(15)	2849.5(3)	11822(4)	3771.8(5)
Z	8	2	2	1	4	2
formula wt	1235.20	1065.17	1191.32	2042.19	2109.33	1334.59
space group	*Pbca*	*P*4/*n*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
t, K	143	296	143	143	296	143
λ, Å	0.71070	1.54178	0.71070	0.71073	0.71070	0.71073
ρ_{calc}, g cm^{-3}	1.283	1.108	1.227	1.190	1.185	1.175
μ, cm^{-1}	4.66	19.81	2.50	2.73	2.59	2.16
no. of measd reflctns	70 888	5894	22 868	19 409	71 859	22 880
no. of unique reflctns	11 412 (R_{int} = 0.0752)	2844 (R_{int} = 0.0542)	11 709 (R_{int} = 0.0294)	9944 (R_{int} = 0.0379)	19 617 (R_{int} = 0.1006)	11 382 (R_{int} = 0.0462)
no. of unique reflctns [$I > 2\sigma(I)$]	7704	2038	9944	7777	10 087	8625
data/params	11 412/778	2844/164	11 709/760	9944/714	19 617/1265	11 382/878
R^a [$I > 2\sigma(I)$]	R = 0.0434, $wR2$ = 0.1056	R = 0.0843, $wR2$ = 0.2356	R = 0.0405, $wR2$ = 0.1105	R = 0.0584, $wR2$ = 0.1453	R = 0.0634, $wR2$ = 0.1469	R = 0.0571, $wR2$ = 0.1206
R^a (all data)	R = 0.0736, $wR2$ = 0.1210	R = 0.1122, $wR2$ = 0.2621	R = 0.0491, $wR2$ = 0.1180	R = 0.0840, $wR2$ = 0.1728	R = 0.1287, $wR2$ = 0.1786	R = 0.0864, $wR2$ = 0.1447
GoF	0.966	1.071	1.072	1.088	0.894	1.083

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

stored at −23 °C for 12 h. **15**·Na(THF)$_6$·C_6H_{14} was collected as a scarlet powder (1.28 g, 37%). Anal. Calcd for **15**·Na(THF)$_6$·C_6H_{14}, $C_{127}H_{175}NNa_2Nb_2O_{14}$: C, 70.24; H, 8.12; N, 0.65. Found: C, 70.60; H, 7.87; N, 0.70. The product is slightly soluble in Et_2O and soluble in THF, DME, and toluene. Crystals suitable for X-ray analysis were grown in a toluene/DME solution at 6 °C and obtained as **15**·$Na_2(DME)_2 \cdot 3C_7H_8$. Solutions of **15** in C_6D_6, py-d_5, CD_2Cl_2, and toluene-d_8 gave ^{1}H NMR spectra with extremely broad signals, even at low temperatures. IR spectra showed no absorption between 3000 and 1700 cm^{-1}.

Synthesis of 16. PhCH═NPh (0.546 g, 3.01 mmol) was added, under an argon atmosphere, to a dark green THF (100 mL) solution of **3**·6THF (2.91 g, 1.49 mmol), and the reaction mixture was stirred at room temperature for 12 h, yielding a dark amber solution with a gray precipitate. Argon was replaced with N_2, and the reaction mixture was stirred for 6 h. Volatiles were then removed in vacuo, and *n*-hexane (30 mL) was added to the yellow residue. **16**·Na(THF)$_3$ was collected and dried in vacuo as a yellow powder (2.43 g, 66%). Anal. Calcd for **16**·Na(THF)$_3$ $C_{69}H_{87}NNaNbO_7$: C, 71.55; H, 7.57; N, 1.21. Found: C, 71.88; H, 8.07; N, 1.23. ^{1}H NMR (C_6D_6, 298 K, ppm): δ 7.83 (br, 5H, Ph), 7.31 (br, 5H, Ph), 7.05 (s, 8H, ArH), 4.60 (br, 4H, *endo*-CH_2), 4.37 (bs, 1H, HC═N), 3.41 (m, 12H, THF), 3.20 (br, 4H, *exo*-CH_2), 1.34 (m, 12H, THF), 1.17 (bs, 36H, Bu^t). ^{1}H NMR (TDF, 298 K, ppm): δ 7.88 (d, 2H, J = 7.6 Hz, ArH(Ph)), 7.26 (d, 2H, J = 7.2 Hz, ArH(Ph)), 7.13 (t, 2H, J = 7.6 Hz, ArH(Ph)), 7.01 (t, 2H, J = 7.2 Hz, ArH(Ph)), 6.90 (s, 8H, ArH), 6.68 (t, 2H, J = 7.6 Hz, ArH(Ph)), 6.62 (t, 2H, J = 7.2 Hz, ArH(Ph)), 4.54 (d, 4H, J = 11.6 Hz, *endo*-CH_2), 3.90 (s, 1H, *H*C═N), 3.61 (m, 12H, THF), 2.89 (d, 4H, J = 11.6 Hz, *exo*-CH_2), 1.77 (m, 12H, THF), 1.16 (s, 36H, Bu^t). The C_{4v} symmetry of the ^{1}H NMR spectrum remained unchanged at low temperatures (TDF, −90 °C). When the reaction was repeated under the same experimental conditions with 1 mol of imine per mole of **3**, ^{1}H NMR (C_5D_5N) analysis of the crude indicated that only half of the moles of **3** were consumed. Complex **16** does not react with **3**, as judged by ^{1}H NMR (C_5D_5N) analysis. Crystals suitable for X-ray analysis were grown in a toluene/TMEDA solution and obtained as **16**·TMEDA·$3C_7H_8$. The product is soluble in THF, benzene, and pyridine; it gives very viscous solutions in toluene in the absence of a coordinating solvent.

