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Calix[4]arene supported group 5 imido complexes

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Abstract

The reaction of imidoyl chlorides $[V(NR)Cl_3](R = Ph 1, Tol 2, tBu 3)$ and calix[4]arene methyl ether H₃Mecalix unexpectedly leads to the formation of the structurally characterized vanadium (IV) complex [VCl(Mecalix)](4). Calix[4]arene methyl ether stabilized imido complexes of the type [V(NR)(Mecalix)](R = Ph 7, Tol 8, tBu 9) were afforded from the reaction of $[V(NR)Cl_3](R = Ph 1, Tol 2, tBu 3)$ and the tris(lithium) or tris(sodium) salt of the calix[4]arene ether. The lithium salt $[{Li_3(Mecalix)}_2](5)$ is a dimer in the solid state, in which two monomeric trianions are bridged by lithium cations. Imido complexes $[M(NR)(Mecalix)](M = Nb: R = tBu, 12, R = Tol 13, R = Mes 14, R = Dipp 15; M = Ta: R = tBu 16, R = Tol 17) (Tol = 4-C_6H_4Me, Mes = 2,6-C_6H_3Me_2; Dipp = 2,6-C_6H_3iPr_2)$ have been prepared from structurally characterized $[NbCl_2(Mecalix)](10)$ and previously known $[TaCl_2(Mecalix)](11)$ via reaction with two equivalents of the appropriately metallated (Li, K) primary amine. The molecular structures of 13 and 15 confirm the mononuclear nature of these complexes.

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1. Introduction

Calix[n]arenes are macrocyclic molecules made of n phenol units connected by ortho methylene groups [1,2]. Calix[4]arenes are the simplest and most common members of this family with four phenolic residues in the macrocyclic ring. These molecules and their derivatives have been extensively studied for their interesting properties, e.g. as hosts to cations, anions and neutral molecules, and for the formation of supramolecular assemblies [3]. Because of the four phenoxyl groups in the calix[4]arenes (p-tert butyl-calix[4]arene = H_4 calix, see Scheme 1), reactions with transition metal complexes can produce metal phenolate complexes with substitution of one to four hydrogen atoms [4]. The fully deprotonated form of the parent calix[4]arene acts as tetraanionic ligands and usually assumes the cone conformation in metalla-calix[4]arenes, which keeps the set of the oxygen donor atoms quasi planar. The charge of the O₄ set can be tuned by etherification or esterification of the lower rim of the calix[4]arene, as pointed out in Scheme 1 for methylation products of H_4 calix.

The degree of functionalization of the metal atom can be controlled by alkylation or silvlation of the oxygen atoms, which also offers steric protection. As a consequence, isoelectronic and structurally closely related transition metal complex fragments are available for metals in neighboring groups of the periodic table. Similar compounds of the complex fragments [M(R₂calix)], [M'(Rcalix)], and [M"(calix)] can be synthesized, if the degree of alkylation of the calix[4]arene ligand is decreased and the central atom of the complex is substituted with a metal atom of the next group of the periodic table or the same metal atom in its next higher oxidation state. In the case of calix[4]arene stabilized imido complexes, closely related metal d⁰ imido compounds of the type $[M(NR)(Me_2calix)]$ (M = group 4 metal), [M'(NR)-(Mecalix)] (M' = group 5 metal), and [M''(NR)(calix)] (M" group 6 metal) should be available. In continuation of our studies on calix[4]arene stabilized group 6 [5] and group 4 [6] metal imido complexes, we report here the synthesis of calix[4]arene stabilized group 5 metal imido complexes.

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Scheme 1. Calix[4]arenes and Calix[4]arene-ethers as ancillary poly-(phenolate)ligands.

2. Experimental

2.1. General methods and instrumentation

All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen or argon atmosphere using standard Schlenk techniques as reported previously [5-7]. Elemental analyses were performed in the microanalytical laboratory of the author's department. EI mass spectra were recorded on a Varian MAT 3830 (70 eV). NMR spectra were recorded on a Bruker AC 250 at 298 K if not stated otherwise. ¹³C NMR spectra are broad-band proton decoupled $({}^{13}C{}^{1}H{})$. Standard DEPT-135 experiments were recorded to distinguish -CH₃ and -CH type carbon atoms from -C or -CH₂ type carbon atoms in the ¹³C NMR spectrum; NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Coupling constants are quoted in Hertz. Residual solvent peaks used as internal standards were as follows: CDCl₃: 7.24 ppm (¹H), C₆D₆: 7.15 ppm (^{1}H) or natural-abundance carbon signal at 77.0 ppm for CDCl₃ and 128.0 ppm for C₆D₆. Infrared spectra were recorded as Nujol mulls between KBr plates or as KBr pellets on a Bruker IFS 28 and are reported in cm^{-1} .

Literature preparations. H₄calix [8], H₂Me₂calix [9], $[V(NR)Cl_3]$ (R = Ph 1, Tol 2, *t*Bu 3) [10], and $[TaCl_2Mecalix]$ [11] were prepared according to established methods, all other reagents were purchased from commercial sources and purified by standard techniques.

2.2. Syntheses

2.2.1. Synthesis of H_3 Mecalix

H₃Mecalix was synthesized according to a modified procedure reported by Floriani et al. [12]. A mixture of H₂Me₂calix (15.8 g, 23.4 mmol) and [TiCl₄(THF)₂] (7.80 g, 23.4 mmol) was dissolved in toluene (120 ml) and the resulting dark red solution was refluxed for two days. After cooling to room temperature, a red powder precipitated ([TiCl(Mecalix) [13]) and HCl (10% water solution, 100 ml) was added to the reaction mixture. The suspension was stirred until it was almost colorless and the organic layer was extracted and washed with water (3 portions of 50 ml). The organic phase was dried over Na₂SO₄ and filtered. After removal of all volatile material, the yellowish residue was dissolved in 10 ml CH₂Cl₂ and the colorless

product was precipitated by addition of 50 ml MeOH, filtered off and washed with two portions (20 ml) MeOH and one portion (5 ml) pentane. The product was dried in vacuo to afford H₃Mecalix as a colorless powder. Yield: 11.1 g (72%) colorless powder. C₄₅H₅₈O₄ [663.0]: Calc.: C, 81.53; H, 8.82. Found: C, 81.48; H, 8.78%. EI/MS m/z (%): 663 (100) [M]⁺, 648 (19) [M - CH₃]⁺, 331 (6) $[M]^{2+}$. IR (Nujol $[cm^{-1}]$): 3263 br vs (O-H), 3164 br vs (O-H), 1600 m, 1298 s, 1264 m, 1240 m, 1205 vs, 1123 s, 1104 m, 1007 s, 944 m, 870 s, 818 s, 781 s, 700 m, 674 w, 588 w, 528 w, 464 w. ¹H NMR (C₆D₆): $\delta = 0.91$ (s, 9H, $C(CH_3)_3$, 0.98 (s, 9H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$), 3.34 (d, 2H, ${}^{2}J_{HH} = 12.9$ Hz, CH_{2}), 3.35 (d, 2H, ${}^{2}J_{\text{HH}} = 13.6 \text{ Hz}, \text{ CH}_{2}$), 3.56 (s, 3H, OCH₃), 4.40 (d, 2H, ${}^{2}J_{\text{HH}} = 12.9 \text{ Hz}, CH_{2}, 4.52 \text{ (d, } 2\text{H}, {}^{2}J_{\text{HH}} = 13.6 \text{ Hz},$ CH₂), 6.90 (s, 2H, aryl-H_m), 6.95 (s, 4H, aryl-H_m), 7.09 (s, 2 H, aryl-H_m), 9.71 (s, 2H, OH), 9.95 (s, 1H, OH). ¹³C NMR (C₆D₆): $\delta = 30.94$, 31.25, 31.72 (C(CH₃)₃), 32.50, 33.10 (CH₂), 33.73, 33.97, 34.02 (C(CH₃)₃), 62.91 (OCH₃), 125.68, 125.97, 126.14, 126.56, 128.10, 128.56, 128.61, 133.55, 143.02, 144.02, 147.24, 148.04, 149.53, 150.83 (aryl-C).