X-ray Crystallography for 6, 9, 11, 13, 15, and 16. Suitable crystals of **6**, **9**, **11**, **13**, **15**, and **16** were mounted in glass capillaries and sealed under nitrogen. Data concerning crystals, data collection, and structure refinement are listed in Table 1. Data collection for complexes **6**, **11**, and **15** was performed at 143 K on a mar345 image plate detector. Diffraction data for compounds **13** and **16** were collected at 143 K on a KUMA diffractometer, having a κ geometry, equipped with a CCD area detector. For compound **9**, data collection was carried out using a Rigaku AFC6S four-circle diffractometer at 296 K. Data reduction for **6**, **11**, and **15** was performed with marHKL release 1.9.1,[14] with KM4RED release 1.5.2[15] for **13** and **16** and teXsan for Windows release 1.0.1[16] for **9**. No data set was corrected for absorption. Structure solutions for compound **6**, **9**, **11**, **13**, and **15** were determined with ab initio direct methods,[17] whereas for compound **16** any attempt, using SHELXS and its ab initio direct methods or its heavy atom location by Patterson interpretation,[18] failed; structure determination was eventually obtained using SIR97.[19] All structures were refined using the full-matrix least-squares on F^2, with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$(C) [where a = 1.5 for methyl hydrogens and 1.2 for others, while C is the parent carbon atom]. In some cases, for methyl hydrogens and for hydrogens belonging to solvent molecules, a common isotropic displacement parameter (U_{iso} = 0.08 Å^2) was used. Structure solution (except **16**), refinement, molecular graphics, and geometrical calculations were carried out for all structures with the SHELXTL software package, release 5.1.[20] Final atomic coordinates, thermal and geometrical parameters, and hydrogen coordinates, and further details about structure refinement, are given in the Supporting Information.[21]

(14) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*, *Vol. 276: Macromolecular Crystallography*, *Part A*; Carter, C. W. Jr., Sweet, R. M., Eds.; Academic: New York, 1997; pp 307−326.

(15) Kuma Diffraction Instruments GmbH, PSE-EPFL module 3.4, CH-1015, Lausanne, Switzerland, 1999.

(16) Molecular Structure Corp., a Rigaku company, 3200 Research Forest Dr., The Woodlands, TX 77381-4238, 1997.

(17) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(18) Sheldrick, G. M.; Dauter, Z.; Wilson, K. S.; Hope, H.; Sieker, L. C. *Acta Crystallogr.* **1993**, *D49*, 18.

(19) Cascarano, G.; Altomare, A.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Siliqi, D.; Burla, M. C.; Polidori, G.; Camalli, M. *Acta Crystallogr.* **1996**, *A52*, C79.

(20) Bruker AXS, Inc., Madison, WI 53719, 1997.

(21) See the paragraph at the end of paper regarding Supporting Information.

Results and Discussion

The parent compound **1** has been synthesized from the reaction of $NbCl_5$ and calix[4]arene in toluene solutions.[22] Its stepwise reduction primarily to **2**, and then to **3**, should be carried out under N_2 and then Ar atmosphere, due to the reactivity of **3** with dinitrogen.[10] Complex **3** has been isolated in the ion-pair form shown in Scheme 1, and its structure has been determined.[23]

The reactivity of **3** is particularly pronounced with a variety of organic substrates, thus causing their overall reduction by four electrons. Among them, particularly interesting is the metathesis of the Nb═Nb double bond with the >C═O ketonic functionality, which corresponds to a four-electron reduction of the carbonyl with the C═O complete cleavage. The reaction, thus, proceeds with the formation of the corresponding alkylidenes **4**−**8** and the oxoniobium(V) derivative, **9**. The reaction has some major peculiarities. It is not very sensitive to the substituent at the carbonyl functionality, thus occurring equally well with aromatic, mixed, or aliphatic ketones. The synthetic value of the reaction rests on the easy separation of the alkylidene from the corresponding oxo compound, **9**, thus allowing the introduction of the metal alkylidene functionality, via the presence of a ketonic group in a variety of organic substrates. Although the reaction with ketones usually led to the formation of the metal−oxo compounds and the corresponding olefin from the coupling,[24] in the present case the isolation of the intermediate metal alkylidene was quite easy. The intermediacy of the metal alkylidene in the deoxygenation has been proven (see below). In this context, it has to be mentioned that the four-electron reduction of ketones by a tungsten(II) complex $[WCl_2(PPhMe_2)_4]$, which adds oxidatively to the >C═O double bond, forms mononuclear oxo-alkylidene complexes.[25] The reaction at tungsten has been shown to be a single-site activation, which is not the case in the reaction of Nb═Nb with ketones and aldehydes (see below).

The alkylidenes **4**−**8** occur either in the ion-pair form, with the sodium cation complexed inside the cavity and at the lower rim, or in the separated ion form, with the countercation fully solvated outside the calix[4]arene cavity, depending on the reaction or crystallization solvent. In the presence of the weakly binding THF, the ion-pair form is the preferred one, as has been reported for Nb^V- and Ta^V-calix[4]arene alkoxo derivatives,[21] while, when compounds are formed or recrystallized from solvents such as DME and diglyme, the sodium cation is completely separated from the metal−calix moiety. For sake of clarity, we preferred to display all the niobium alkylidene derivatives in Schemes 1 and 2 in their ion-separated forms. The ^{13}C NMR spectra show the expected chemical shift for the alkylidene carbon. The ^1H NMR spectra reveal a pseudo-C_{4v} symmetry with two doublets for the exo and endo methylene protons and a singlet for the Bu^t substituents. This is due, probably, to the almost free rotation through a very low energy barrier of the alkylidene functionality between the two equivalent positions, expressed by the degenerate d_{xz} and d_{yz} orbitals at the metal, the *z* direction being the Nb═C direction.[8] Lowering the temperature, we did not see any significant change in the ^1H NMR spectra. The structure of the niobium alkylidene functionality is exemplified by the X-ray structure of **6**.

(22) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Commun.* **1997**, 183.

(23) Details of the structure will be reported in a forthcoming publication.

(24) For the reductive cleavage of C−O of ketones, see: Chisholm, M. H.; Folting, C.; Klang, J. A. *Organometallics* **1990**, *9*, 602, 609, and references therein.

(25) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298.

Scheme 2

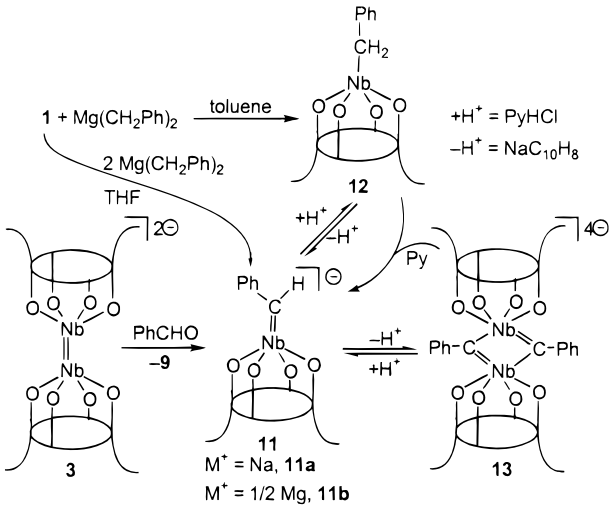
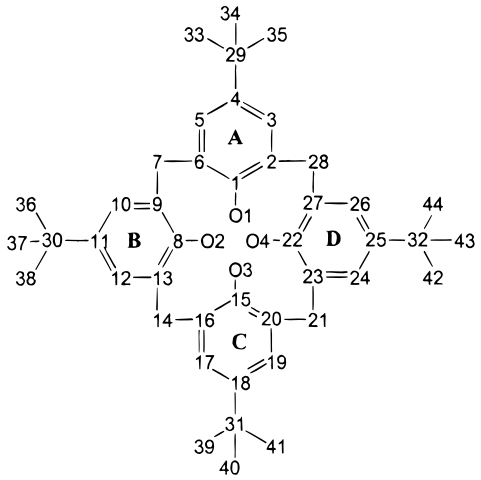


Chart 1



The labeling scheme of the calix[4]arene skeleton is given in Chart 1. In Table 2, the most relevant conformational parameters are quoted. Selected bond distances and angles for complexes **6**, **9**, **11**, **13**, **15**, and **16** are presented in Table 3. The structure of **6** is displayed in Figure 1. It shows the cone conformation (see Table 2) of the calix[4]arene fragment according to the presence of a five-coordinated metal, which has an out-of-O_4-plane of −0.444(1) Å. Two pairs of Nb−O bond distances have been observed, averaging to 1.919(2) and 2.072(2) Å. Such a dissymmetry depends on the fact that one of the d_π orbitals of the metal, either the d_{xz} or the d_{yz}, is engaged by the alkylidene carbon,[8] in particular that perpendicular to the metal−alkylidene plane [Nb1, C45, C46, C47], forming a dihedral angle of 76.9(2)° with the Nb, O1, O3 plane. This finding is in agreement with the shorter Nb−O distance found for Nb1−O2 and Nb1−O4 (Table 3). The Nb═C distance is close to the few reported in the literature.[5] All the other structural parameters, including those related to the ferrocenyl substituent (Table 3), are in the usual range and do not deserve a special comment. The sodium cation is associated to one of the calix[4]arene oxygens and binds three THF molecules. The oxoniobium complex **9** (Figure 2) has an overall geometry quite close to that of the alkylidene complexes **4**−**8**, with a cone conformation for the calix[4]arene moiety (Table 2) and the Nb−O bond of 1.963(4) Å which, according to the 4-fold symmetry of the anion, is close to the average of Nb−O bond distances in niobium alkylidenes **4**−**8** (see Table 3). The Nb═O distance is

Table 2. Comparison of Relevant Conformational Parameters within the Calix[4]arene for **6**, **9**, **11**, **13**, **15**, and **16**