2.2.2. Synthesis of [VCl(Mecalix)] (4)

A solution of H_3 Mecalix (1.04 g, 1.56 mmol) and [V(NPh)Cl₃] (389 mg, 1.60 mmol) in toluene (20 ml) was stirred at 65 °C overnight. The reaction mixture was cooled to room temperature and all volatile material was removed in vacuo. The remaining dark brown residue was suspended in hexane (20 ml) and stirred at 65 °C for 1 h. The brown product was filtered off and dried in vacuo. Yield: 1.01 g (87%) brown solid. Single crystals have been obtained by cooling concentrated solutions of the product in benzene/hexane (1:1) to $-40 \,^{\circ}\text{C}$. C₄₅H₅₅O₄VCl [746.32]: Calc.: C, 72.42; H, 7.43. Found: C, 72.22; H, 7.43%. EI/ MS: m/z (%): 745 (100) [M]⁺, 730 (31) [M – CH₃]⁺, 709 (26) $[M - Cl]^+$. UV–Vis: $\lambda_{max} = 395 \text{ nm}, \epsilon_{max} = 714 \text{ L}$ $mol^{-1} cm^{-1}$. IR (Nujol [cm⁻¹]): v = 1972 w, 1430 m, 1310 w, 1296 m, 1257 m, 1193 m, 1164 w, 1081 m, 1006 m, 940 m, 869 m, 796 m, 585 w, 446 w.

2.2.3. Synthesis of $[{Li_3(Mecalix)}_2]$ (5)

A solution of *n*butyl lithium (1.60 m, 5.90 ml, 9.40 mmol) in hexane was slowly added at room temperature to a solution of H₃Mecalix (2.08 g, 3.10 mmol) in tetrahydrofurane (60 ml). The yellowish colored reaction mixture was stirred for 4 h at 65 °C. The resulting solution was cooled to room temperature and all volatile components were removed in vacuo. The colorless residue was suspended in hexane (30 ml), stirred for 1 h and the insoluble colorless product was filtered off and dried in vacuo. Yield: 1.64 g, (66%) colorless powder. Single crystals were obtained from diffusion of hexane into a concentrated solution of **5** in toluene. [{C₄₅H₅₅O₄Li₃}] · C₆H₁₄ · 2C₄H₈O [1591.9]: Calc.: C, 78.47; H, 8.86. Found: C, 78.35; H, 8.74%. EI/MS: m/z (%): 1361 (100) [M]⁺, 1346 (43) [M – CH₃]⁺, 681 (14) [M]²⁺. IR (Nujol [cm⁻¹]): 1728 w,

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1310 vs, 1260 s, 1205 s, 1181 w, 1166 m, 1154 w, 1141 w, 1125 m, 1094 s br, 1041 s, 1024 s, 973 w, 932 w, 910 m, 885 m. 872 s. 825 s. 801 s. 791 s. 748 s. 711 m. 665 w. 613 w, 602 w, 595 m, 565 s, 553 m, 525 m, 499 m, 491 m, 446 m, 419 w. ¹H NMR (CDCl₃, 298 K): $\delta = 0.79$ (s, 9H, C(CH₃)₃), 0.92 (s, 9H, C(CH₃)₃), 1.29 (s, 18H, C(CH₃)₃), 3.18 (d, 2H, ${}^{2}J_{HH} = 14.5$ Hz, CH₂), 3.20 (d, 2H, $^{2}J_{HH} = 13.0$ Hz, CH_{2}), 3.79 (s, 3H, OCH₃), 4.15 (d, 2H, ${}^{2}J_{\rm HH} = 14.5$ Hz, CH_{2} , 3.0 (c, $2J_{\rm HH} = 13.0$ Hz, 2H, 2H, CH₂), 6.62 (s, 2H, aryl-H_m), 6.71 (s, 2 H, aryl-H_m), 7.01, 7.03 (s, 4H, aryl- $H_{\rm m}$). ¹H NMR (d^8 -THF, 353 K): $\delta =$ 0.94 (s, 9H, C(CH₃)₃), 1.01 (s, 9H, C(CH₃)₃), 1.23 (s, 18H, C(CH₃)₃), 3.20–3.24 (br, 4H, CH₂), 3.58 (s, br, 3H, OCH_3 , 4.25–4.45 (br, 4H, CH_2), 6.83 (s, 4H, aryl- H_m), 7.00–7.15 (br, 4H, aryl- $H_{\rm m}$). ¹H NMR (d^{8} -THF, 300 K): species 1: $\delta = 0.97$ (br, C(CH₃)₃), 1.23 (s, C(CH₃)₃), 3.00-3.45 (br, CH₂), 3.55 (s, OCH₃), 4.00-4.75 (br, CH₂), 6.87 (s, aryl- H_m), 6.98 (s, aryl- H_m), 7.18 (s, aryl- H_m); species 2: 1.03 (br, $C(CH_3)_3$), 1.20 (s, $C(CH_3)_3$), 3.00–3.45 (br, CH₂), 3.52 (s, OCH₃), 4.00–4.75 (br, CH₂), 6.87 (s, aryl- $H_{\rm m}$), 6.98 (s, aryl- $H_{\rm m}$), 7.18 (s, aryl- $H_{\rm m}$). ¹H NMR (d^8 -THF, 193 K): species 1: $\delta = 1.03$ (s, C(CH₃)₃), 1.14 (s, $C(CH_3)_3)$, 3.08 (d, ${}^2J_{HH} = 10.6$ Hz, 2H, CH_2), 3.16 (d, $^{2}J_{\text{HH}} = 10.6 \text{ Hz}, 2\text{H}, CH_{2}$, 3.52 (s, OCH₃), 4.35 (d, ${}^{2}J_{\text{HH}} = 10.6 \text{ Hz}, 2\text{H}, CH_{2}), 4.79 \text{ (d, } {}^{2}J_{\text{HH}} = 10.6 \text{ Hz}, 2\text{H},$ CH_2), 6.83 (s, aryl- H_m), 6.94 (s, aryl- H_m). ⁷Li NMR (d^8 -THF, 353 K): $\delta = 0.92$ (br); ⁷Li NMR (d^{8} -THF, 300 K): $\delta = -1.87, 1.57, 2.23$ (all br); ⁷Li NMR (d^8 -THF, 193 K): $\delta = 3.45, 2.45, 2.20, 1.61, 1.22, -2.02$ (all br).

2.2.4. Synthesis of $[\{Na_3(Mecalix)\}_2]$ (6)

A mixture of H₃Mecalix (653 mg, 0.99 mmol) and sodium hydride (71.0 mg, 2.96 mmol) was dissolved in tetrahydrofurane (20 ml) and the reaction mixture was refluxed for 12 h. During this time, a colorless solid precipitated, which was filtered off, washed with tetrahydrofurane (5 ml) and dried in vacuo. Yield: 454 mg (63%) colorless powder. [{C₄₅H₅₅O₄Na₃}₂] (1457.76): Calc.: C, 74.15; H, 7.61. Found: C, 74.27; H, 7.48%. IR (Nujol $[cm^{-1}]$): 1728 w, 1590 m, 1312 vs, 1202 m, 1167 m, 1098 m, 1008 m, 876 m, 822 m, 800 m, 726 s, 720 s, 564 w, 521 w, 488 w, 429 w. ¹H NMR (CDCl₃): $\delta = 0.76$ (s, 9H, C(CH₃)₃), 0.97 (s, 9H, C(CH₃)₃), 1.30 (s, 18H, C(CH₃)₃), 3.10 (d, 2H, ${}^{2}J_{\text{HH}} = 14.5 \text{ Hz}, CH_2$, 3.16 (d, 2H, ${}^{2}J_{\text{HH}} = 13.1 \text{ Hz},$ CH_2), 3.49 (d, 2H, ${}^2J_{HH} = 14.5$ Hz, CH_2), 3.87 (s, 3H, OCH₃), 4.18 (d, 2H, ${}^{2}J_{HH} = 12.9$ Hz, CH₂), 6.48 (s, 2H, aryl-H_m), 6.63 (s, 2H, aryl-H_m), 7.04, 7.06 (s, 4H, aryl-H_m).