	6	**9**[a]	**11**	**13**	**15**[b]	**19**
			(a) Angles (deg) between Planar Moieties[c]			
E∧**A**	64.98(7)	55.15(13)	60.16(6)	16.02(12)	67.47(14) [48.99(13)]	64.75(10)
E∧**B**	50.56(8)	55.15(13)	50.11(5)	66.51(10)	17.06(21) [65.96(13)]	38.19(12)
E∧**C**	59.83(8)	55.15(13)	62.65(5)	23.24(6)	64.48(13) [49.88(16)]	64.46(11)
E∧**D**	44.50(9)	55.15(13)	49.66(7)	64.75(12)	11.62(23) [63.06(15)]	52.25(9)
A∧**C**	55.21(10)	69.70(16)	57.19(6)	39.26(10)	48.05(17) [81.14(15)]	50.90(12)
B∧**D**	84.94(9)	69.70(16)	80.24(6)	48.74(13)	28.59(24) [50.98(18)]	89.56(11)
			(b) Contact Distances (Å) between p-Carbon Atoms of Opposite Aromatic Rings			
C29···C31	9.378(5)	10.251(17)	9.426(4)	13.367(8)	8.963(10) [11.067(11)]	8.954(6)
C30···C32	11.300(5)	10.251(17)	10.949(5)	8.960(7)	13.615(10) [9.027(12)]	11.579(7)

[a] Such values are due to the fact that compound **9** lies on a 4-fold axis. [b] Values in brackets refer to the second calix[4]arene bonded to Nb2. [c] **E** (reference plane) refers to the least-squares plane defined by the bridging CH_2 [C7, C14, C21, C28]. **A**, **B**, **C**, and **D** refer to the least-squares planes defined by the aromatic rings bonded to O1, O2, O3, and O4, respectively.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **6**, **9**, **11**, **13**, **15**, and **16**

		Complex **6**			
Nb1−O1	2.108(2)	Nb1−O3	2.036(2)	Nb1−C45	1.965(3)
Nb1−O2	1.930(2)	Nb1−O4	1.907(2)	Fe1−η^5(Cp)$_{av}$	1.654(2)
η^5(Cp)−Fe1−^{5}(Cp)[a]	178.3(1)				
		Complex **9**[b]			
Nb1−O1	1.963(4)	Nb1−O1B	1.963(4)	Nb1−O2	1.706(8)
Nb1−O1A	1.963(4)	Nb1−O1C	1.963(4)	Nb1−O2···Na	180
		Complex **11**			
Nb1−O1	2.048(2)	Nb1−O3	2.044(2)	Nb1−C45	1.954(2)
Nb1−O2	1.925(2)	Nb1−O4	1.926(2)		
Nb1−O1	2.084(3)	Nb1−O3	2.106(3)	Nb1−C45	1.945(4)
Nb1−O2	2.130(3)	Nb1−O4	2.120(3)	Nb1−C45[c]	2.194(4)
Nb···Nb	2.9477(7)				
		Complex **15**[d]			
Nb1−O1	2.139(3) [1.945(3)]	Nb1−O4	1.988(3) [2.001(3)]	Nb2−N1	2.041(4)
Nb1−O2	2.078(3) [2.171(3)]	Nb1−O6	2.048(3) [2.171(3)]	C89−N1	1.374(6)
Nb1−O3	2.029(3) [1.892(3)]	Nb1−C89	1.958(5) [2.134(5)]	Nb···Nb	3.0469(9)
		Complex **16**			
Nb1−O1	2.110(3)	Nb1−O3	2.043(3)	Nb1−C45	2.210(4)
Nb1−O2	1.912(3)	Nb1−O4	1.926(3)	Nb1−N1	1.963(3)
C45−N1	1.407(5)				

[a] η^5(Cp) indicates the centroid. [b] Compound **9** lies on a crystallographic 4-fold axis. [c] Symmetry operation used to obtain equivalent atoms: $-x$, $-y$, $-z$. [d] Values in brackets refer to the second calix[4]arene connected to Nb2.

close to those of the well-known oxoniobium(V) derivatives,[26] with the metal displaced toward the oxo group by 0.472(4) Å from the O_4 average plane. The location of the sodium cation is rather unusual, being associated with the niobyl oxygen, which in such an anionic form is probably the most basic site.

Aldehydes usually behave differently and in a more complex manner in their reaction with low-valent metals,[25] while, with reactive metal−metal bonds, the presence of the hydrogen at the carbonyl functionality does not induce a different pathway of reactivity.[27] Unlike previous reports in the field, the reaction of **3** with aldehydes (see Schemes 1 and 2), leading to **10** and **11** and the corresponding oxoniobium(V) complex **9**, parallels the reactions with ketones. The structure of **11** has been completely elucidated, including an X-ray analysis on **11a**, which, when recrystallized from diglyme, occurs in the ion-separated form shown in Scheme 2 with $[Na(digly)_2]^+$ as countercation. A picture of the anion is given in Figure 3. The metal is in a quasi-square-pyramidal environment (Table 2), sitting out of the O_4 plane by −0.4486(8) Å. The Nb−O bond distances occur in couples, being two short [average 1.925(2) Å] and two long [average 2.046(2) Å]. This type of C_{2v} symmetry is not revealed in the ^{1}H NMR spectrum, which is rather in agreement with a C_{4v} symmetry, namely with a single