2.2.5. Synthesis of [V(NPh)(Mecalix)] (7)

At room temperature, a solution of *n*-butyl lithium (1.60 M, 2.00 ml, 3.14 mmol) in hexane was slowly added to a solution of H₃Mecalix (694 mg, 1.05 mmol) in tetrahydrofurane (20 ml). The slightly yellow colored reaction mixture was stirred at 65 °C for 4 h. After cooling to room temperature, the resulting solution was transferred to a solution of $[V(NPh)Cl_3]$ (260 mg, 1.00 mmol) in tetrahydrofurane (20 ml) and stirred at 70 °C for another 4 h, cooled to room temperature and all volatile components were removed in vacuo. The remaining red-brown solid was suspended in toluene (20 ml) and undissolved components were filtered off through a pad of Celite. The filtrate was evaporated to dryness, the resulting solid was suspended in hexane (20 ml) and the suspension was stirred at 65 °C for 1 h. The product was filtered off and dried in Yield: 422 mg (53%) red-brown powder. vacuo. C₅₁H₆₀O₄NV (801.98): Calc: C, 76.38; H, 7.54; N, 1.75. Found: C, 76.26; H, 7.43; N, 1.44%. EI/MS: m/z (%): 801 $(100) [M]^+$, 786 (41) $[M - CH_3]^+$. IR (Nujol $[cm^{-1}]$): 1588 vw, 1298 m, 1266 m, 1259 m, 1246 m, 1201 m, 1113 m, 1091 m br, 1012 m br, 969 w, 943 w, 914 w, 872 m, 823 m, 797 m, 756 w, 726 w, 690 w, 678 w, 596 w, 583 w, 566 w, 550 w, 486 vw, 461 w, 429 vw, 427 vw. ¹H NMR (C_6D_6): $\delta = 0.78$ (s, 9H, C(CH₃)₃), 0.85 (s, 9H, C(CH₃)₃), 1.43 (s, 18H, C(CH₃)₃), 3.30 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 3.32 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 3.80 (s, 3H, OCH₃), 4.49 $(d, 2H, {}^{2}J_{HH} = 12.6 \text{ Hz}, CH_{2}), 5.03 (d, 2H, {}^{2}J_{HH} = 12.6 \text{ Hz},$ CH₂), 6.65 (t, 1H, ${}^{2}J = 7.41$, aryl-H_{p(Ph)}), 6.87 (m, 4H, 7.8 Hz, aryl- $H_{m(Ph)}$ and aryl- H_m) 6.95 (d, 4H, ${}^{2}J_{\text{HH}} = 10.3$, aryl- $H_{o(\text{Ph})}$ and aryl- H_{m}), 7.27 (s, 2H, aryl-H_m), 7.28 (s, 2H, aryl-H_m). ¹³C NMR (C₆D₆): δ = 31.57, 31.87, 32.76 (C(CH₃)₃), 34.32, 34.53, 34.60 (C(CH₃)₃), 34.75, 35.19 (CH₂), 66.12 (OCH₃), 125.31, 126.02, 126.44, 127.28, 129.58, 130.20, 131.12, 131.41, 133.56, 145.71, 146.92, 149.33, 149.54, 152.25, 159.61, 162.48 (aryl-C).

2.2.6. Synthesis of [V(NTol)(Mecalix)](8)

A procedure identical to that described for the preparation of [V(NPh)(Mecalix)] using $[V(NTol)Cl_3]$ (262 mg, 1.00 mmol) instead of [V(NPh)Cl₃] afforded [V(NTol)-(Mecalix)] as a red-brown powder. Yield: 436 mg (53%). C₅₂H₆₂O₄NV (815.99): Calc.: C, 76.54; H, 7.66; N, 1.72. Found: C, 76.88; H, 7.56; N, 1.58%. EI/MS: m/z (%): 815 (100) $[M]^+$, 800 (55) $[M - CH_3]^+$, 770 (5) $[M - CH_3]^+$ $3CH_3^{+}$. IR (Nujol [cm⁻¹]): 1586 w, 1302 m, 1260 m, 1205 m, 1095 m, 1015 m br, 920 w, 871 w, 799 m, 580 w, 553 vw, 430 vw. ¹H NMR (C₆D₆): $\delta = 0.77$ (s, 9H, C(CH₃)₃), 0.85 (s, 9H, C(CH₃)₃), 1.42 (s, 18H, C(CH₃)₃), 1.96 (s, 3H, CH₃), 3.29 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 3.33 (d, 2H, ${}^{2}J_{\text{HH}} = 12.6 \text{ Hz}, \text{ CH}_{2}$), 3.84 (s, 3H, OCH₃), 4.51 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 5.04 (d, 2H, ${}^{2}J_{HH} =$ 12.6 Hz, CH_2), 6.65 (d, 2H, ${}^2J = 8.1$ Hz, aryl-H_{m(Tol)}), 6.94 (d, 4H, ${}^{2}J = 9.5$ Hz, aryl-H_{o(Tol)} and aryl-H_m), 7.27 (s, 2H, aryl- $H_{\rm m}$), 7.28 (s, 4H, aryl- $H_{\rm m}$). ¹³C NMR $(C_6D_6): \delta = 31.57, 31.87, 32.77 (C(CH_3)_3), 34.51, 34.59,$ 34.71 (C(CH₃)₃), 34.79, 35.17 (CH₂), 66.03 (OCH₃), 125.27, 126.16, 126.41, 127.24, 130.08, 131.08, 131.47, 133.59, 139.17, 145.55, 146.74, 149.29, 152.27, 159.60, 162.39, 166.52 (aryl-C).

2.2.7. Synthesis of [V(Mecalix)(NtBu)] (9)

A procedure identical to that described for the preparation of [V(NPh)(Mecalix)] using $[V(NtBu)Cl_3]$ (228 mg, 1.00 mmol) instead of $[V(NPh)Cl_3]$ afforded [V(NtBu)-(Mecalix)] as a red-brown powder. Yield: 835 mg (92%). C₄₉H₆₄O₄NV (781.99): Calc.: C, 75.26; H, 8.25; N, 1.79. Found: C, 75.20; H, 8.10; N, 1.57%. EI/MS: m/z (%): 781 (100) $[M]^+$, 766 (29) $[M - CH_3]^+$, 710 (16) $[M - NC(CH_3)_3]^+$. IR (Nujol $[cm^{-1}]$): 1600 w, 1307 m, 1260 m, 1203 s, 1095 br m, 1014 br m, 919 w, 872 m, 798 m, 678 vw, 567 w, 428 vw. ¹H NMR (C_6D_6): $\delta = 0.77$ $(s, 9H, C(CH_3)_3), 0.84 (s, 9H, C(CH_3)_3), 1.41 (s, 18H, 18H)$ $C(CH_3)_3)$, 1.45 (s, 9H, (NC(CH_3)_3)), 3.26 (d, 2H, ${}^2J_{HH} = 12.6$ Hz, CH_2), 3.35 (d, 2H, ${}^2J_{HH} = 12.6$ Hz, CH_2), 3.96 (s, 3H, OCH₃), 4.46 (d, 2H, ${}^2J_{HH} = 12.6$ Hz, CH_2), 4.90 (d, 2H, ${}^2J_{HH} = 12.6$ Hz, CH_2), 6.93 (s, 4H, aryl- $H_{\rm m}$), 7.25 (s, 4H, aryl- $H_{\rm m}$). ¹³C NMR (C₆D₆): $\delta = 31.07$ (NC(*C*H₃)₃), 31.58, 31.89, 32.77 (C(*C*H₃)₃), 34.48, 34.61, 34.71 (C(CH₃)₃), 34.78, 34.89 (CH₂), 67.37 (OCH₃), 85.98 (NC(CH₃)₃), 125.32, 126.14, 126.46, 127.11, 129.28, 130.07, 130.93, 131.18, 133.55, 138.62, 144.96, 146.30, 149.27, 152.30, 158.56, 161.44 (aryl-C).