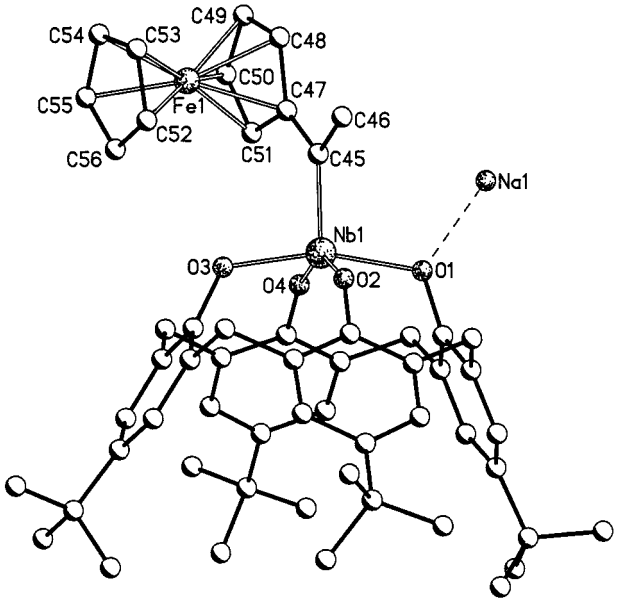


Figure 1. XP drawing of **6**, showing the anion having $Na(THF)_3^+$ as countercation.

(26) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; pp 162−163.

(27) Chisholm, M. H.; Huffman, J. C.; Lucas, E. A.; Sousa, A.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 2710.

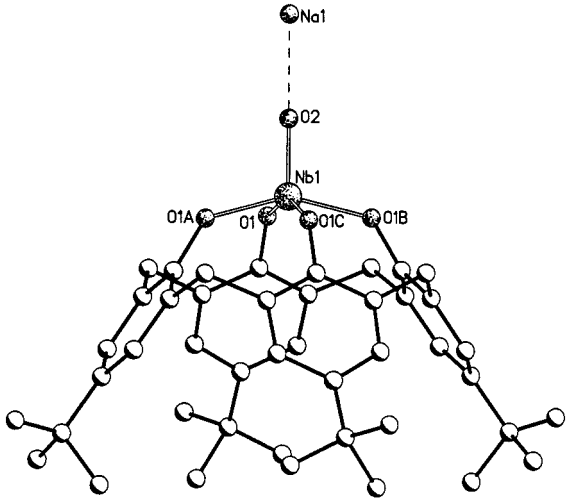


Figure 2. XP drawing of **9**. The letters A, B, and C indicate the following symmetry operation: $-y + {}^1/_2, x, z; y, -x + {}^1/_2, z; -x + {}^1/_2, -y + {}^1/_2, z$.

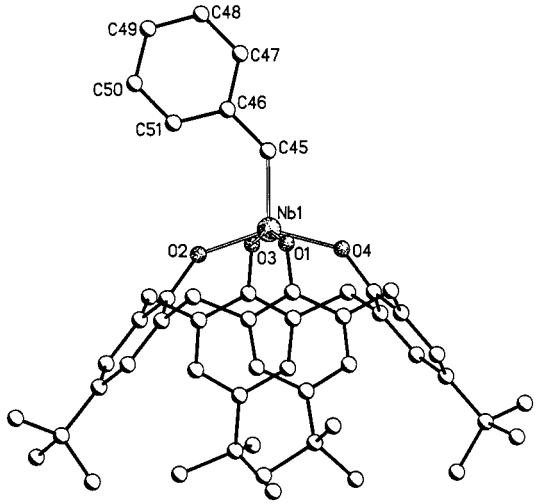


Figure 3. XP drawing of **11**, showing the anion having $Na(diglyme)_2^+$ as countercation.

pair of doublets for the bridging methylenes and a singlet for the Bu^t substituents.[8] We suppose, even in the present case, a very low energy barrier for the rotation of the alkylidene functionality between the two isoenergetic positions for the formation of the metal−C π-bonding. The Nb═C distance is in the range of those of the few niobium alkylidenes reported.[5] One of the peculiarities of the alkylidene or alkylidyne functionality anchored to a metallacalix[4]arene is the occurrence of protonation and deprotonation at the carbon without the metal−ancillary ligand fragment undergoing any change.[8] The protonation of **11** using PyHCl led to the formation of the corresponding benzyl derivative **12**, which was deprotonated back to the alkylidene form using sodium naphthalene. Complex **12** has a monomeric form according to the ^{1}H NMR spectrum in solution, likewise the analogous Ta derivative.[28] The independent synthesis of **12** was performed from the alkylation of **1** using $[Mg(CH_2Ph)_2]$ in benzene. However, when such an alkylation was carried out in THF with 2 equiv of Grignard reagent, the formation of the benzyl derivative was followed by the deprotonation of the benzyl group by the alkylating agent itself, thus forming the alkylidene **11**. In this case, the countercation is magnesium (see the Experimental Section) instead of sodium. Alkylidene **11** underwent, by sodium naphthalenide, the deprotonation to the alkylidyne dimer **13**, which can be quite easily protonated back to **11**. We should emphasize that all the protonations of the alkylidyne carbon in the metallacalix[4]arene chemistry may be assisted by one of the basic oxygens in the metal coordination environment.[8] Such an event is quite similar to oxygen-assisted protonation and deprotonation of alkyl and alkene functionalities supposed to occur on metal−oxo surfaces.[29]