2.2.8. Synthesis of $[NbCl_2(MeCalix)]$ (10)

A mixture of [H₂Me₂calix] (18.0 g, 26.6 mmol) and NbCl₅ (7.17 g, 26.6 mmol) was dissolved in toluene (300 ml) and stirred at 80 °C overnight. After cooling the reaction mixture to room temperature all of the volatile components were removed in vacuo. The remaining red residue was suspended in hexane (-20 °C, 20 ml), filtered off and dried in vacuo to afford the toluene adduct of [NbCl₂(MeCalix)]. Yield: 22.1 g (91%) red powder. Single crystals were obtained from cooling hot saturated toluene solutions of the product to room temperature. C45H45O4-Cl₂Nb · C₇H₈ [915.88]: Calc.: C, 68.19; H, 6.99. Found: C, 68.13; H, 6.99%. EI/MS m/z (%): 822.2 (100) [M]⁺, 807.3 (39) $[M - CH_3]^+$, 787.2 (10) $[M - Cl]^+$, 772.2 (11) $[M - CH_3 - Cl]^+$. IR (Nujol $[cm^{-1}]$): 1580 w, 1320 m br, 1206 s, 1166 m, 1122 m, 988 w, 940 m, 875 m, 829 w, 795 m, 755 w, 681 w, 585 w, 584 m, 464 w, 422 w, 353 w, 307 w. ¹H NMR (C₆D₆): $\delta = 0.67$ (s, 9H, C(CH₃)₃), 0.73 (s, 9H, C(CH₃)₃), 1.34 (s, 18H, C(CH₃)₃), 3.14 (d, 2H, ${}^{2}J_{\rm HH} = 13.2$ Hz, CH₂), 3.24 (d, 2H, ${}^{2}J_{\rm HH} = 13.8$ Hz, CH_2), 3.96 (s, 3H, OCH₃), 4.46 (d, 4H, ${}^2J_{HH} = 13.2$ Hz, CH_2), 4.99 (d, 2H, ${}^2J_{HH} = 13.8$ Hz, CH_2), 6.81 (d, 2H, $^{2}J_{\rm HH} = 6.8$ Hz, aryl- $H_{\rm m}$), 6.99–7.14 (aryl- $H_{\rm m}$). 13 C NMR $(C_6D_6): \delta = 30.92, 31.21, 32.18 (C(CH_3)_3), 34.04, 34.15,$ 34.58 (C(CH₃)₃), 34.67, 35.07 (CH₂), 69.90 (OCH₃), 124.68, 125.73, 126.85, 127.72, 129.68, 132.89, 133.18, 136.28, 147.29, 147.37, 149.53, 155.29, 160.41, 166.36 (aryl-*C*).

2.2.9. Synthesis of [Nb(NtBu)(MeCalix)] (12)

A mixture of [NbCl₂(MeCalix)] (2.75 g, 3.00 mmol) and LiNH*t*Bu (475 mg, 6.00 mmol) was dissolved in toluene (30 ml) at -30 °C and stirred for 2 h. The resulting solution was allowed to reach room temperature within 12 h and was filtered through a pad of Celite. The volatile components of the filtrate were removed in vacuo and the remaining residue was washed with 10 ml cold (-20 °C) hexane and dried in vacuo. Yield: 1.18 g (85%) orange powder. C₄₉H₆₄NNbO₄ [823.96]: Calc.: C, 71.43; H, 7.83; N, 1.70.

Found: C, 71.83; H, 7.66; N, 1.56%. EI/MS m/z (%): 823.3 (10) $[M]^+$, 809.3 (13) $[M - CH_3]^+$. IR (Nujol $[cm^{-1}]$: 1607 w. 1322 m. 1304 m. 1276 m. 1206 m. 1164 w, 1123 m, 1108 w, 987 w, 938 w, 920 m, 876 w, 858 w, 830 w, 797 m, 754 w, 673 w, 584 w, 584 m, 563 m 551 m, 502 w, 463 w, 427 w, 384 w. ¹H NMR (C_6D_6): $\delta = 0.71$ (s, 9H, C(CH₃)₃), 0.80 (s, 9H, C(CH₃)₃), 1.43 (s, 18H, C(CH₃)₃), 1.53 (s, 9H, N(CH₃)₃), 3.26 (d, 2H, $^{2}J_{\text{HH}} = 12.3 \text{ Hz}, CH_{2}$, 3.30 (d, 2H, $^{2}J_{\text{HH}} = 12.5 \text{ Hz}, CH_{2}$), 4.12 (s, 3H, OCH₃), 4.38 (d, 2H, $^{2}J_{\text{HH}} = 12.3 \text{ Hz},$ CH_2), 5.00 (d, 2H, ${}^2J_{HH} = 12.5$ Hz, CH_2), 7.05–7.23 (aryl- $H_{\rm m}$). ¹³C NMR (C₆D₆): $\delta = 30.82$ (NC(CH_3)₃), 30.93, 31.25, 31.36 (C(CH₃)₃), 32.37, 33.42, 33.73 (C(CH₃)₃), 34.16, 34.66 (CH₂), 70.88 (NC(CH₃)₃), 73.22 (OCH₃), 124.27, 126.07, 126.46, 127.80, 129.43, 130.41, 131.93, 133.91, 143.58, 144.18, 149.78, 150.43, 151.06, 156.21 (aryl-C).

2.2.10. Synthesis of [Nb(NTol)(MeCalix)] (13)

A mixture of [NbCl₂(MeCalix)] (2.75 g, 3.00 mmol) and LiNHTol (679 mg, 6.00 mmol) was dissolved in toluene (30 ml) at $-30 \degree$ C and stirred for 2 h. The resulting solution was allowed to reach room temperature and filtered through a pad of Celite. All volatile components of the remaining solution were removed in vacuo and the orange residue was washed with 10 ml cold ($-20 \,^{\circ}$ C) hexane and dried in vacuo. Yield: 1.48 g (58%) orange powder. Single crystals were obtained from concentrated solutions of the product in toluene at -40 °C. $C_{52}H_{62}NNbO_4$ [857.97]: Calc.: C, 72.80; H, 7.28; N, 1.48. Found: C, 72.45; H, 7.42; N, 1.43%. EI/MS m/z (%): 857.4 (100) [M]⁺, 842.5 (33) $[M - CH_3]^+$, 812.4 (8.9) $[M - 3 CH_3]^+$. IR (Nujol $[cm^{-1}]$: 1580 w br, 1302 m br, 1210 s, 1120 m, 995 w, 919 m, 872 m, 819 m, 796 m, 756 w, 624 m, 550 m, 406 w, 469 w. ¹H NMR (CDCl₃): $\delta = 1.18$ (s, 9H, C(CH₃)₃), 1.19 (s, 9H, C(CH₃)₃), 1.25 (s, 18H, C(CH₃)₃), 2.36 (s, 3H, tolyl-CH₃), 3.28 (d, 2H, ${}^{2}J_{HH} = 12.8$ Hz, CH₂), 3.41 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 4.37 (d, 2H, ${}^{2}J_{HH} =$ 12.6 Hz, CH₂), 4.55 (s, 3H, OCH₃), 4.59 (d, 2H, $^{2}J_{\text{HH}} = 12.8 \text{ Hz}, \text{ CH}_{2}, 7.03-7.24 \text{ (aryl-}H\text{)}.$ $^{13}\text{C} \text{ NMR}$ (CDCl₃): $\delta = 21.19$ (NC₆H₄ - CH₃), 31.23, 31.52, 31.83 (C(CH₃)₃), 31.95, 32.92, 33.22 (C(CH₃)₃), 34.26, 34.50 (CH₂), 70.01 (OCH₃), 124.11, 124.22, 125.45, 125.56, 125.75, 127.77, 128.38, 128.57, 129.08, 129.19, 130.02, 130.27, 133.54, 133.89, 143.90, 144.19, 149.46, 150.44, 152.10, 155.03 (aryl-C).

2.2.11. Synthesis of [Nb(NMes)(MeCalix)] (14)

A mixture of [NbCl₂(MeCalix)] (1.37 g, 1.50 mmol) and KNHMes (520 mg, 3.00 mmol) was dissolved in toluene (20 ml) at -30 °C and stirred for 2 h. The resulting solution was allowed to reach room temperature and filtered through a pad of Celite. All of the volatile material of the mother liquor was removed in vacuo and the remaining residue was washed with 10 ml cold (-20 °C) hexane and dried in vacuo. Yield: 500 mg (55%) yellow powder. C₅₄H₆₆NNbO₄ [886.03]: Calc.: C, 73.20; H, 7.51; N, 1.58. Found: C, 73.64, H, 7.86; N, 1.82%. EI/MS m/z (%): 885.0 (100) $[M]^+$, 870.5 (5.67) $[M - CH_3]^+$. IR (Nujol $[cm^{-1}]$): 1601 w. 1308 m. 1269 m. 1209 s. 1123 m. 1110 w. 1030 w. 986 w, 936 w, 920 m, 871 m, 850 m, 823 m, 754 w, 694 w, 674 w, 586 w, 560 s, 523 w, 464 m, 427 w. ¹H NMR (CDCl₃): $\delta = 1.19$ (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃), 2.17 (s, 3H, p-CH₃), 2.32 (s, 6H, o-CH₃), 3.30 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 3.42 (d, 2H, ${}^{2}J_{HH} =$ 12.5 Hz, CH_2), 4.38 (d, 2H, ${}^2J_{HH} = 12.5$ Hz, CH_2), 4.46 (s, 3H, OCH₃), 4.61 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH₂), 6.86 (s, 2H, mesityl- H_m), 7.05–7.25 (aryl- H_m). ¹³C NMR $(CDCl_3)$: $\delta = 31.20, 31.50, 31.86 (C(CH_3)_3), 32.91, 33.25,$ 34.14 (C(CH₃)₃), 34.28, 34.50 (CH₂), 71.86 (OCH₃), 123.99, 125.47, 125.76, 127.84, 128.35, 128.99, 129.19, 130.11, 130.16, 133.72, 134.00, 134.39, 143.79, 150.45, 155.25 (aryl-C).

2.2.12. Synthesis of [Nb(NDipp)(MeCalix)] (15)

A solution of [NbCl₂(MeCalix)] (950 mg, 1.00 mmol) in toluene (30 ml) and a solution of LiNHDipp (366 mg, 2.00 mmol) in tetrahydrofurane (30 ml) were cooled to -40 °C, then combined and stirred for 2 h at this temperature. Afterwards, the solution was allowed to reach room temperature within 12 h and all volatiles were removed in vacuo. The residue was dissolved in 10 ml hexane and undissolved components were filtered off. The solvent of the filtrate was removed in vacuo, the remaining yellow residue was washed with 5 ml cold pentane $(-20 \,^{\circ}\text{C})$ and dried in vacuo. Yield: 451 mg (49%) yellow powder. Single crystals were obtained from concentrated solutions of the product in hexane at -40 °C. C₅₇H₇₂NNbO₄ [928.11]. EI/ MS m/z (%): 927.4 (100) [M]⁺, 912.4 (11) [M - CH₃]⁺, 753.3 (5) $[M - C_{12}H_{17}N]^+$. IR (KBr $[cm^{-1}]$): 1753 w, 1598 w, 1477 s, 1428 m, 1358 m, 1299 s, 1266 s, 1205 s, 1115 m, 992 m, 918 m, 871 w, 824 m, 795 s, 752 m, 676 w, 590 w, 554 m, 506 w, 429 w. ¹H NMR (C_6D_6): $\delta = 0.72$ (s, 9H, C(CH₃)₃), 0.81 (s, 9H, C(CH₃)₃), 1.40 (s, 18H, $C(CH_3)_3$, 1.54 (d, 12H, ${}^2J_{HH} = 3.44$ Hz, *i*Pr-CH₃), 3.29 (d, 2H, ${}^{2}J_{\rm HH} = 12.5$ Hz, CH₂), 3.36 (d, 2H, ${}^{2}J_{\text{HH}} = 12.7 \text{ Hz}, \text{ CH}_{2}$, 3.95 (s, 3H, OCH₃), 4.44 (d, 2H, $^{2}J_{\text{HH}} = 12.4 \text{ Hz}, \text{ CH}_{2}, 4.60 \text{ (sept, 1H,$ *i*Pr-*H*), 5.01 (d,2H, ${}^{2}J_{\text{HH}} = 12.6 \text{ Hz}, \text{ CH}_{2}$), 6.88–7.29 (aryl-*H*). ¹³C NMR (C_6D_6) : $\delta = 28.91$ (*i*Pr-*C*H₃), 30.38 (*i*Pr-*C*H), 31.33, 31.75, 32.81 (C(CH₃)₃), 33.86, 34.21 (CH₂), 34.39, 34.63, 35.15 (C(CH₃)₃), 71.66 (OCH₃), 123.60, 124.80, 126.39, 126.54, 127.17, 129.30, 129.71, 130.07, 130.68, 132.10, 134.24, 144.53, 145.22, 145.67, 151.00, 154.55 (aryl-C).

2.2.13. Synthesis of [Ta(NtBu)(MeCalix)] (16)

A mixture of $[TaCl_2(MeCalix)]$ (3.01 g, 3.00 mmol) and LiNH*t*Bu (475 mg, 6.00 mmol) was dissolved in toluene (30 ml) at -30 °C and stirred for 2 h. The resulting solution was allowed to reach room temperature within 12 h and was filtered through a pad of Celite. All of the volatile components of the filtrate were removed in vacuo and the remaining residue was washed with 10 ml cold (-20 °C) hexane and dried in vacuo. Yield, 1.35 g, 49%, colorless powder. C₄₉H₆₄NO₄Ta [912.00]: Calc.: C, 64.53; H, 7.07; N, 1.54. Found: C, 63.72; H, 7.42; N, 1.67%. EI/MS m/z (%): 911.2 (29) $[M]^+$, 896.2 (90) $[M - CH_3]^+$, 866.2 (19) $[M - 3CH_3]^+$. IR (Nujol $[cm^{-1}]$): 1598 w, 1315 m, 1209 m, 1120 m, 994 w, 937 w, 922 w, 872 m, 855 w, 827 w, 758 w, 695 w, 674 w, 665 w, 583 w, 555 w, 428 w, 403 w. ¹H NMR (C₆D₆): $\delta = 0.70$ (s, 9H, C(CH₃)₃), 0.80 (s, 9H, C(CH₃)₃), 1.43 (s, 18H, C(CH₃)₃), 1.59 (s, 9H, $N(CH_3)_3)$, 3.25 (d, 2H, ² $J_{HH} = 12.6$ Hz, CH_2), 3.29 (d, 2H, ${}^{2}J_{HH} = 12.6$ Hz, CH_{2}), 4.25 (s, 3H, OCH₃), 4.37 (d, 2H, ${}^{2}J_{HH} = 12.5$ Hz, CH₂), 5.02 (d, 2H, ${}^{2}J_{HH} = 12.5$ Hz, CH_2), 6.86 (d, ${}^2J_{HH} = 2.20$ Hz, aryl-H), 7.05–7.23 (aryl-*H*). ¹³C NMR (C₆D₆): $\delta = 31.20, 31.67, 32.72$ (C(*C*H₃)₃), 32.88 (NC(CH₃)₃), 33.73, 34.16, 34.69 (C(CH₃)₃), 35.03, 35.10 (CH₂), 67.47 (NC(CH₃)₃) 75.14 (OCH₃), 124.46, 126.35, 126.76, 129.21, 129.99, 130.99, 132.23, 134.21, 144.19, 144.48, 150.16, 150.64, 151.06, 156.34 (aryl-C).