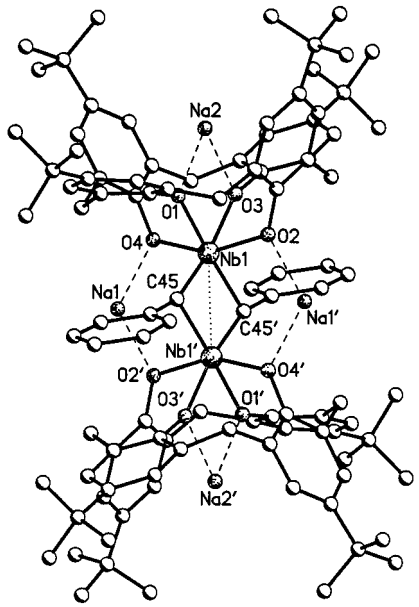


Figure 4. XP drawing of complex **13**. Prime denotes the following symmetry transformation: $-x, y, z$.

An interesting observation in this context is the proton transfer occurring between **12** and **13**, which can be assisted by a quite basic solvent such as pyridine and leads to the formation of **11** (Scheme 2) (see the Experimental Section). Such a finding is diagnostic of the easy protonation−deprotonation of M−C functionalities bonded to a calix[4]arene moiety.[8b,c]

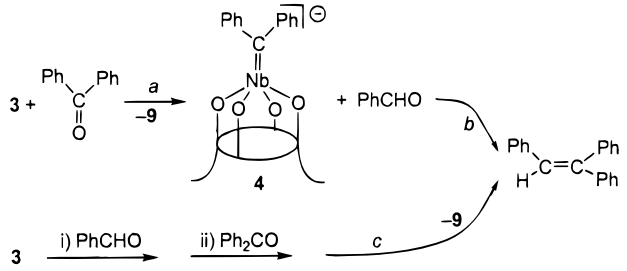
The bridging niobium alkylidyne **13** has precedents in the literature.[7] Complex **13** occurs in a rather tight ion-pair form, with two sodium cations within the calix[4]arene cavities and the other two across the two calix[4]arene O_4 environments. A picture of **13** is given in Figure 4. The hexacoordinated metal led to the elliptical deformation of the calix[4]arene ligand[21,30] (see Table 2). The Nb−O bond distances all became rather similar in length, and in the range where there is no metal−oxygen π-binding interaction, the three more accessible metal orbitals, namely the d_{z^2}, d_{xz}, and d_{yz} being engaged with the binding to the alkylidyne functionality.[8] The structural parameters (see Table 3) support the 1,3-dimetallcyclobutadiene proposed structure, with a quite unexpected and significant difference between the two Nb−C bond distances [Nb═C, 1.945(4) Å vs Nb−C, 2.194(4) Å], unlike that found in a previous structure.[7a] Such a finding rules out any delocalization effect.

(28) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Eur. J.* **1999**, *5*, 722.

(29) (a) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; VCH: Weinheim, Germany, 1997. (b) Gates, B. *Catalytic Chemistry*; Wiley: New York, 1992. (c) *Mechanisms of Reactions of Organometallic Compounds with Surfaces*; Cole-Hamilton, D. J., Williams, J. O., Eds.; Plenum: New York, 1989. (d) Campbell, I. M. *Catalysis at Surfaces*; Chapman & Hall: London, U.K., 1988.

(30) (a) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198. (b) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709.

Scheme 3



The dimetallacyclobutadiene plane [Nb1, C45, Nb1′, C45′] forms a dihedral angle with the O4, Na1, O2′, O2, Na1′, O4′ plane of 85.8(1)°. For both kinds of sodium, Na1 and Na2, solvation is assured by the oxygens outside or inside the cavity and, in the case of Na2, also by the π-interaction with the arene rings of the calix[4]arene.

The synthetic method leading to niobium alkylidenes and niobium alkylidynes was particularly successful, due to a quite remarkable difference in the reaction rate of **3** with ketones or aldehydes, vs the subsequent reaction of the alkylidene with ketones and aldehydes (see Scheme 3). The former reaction takes a few minutes at −40 °C, while the latter one occurs in hours at room temperature. The reaction between an early transition metal alkylidene and a ketone to yield a metal-oxo group and an olefin was first noted by Schrock.[31] The reaction between **4** and benzaldehyde led to triphenylethylene and the niobyl derivative **9**. Due to the difference in rates between reactions a and b in Scheme 3, we found that the sequential addition of two different ketones or aldehydes to a THF solution of **3** produces a nonsymmetric olefin in a stepwise McMurry-type reaction.[12,24] This is exemplified in the coupling shown in reaction c (Scheme 3). The proposed reaction pathway does not involve the intermediacy of a pinacolato ligand and, therefore, differs from the mechanism of the McMurry reaction and related reductive couplings at activated metal sites.[32]

As far as the M═M reactivity is concerned, the reactivity of **3** has very few analogues,[33] the closest one being the $[W_2(OR)_8]$, containing a d^2-d^2 W═W unit.[34] The major difference with the latter, besides the difference in the metal−metal bond energy, lies in the presence, in the case of tungsten, of strong bridging alkoxo groups. In the case of $[W_2(OR)_8]$,[34a] reactions with C_2H_4, CO, and Ph_2CO occurred preferentially at a single metal center rather than at the M═M double bond and led to terminal CO, ethylene, and η^2-ketone derivatives. In contrast with the one for $[W_2(OR)_8]$, the reaction for **3** occurred with two distinctive characteristics, namely the complete cleavage of the M═M bond and the four-electron reduction of the substrate, as was the case for N_2,[10] R_2CO, and RCHO. Those two peculiarities were confirmed by the reaction of **3** with isocyanides (Scheme 4), which additionally provided structural models for the preliminary stage of its reaction with ketones and aldehydes.[24,35] The four-electron reduction of isocyanides led to the dimetalla-imino-alkylidyne dianions **14** and **15** shown in Scheme 4. The reaction occurs with the complete cleavage of the Nb═Nb, the Nb···Nb distance being 3.0469(9) Å in complex **15**.

A picture of the structure of **15** is given in Figure 5. The two niobium ions are bridged by the imino-alkylidyne, and they share O6, giving rise to a nonsymmetric dimer. The two calix[4]arene tetraanions, due to the hexacoordination of the metal, underwent

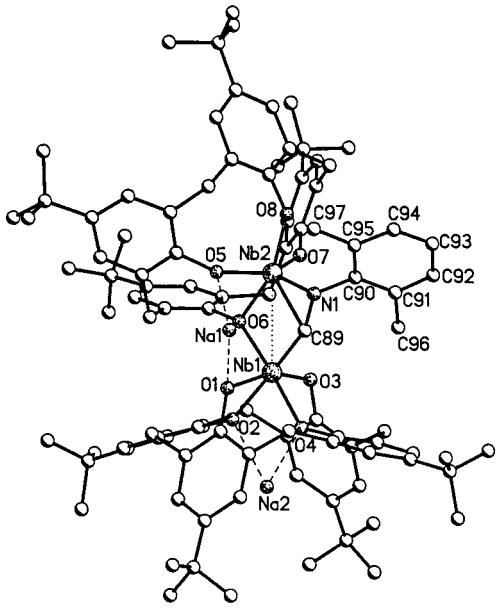
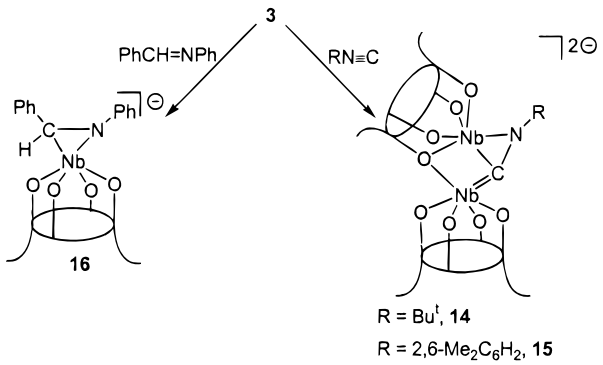


Figure 5. XP drawing of **15**, showing the anion.

Scheme 4



a high distortion from their usual cone conformation, with the Nb−O bond distances varying without any regular trend. The structural parameters (Table 3) support the bridging bonding mode of the imino-alkylidyne [Nb1−C89, 1.958(5) Å; Nb2−C89, 2.134(5) Å; Nb2−N1, 2.041(4) Å; C89−N1, 1.374(6) Å]. Complex **15** occurs in the ion-pair form, with one Na counter-cation inside the cavity and the other one bridging the two metal−calix[4]arene interactions with O1 and O5. The Ph−N═CHPh and R−N≡C functionalities would help in defining, eventually, the preliminary interaction with the Nb═Nb unit, because, unlike in the case of organic carbonyls and carbon monoxide,[24,35] the reaction will not be driven by the oxophilicity of the metal and the presence of alkali cations. The reaction of **3** with PhCH═NPh leads to the formation of the monomeric η^2-imino complex **16**. The overall reaction is a four-electron reduction of two imino groups by a single Nb═Nb unit. The reaction proceeds as shown in Scheme 4, regardless of the imine/

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(35) For the reductive cleavage of CO and its mechanism, reference is made to the pioneering work of Wolczanski and Chisholm: (a) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056. (b) Miller, R. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1993**, *115*, 10422. (c) Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 7056.