2.2.14. Synthesis of [Ta(NTol)(MeCalix)] (17)

A mixture of [TaCl₂(MeCalix)] (3.01 g, 3.00 mmol) and LiNHTol (679 mg, 6.00 mmol) was dissolved in toluene (30 ml) at -30 °C and stirred for 2 h. The resulting solution was allowed to reach room temperature within 12 h and was filtered through a pad of Celite. All of the volatile components of the mother liquor were removed in vacuo and the remaining yellow residue was washed with 10 ml cold (-20 °C) hexane and dried in vacuo. Yield: 1.14 g (40%) yellow powder. C₅₂H₆₂NTaO₄ [946.02]: Calc.: C, 66.02; H, 6.61; N, 1.48. Found: C, 66.74; H, 6.28; N, 1.43%. EI/ MS m/z (%): 946.4 (69) [M]⁺, 931.4 (33) [M - CH₃]⁺. IR (Nujol [cm⁻¹]): 1657 w, 1606 w, 1497 m, 1320 s, 1277 m, 1237 w, 1212 s, 1177 w, 1119 m, 1092 m, 997 m, 939 m, 921 m, 871 w, 871 m, 862 m, 817 m, 795 m, 754 w, 678 w, 654 m, 634 m, 599 w, 587 w, 557 m, 547 w, 505 w, 478 w, 445 w, 422 w, 407 w, 361 w. ¹H NMR (C₆D₆): $\delta = 0.68$ (s, 9H, C(CH₃)₃), 0.79 (s, 9H, C(CH₃)₃), 1.37 (s, 18H, $C(CH_3)_3)$, 2.11 (s, 3H, Tol- CH_3), 3.28 (d, 2H, ${}^2J_{HH} = 11.0$ Hz, CH_2), 3.32 (d, 2H, ${}^2J_{HH} = 12.1$ Hz, CH_2), 4.57 (d, 2H, ${}^2J_{HH} = 12.1$ Hz, CH_2), 4.94 (d, 2H, $^{2}J_{\rm HH} = 11.0$ Hz, CH₂), 4.96 (s, 3H, OCH₃), 6.57–7.41 (aryl-*H*). ¹³C NMR (C₆D₆): $\delta = 21.40$ (Tol-*C*H₃) 25.17 (CH₂), 31.62, 31.06, 32.08 (C(CH₃)₃), 33.37, 33.64, 34.33 (C(CH₃)₃), 34.66, 35.01, 67.86 (CH₂), 70.17 (OCH₃), 121.66, 123.15, 124.42, 125.66, 129.30, 131.80, 132.64, 133.39, 137.86, 143.68, 144.11, 148.93, 154.39, 156.04, 156.79, 158.60 (aryl-C).

2.3. Crystal structure determination of $[V(NTol)Cl_3]$ (2), $[VCl(Mecalix)] \cdot (0.5C_6H_6) \cdot (C_6H_{16}) (4 \cdot (0.5C_6H_6) \cdot (C_6H_{16})), [{Li_3(Mecalix)}_2] \cdot (2C_7H_8) (5 \cdot (2C_7H_8)),$ $[NbCl_2(MeCalix)] \cdot (2C_7H_8) (10 \cdot (2C_7H_8)),$ $[Nb(NTol)(Mecalix)] \cdot (0.5C_7H_8) (13 \cdot (0.5C_7H_8))$ and [Nb(NDipp)(Mecalix)] (15)

Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a STOE

Table 1 X-ray data collection and processing parameters

	2	${\bf 4} \cdot (0.5 C_6 H_6) \cdot (C_6 H_{16})$	$0.5\boldsymbol{5}\cdot(2C_7H_8)$	$10\cdot(\mathbf{2C_7H_8})$	$13 \cdot (0.5 C_7 H_8)$	15
Formula	C7H7Cl3NV	C ₅₄ H ₇₂ ClO ₄ V	C59H71Li3O4	C ₅₉ H ₇₁ Cl ₂ NbO ₄	C55.5H65.5NNbO4	C57H72NNbO4
Formula weight	262.43	871.51	864.98	1007.97	930.50	928.07
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	5.8905(8)	16.8594(7)	13.4916(11)	12.7115(8)	12.7309(11)	12.2677(14)
b (Å)	9.8972(14)	13.0622(6)	14.3860(15)	18.4227(9)	18.4040(14)	15.1302(14)
c (Å)	10.1573(16)	22.7705(10)	16.9147(17)	23.4189(14)	21.543(3)	15.8064(15)
α (°)	112.947(16)		93.609(12)			99.315(11)
β (°)	101.240(17)	93.049(4)	112.717(11)	100.551(5)	97.717	101.171(12)
γ (°)	105.142(16)		114.557(10)			109.937(12)
$V(\text{\AA}^3)$	496.17(12)	5007.4(4)	2654.9(4)	5391.5(5)	5001.7(9)	2621.8(5)
Ζ	2	4	2	4	4	2
$\mu (\mathrm{mm}^{-1})$	0.891	0.293	0.042	0.366	0.780	0.273
Independent reflections	2955	7162	7341	9138	8825	8421
Observed reflections	2433	5537	3387	8121	4930	5936
Parameters	110	511	528	610	550	566
Final R , ^a wR_2^{b}	0.0302, 0.0691	0.0775, 0.2062	0.1029, 0.2597	0.0591, 0.1457	0.0874, 0.1717	0.0527, 0.1209

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|.$ ^b $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}; \text{ for data with } I > 2\sigma(I).$

STADI IV CDD diffractometer (Mo Kα radiation: 4, 10) equipped with an Oxford Cryosystems low-temperature device or a STOE IPDS I image plate diffractometer (Ag K α radiation: 2, 5, 13; Mo K α radiation: 15) equipped with a FTS AirJet low temperature device. Data were collected at 200 K; equivalent reflections were merged and the images were processed with the STOE IPDS or CCD software package. Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using shelxs-97 and SHELXL-97 [14].

The calix [4] arene *tert* butyl groups containing C(17) to C(19) were positionally disordered for compound 5. $(2C_7H_8)$. These carbon atoms were refined in an isotropic approximation with occupancy factors of 70% and 30%. For compound $10 \cdot (2C_7H_8)$, the calix[4]arene tert butyl groups containing C(27) to C(29) and C(47) to C(49) were positionally disordered. These carbon atoms were refined in an isotropic approximation with occupancy factors of 50% each and 70% and 30%, respectively. The calix[4]arene *tert* butyl groups of 15 containing C(27) to C(29) were positionally disordered and refined in an isotropic approximation with occupancy factors of 67% and 33%.