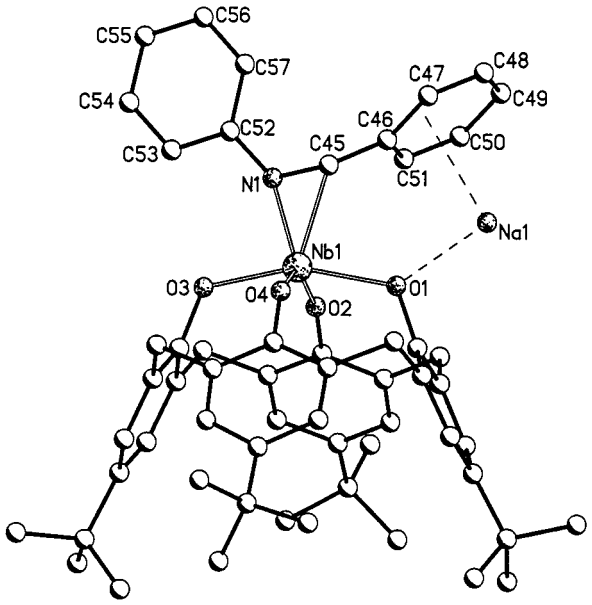
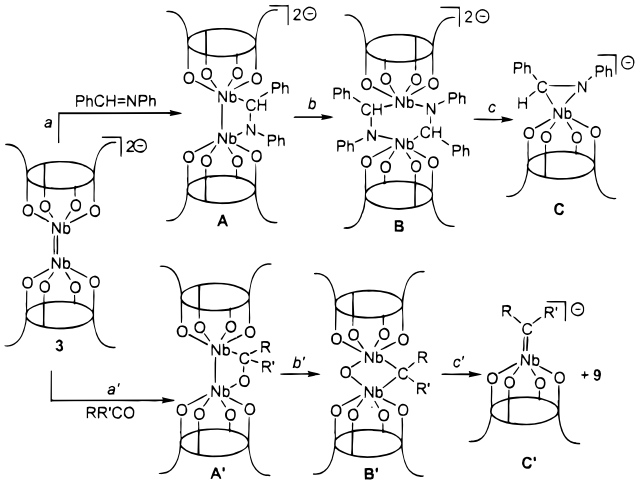


Figure 6. XP drawing of complex **16**.

Nb ratio. In addition, complex **16** does not react with an excess of **3**. The structure of **16** is shown in Figure 6. Although the metal is formally hexacoordinated, the calix[4]arene maintains its cone conformation (Table 2), thus the η^2-imine seeming to account for a monodentate ligand.[30] Complex **16** occurs in a tight ion-pair form, the sodium being solvated by TMEDA, O1 from the calix[4]arene, and by the η^4-bonded phenyl ring [Na1-η^4(C46, C47, C48, C51), 2.653(3) Å]. The Nb−O bond distances occur in pairs, with the two shorter [Nb1−O2 and Nb2−O4] and the two longer [Nb1−O1 and Nb1−O3] averaging to 1.919(3) and 2.076(3) Å, respectively. The Nb-imine parameters reveal a Nb1−N1 distance [1.964(3) Å] much shorter than the corresponding Nb1−C45 [2.210(4) Å] interaction. This unusual Nb−C vs Nb−N dissymmetry is supported by the *wR*2 value and the thermal and structural parameters of the related atoms. The very short Nb−N distance is in agreement with the high affinity of niobium for nitrogen donor atoms in the Nb-calix[4]arene chemistry.[10] The C45−N1 distance [1.407(5) Å] is in agreement with the two-electron reduction of the imine.

The reaction of **3** with the imine PhCH═NPh suggests that the oxophilicity of Nb is, probably, the major factor determining the complete cleavage of the R_2C═O functionality, while in the present case only a two-electron reduction of the substrate is achieved, without the complete cleavage of the C−N bond. Based on the results for ketones and isocyanides, complex **16** is probably not the primary compound forming from the reaction of **3** with the imine. In both cases, we feel that the reactivity occurs at the Nb═Nb bond in a similar manner, as shown in Scheme 5. In the case of ketones, according to Chisholm's hypothesis,[24] we do not believe that the η^2-ketone is an intermediate in the formation of the oxo and alkylidene fragments. The data outlined above are much more in favor of the concerted addition to both metal centers, as shown in Scheme 5. The major difference between the two parallel pathways remains in the steps b and b′. In the former case, the two electrons stored in the remaining Nb−Nb bond are not transferred, thus cleaving

Scheme 5



the N−C bond, and a second molecule of imine adds to it, while in the latter case the oxophilicity of the metal drives the C−O bond cleavage via the transfer of the residual electron to the C−O single bond. The rearrangement of the two dimers **B** and **B′** into the monomeric forms **C** and **C′** is highly favored by the nature of frontier orbitals of the metallacalix[4]arene fragment, particularly adapted to form π-bonds in the metal-to-substrate axial direction.[8]

Conclusions

This paper deals with a synthetic entry to the metal alkylidene and alkylidyne field using the ubiquitous organic ketone and aldehyde functionalities without substituent restrictions. The usefulness of the reaction between complex **3** and ketones/aldehydes rests on (i) the easy separation of the niobium alkylidene from the Nb-oxo species in the case of ketones and (ii) the large reaction rate difference between the reaction of complex **3** and the reaction of niobium alkylidene derivatives with ketones/aldehydes. The latter characteristic of the reaction permits us to perform a stepwise McMurry-type coupling between ketones and/or aldehydes, leading to nonsymmetric olefins. The high inertness of the metallacalix[4]arene fragment allowed us to establish the alkyl ↔ alkylidene ↔ alkylidyne acid−base relationship via a reversible protonation−deprotonation sequence. The four-electron reduction of isocyanides led to a dimetallaimino-alkylidyne and sheds light, along with the reaction with PhCH═NPh, on the mechanism of the ketone/aldehyde deoxygenation reactions.

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Supporting Information Available: Details of the structures refinement; ORTEP drawings; tables giving crystal data and details of the structure determination, atomic coordinates, bond distances, and angles; and anisotropic thermal parameters for **6**, **9**, **11**, **13**, **15**, and **16** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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