3. Results and discussion

For a preparation of complexes of the type [M(NR)-(Mecalix)] (M = V, Nb, Ta, R = alkyl, aryl), synthetic routes starting from a suitable metallacalix[4]arene precursor such as $[d^0-MCl_2(Mecalix)]$ or $[\{d^2-M(Mecalix)\}_2]$ or starting from imidoyl chlorides [M(NR)Cl₃] or their base adducts, respectively, are conceivable. Similar strategies

have been proven to be successful in the synthesis of other calix[4]arene stabilized imido complexes [5,6].

The reaction of suitable calix[4]arene stabilized metal d² complexes with organic azides RN₃ should result under N₂ elimination in the formation of two equivalents of the corresponding imido complex. This method has already been successfully applied in the synthesis of calixarene phenylimido complexes of the metals zirconium, tantalum and tungsten using $[Zr(\eta^4-C_4H_6)(Me_2calix)]$ [15], $[Ta(\eta^4-C_4H_6)(Mecalix)]$ [11b], and $[W(\eta^2-C_6H_{10})-$ (calix)] [16] as starting materials. In the case of tantalum, the reaction of $[Ta(\eta^4-C_4H_6)(Mecalix)]$ and phenyl azide afforded the dinuclear complex $[{Ta(\mu-NPh)(Mecalix)}_2],$ which was structurally characterized as an imido bridged centrosymmetric dimer. This method, however, is limited by the availability of the corresponding azide RN₃. For the sake of generality we thus focused on non azide routes to complexes [M(NR)(Mecalix)] (M = V, Nb, Ta, R = alkyl, aryl).

One standard method successfully employed in group 4 imido chemistry was the reaction of the complex [TiCl₂-(Me₂calix)] with two equivalents of a primary lithium amide, which led to the desired products [Ti(NR)(Me₂calix)] and one equivalent of the corresponding amine by salt elimination [6]. In the case of titanium, these reactions proceeded cleanly and in high yields under formation of the corresponding aryl- and alkylimido complexes and one equivalent of the corresponding amine RNH₂, which is eliminated during the reaction. There was no evidence for an interaction between RNH₂ and the imido complexes, which, in principle, could form either an adduct with the free amine or significant equilibrium concentrations of bis(amido) species [Ti(NHR)2(Me2calix)].

Furthermore, we considered the introduction of the calix[4]arene ether ligand into imidoyl chlorides [M(NR)Cl₃] or $[M(NR)Cl_3L_n]$ as a convenient way to imido complexes,

since this route also was successfully applied in the synthesis of group 4 and group 6 metal calix[4]arene imido complexes. Especially for calix[4]arene vanadium chemistry, where a suitable precursor of the type [VCl₂(Mecalix)] is presently unknown [17], this strategy was attractive. Complexes of the type [V(NR)Cl₃] ($R = Ph \ 1$, Tol 2, *t*Bu 3) can be readily prepared from the reaction of [VOCl₃] with isocyanates RNCO [10]. The molecular structure of the *p*-tolyl substituted imido complex emerging from an X ray structural analysis on single crystals of the complex [V(NTol)Cl₃] (Tol = 4-C₆H₄Me) (2) as well as a view along the crystallographic *c*-axis of the elemental cell is shown in Fig. 1.

Complex 2 crystallizes in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit. In analogy to the *tert* butyl imido derivative 3 [18], the tolyl substituted complex is a polymer in the solid state. Regarding the imido ligand as a six electron donor, which is in accordance with a short V–N distance of 165.3(2) pm and a close to linear V–N–C angle of 173.01(2)° [19], the coordinatively unsaturated 12 VE complex fragment [V(NTol)Cl₃] oligo-



Fig. 1. Schakal plot of the molecular structure of $[V(NTol)Cl_3]$ (2) (left side) and a view along the crystallographic *c*-axis (right side). H atoms have been omitted for clarity. Selected bond lengths (pm) and angles (°): V–N 165.3(2), V–Cl(1) 238.8(1), V–Cl(2) 222.2(1), V–Cl(3) 229.0(1), V–Cl(1') 247.4(1), V–Cl(3') 267.1(1); V–N–C(1) 173.01(2), N–V–Cl(1) 96.96(7), N–V–Cl(2) 95.27(6); N–V–Cl(3) 98.43(7), N–V–Cl(1') 94.31(6), N–V–Cl(3') 178.19(6) Cl(1)–V–Cl(2) 91.15(3), Cl(1)–V–Cl(3) 86.14(2), Cl(2)–V–Cl(3) 100.20(3), V–Cl(1)–V' 100.13(2).

merizes in the solid state with two chloride bridges (Cl(1) and Cl(3)) to build a chain of edge sharing [V(NTol)Cl(μ -Cl)₄] octahedrons. These chains are interconnected with weak interactions to result in a three dimensional network as presented on the right side of Fig. 1. The chloride atoms bridge asymmetrically with vanadium chloride bond lengths of 238.8, 222.2 and 229.0 pm to the chloride atoms Cl(1), Cl(2) and Cl(3), respectively, and much longer distances of 247.4 and 267.1 pm to the chloride atoms Cl(1') and Cl(3') of the neighboring unit. The distance V–Cl(3') is particularly long due to the excellent *trans* effect of the imido ligand.

The compounds $[{V(NR)Cl_3}_n](R = Ph 1, Tol 2, tBu 3)$ react with the calix[4]arene monomethyl ether H₃Mecalix in toluene at 70 °C to afford the paramagnetic vanadium (IV) complex [VCl(Mecalix)] (4) in high yields (see Scheme 2). This compound has already been synthesized independently by Floriani et al. by an iodine oxidation/dealkylation reaction starting from the calix[4]arene bis(methyl)ether vanadium(III) complex [VCl(Me₂calix)] [17a], and Limberg et al. reported the formation of this compound starting from [VOCl₂(THF)₂] and H₂Me₂calix as well as the structure of the toluene solvate just recently [17c]. Crystals suitable for X ray analysis were grown from hexane/benzene (1:1) solutions of the product. The molecular structure of complex 4 is depicted in Fig. 2.

Compound 4 crystallizes in the space group $P2_1/c$ with four formular units, four molecules of hexane and two molecules of benzene in the elemental cell. The coordination polyhedron at the vanadium atom resembles a distorted trigonal bipyramid with the oxygen atoms of the calix[4]arene phenolate entities O(2) and O(4) and the chlorine atom defining the equatorial plane and the atoms O(1) and O(3) in axial positions. The distance V-Cl (222.6 pm) is slightly shorter compared to the bond length found in [VCl(Me₂calix)] (226.5 pm) [17a], which is likely due to the different charge density on the metal atom. The angle O(1)-V-O(3) of 172.4° reveals the distortion of the atoms from a regular trigonal bipyramid. In comparison to the analogous titanium complex [TiCl(Mecalix)] [13], the distortion of the polyhedron in 4 is less pronounced, which is also reflected in the metal oxygen distance to the atom O(1) of the calix[4]arene anisole unit. In case of the



Scheme 2. Reactions of $[\{V(NR)Cl_3\}_n]$ (R = Ph 1, Tol 2, tBu 3) with H₃Mecalix and $[\{Li_3Mecalix\}_n]$.



Fig. 2. Schakal plot of [VCl(Mecalix)] (4). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): V–O(1) 226.2(3), V–O(2) 174.7(3), V–O(3) 183.3(3), V–O(4) 174.4(3), V–Cl 222.6(1); O(1)–V–Cl 90.74(8), O(2)–V–Cl 107.79(11), O(3)–V–Cl 96.73(10), O(4)–V–Cl 110.46(13), O(2)–V–O(3) 95.76(14), O(2)–V–O(4) 138.01(16), O(3)–V–O(4) 96.36(14), O(1)–V–O(2) 83.23(12), O(1)–V–O(3) 172.40(12), O(1)–V–O(4) 79.64(12), C(10)–O(1)–V 118.1(2), C(5)–O(1)–V 128.7(3), C(20)–O(2)–V 149.6(3), C(30)–O(3)–V 116.9(3), C(40)–O(4)–V 158.4(3).

titanium complex case this Ti–O bond length is 242.4 pm, whereas in the vanadium complex this distance is 226.2 pm.

The formation of 4 might be explained by an initial loss of the imido group during the protolysis of $[V(NR)Cl_3]$. Similar reactions have been observed for the preparation of molybdenum and tungsten imido complexes, where compounds of the type $[M(NR)_2Cl_2](M = Mo, W)$ or their base adducts react with calix[4]arene H₄calix by elimination of one imido group to yield monoimido complexes [M(NR)(calix)] [5b]. This is in accordance with NMR investigations on the reaction of $[V(NR)Cl_3]$ (R = Ph, Tol) with H₃Mecalix at lower temperatures, that indicated the formation of a C_s symmetrical intermediate, which is not a calix[4]arene imido complex. This was verified by comparison with authentical samples of the imido complexes (see below). At the initial stage of this reaction, species which are still protonated at the calix[4]arene ligand can be detected, and further reactions lead to a diamagnetic calix[4]arene complex. Although a likely intermediate of the type [VCl₂(Mecalix)] defied reproduction so far, we isolated this thermolabile complex once. The NMR spectrum of this compound reveals three resonances for the protons of the calix[4]arene tert butyl groups in an integration ratio of 1:1:2 (9:9:18 H) at 1.15, 1.17 and 1.39 ppm, four doublets at 3.40, 4.73 (coupling constant 13.9 Hz), 3.55, and 5.17 ppm (coupling constant 14.0 Hz) (2H each) for the diastereotopic protons of the methylene groups and a resonance for the methoxy group at 4.02 ppm (3H). No further signals were detected for an imido or amido intermediate and hydrolysis can be ruled out by comparison with the NMR data published by Floriani et al. for [VO(Mecalix)] [17b]. Therefore, we speculate that the imido group was attacked during the first step of the incorporation of the calix[4]arene ligand by either elimination of the imido group and formation of a dichloro complex [VCl₂(Mecalix)] or by formation of an amido chloro complex which leads to the dichloro compound under the

given reaction conditions. Generally, it is known that vanadium (V) complexes are stable if they are coordinated with good π donor ligands such as oxo, sulfido or imido. When they are coordinated with ligands of poor π donor capabilities, they tend to decompose into vanadium (IV) compounds [20]. With this in mind, it is likely that the vanadium (V) dichloro complex [VCl₂(Mecalix)] should readily eliminate chlorine to give the main product of this reaction, the vanadium (IV) chloride [VCl(Mecalix)] (4). This parallels similar observations in molybdenum chemistry, where the hexachloride [MoCl₆] is presently unknown and the molybdenum complex [MoCl₂(calix)] eliminates chlorine at temperatures above 50 °C [21].

To circumvent the problems encountered with the reaction of the calixarene and the vanadium imidoyl chlorides, the lithium and sodium salt of the calix[4]arene methyl ether were prepared via deprotonation of H₃MeCalix with three equivalents of BuLi or NaH, respectively. These reactions proceed smoothly at 65 °C in THF and the colorless salts [{Li₃(Mecalix)}₂] (5) and [{Na₃(Mecalix)}₂] (6) have been isolated in approximately 65% yield. The IR spectra of these compounds reveal no absorption in the O–H region and no OH resonance was observed in the proton NMR spectra, which confirms the complete deprotonation. The EI mass spectrum of the lithium salt shows a signal at m/z = 1361 with a typical isotopical distribution which can be assigned to the dimeric species. The sodium salt is not volatile under the conditions of EI mass spectroscopy.

The room temperature ¹H and ¹³C NMR spectra of **5** and 6 in deuterochloroform show sharp resonances, featuring signals typically found for C_s symmetrical calix[4]arene compounds. The proton and lithium NMR spectrum of 5 in d^8 -THF, however, is temperature dependent comprising of two dynamic processes: An equilibrium between a monomeric and a dimeric form in THF solutions as well as an intramolecular exchange of exohedrally and endohedrally coordinated lithium atoms in the monomer. The room temperature ¹H NMR spectrum of 5 contains two sets of broadened calixarene resonances, especially in the methylene proton region. The intensity ratio of the two sets of resonances is approximately 3:4. The ⁷Li NMR spectrum reveals three broad resonances at -1.87, 1.57, and 2.23 ppm, which is in accordance with three chemically different lithium cations as observed in the solid state structure of the dimer (see below). This implies, however, that ⁷Li NMR spectroscopy does not resolve the equilibrium of the monomeric and the dimeric form of 5, which is likely due to the very narrow chemical shift range of ⁷Li NMR. At 373 K, we observe one set of calix[4]arene resonances, in which the signals of the methylene protons and the aryl meta protons are still broadened. Heating the sample to 353 K also leads to a collapse of the three resonances in the ⁷Li NMR spectrum to a broad resonance at 0.92 ppm, which implies an exchange of the Li cations between endo and exo sites (see structure below). Both findings led us to propose a mononuclear structure of the lithium salt in THF at high temperatures. NMR experiments at lower temperatures were frustrated

by the low solubility of at least one form of the lithium salt in THF solution. The resonances in the proton NMR, however, sharpen on cooling the solution down to 193 K, and in the ⁷Li NMR the three resonances observed at room temperature split into broad resonances.

The molecular structure of 5 is shown in Fig. 3. Compound 5 crystallizes in the space group $P\bar{1}$ with one molecular unit and two toluene molecules in the elemental cell. The overall structure of 5 in the solid state can be viewed as that of dimers, in which two monomeric trianions are bridged by lithium cations. The cocrystallized toluene solvent molecules occupy general positions in the lattice and are omitted in Fig. 3. Both calix[4]arene ligands are fully deprotonated and bind the lithium atoms Li(2) and Li(3)exohedrally, whereas Li(1) is endohedrally located within the calix [4] arene cavities. Li(3) and Li(3)' and the phenolate oxygen atoms O(3) and O(3') form a central, four membered $[Li_2O_2]$ ring with the crystallographically imposed center of inversion in its center. In addition to the coordination with O(3) and O(3'), Li(3) is coordinated with phenolate oxygen atoms O(2) and O(4). Li(2) bridges both calixarene entities as well and is coordinated with the phenolate oxygen atoms O(2), O(4), O(3)', and the anisole oxygen atom O(1). Whereas the coordination sphere at Li(2)can be described as a distorted tetrahedron, Li(3) is disphenoidally coordinated, with angles O(3)-Li(3)-O(3)' of $101.2(5)^{\circ}$ in the 'equatorial plane' and O(2)-Li(3)-O(4)' of $167.6(6)^{\circ}$ in the 'axis'. The endohedrally located Li(1) atom is stabilized by the coordination of O(2) and O(4)



Fig. 3. Schakal plot of $[\{Li_3(Mecalix)\}_2]$ (5). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): Li(1)–O(2) 188.8(1), Li(1)–O(4) 190.2(1), Li(2)–O(1) 191.1(1), Li(2)–O(2) 199.7(1), Li(2)–O(3') 182.9(1), Li(2)–O(4) 199.8(1), Li(3)–O(2) 204.7(9), Li(3)–O(3) 197.2(1), Li(3)–O(3') 196.1(1), Li(3)–O(4') 199.8(9), Li(1)–C(30) 232.8(1), Li(1)–C(31) 262.3(1), Li(1)–C(32) 264.8(1), Li(1)–C(20) 269.0(1), Li(1)–C(40) 266.6(1), Li(1)–Li(3) 310.8(1), Li(2)–Li(3) 263.4(1), Li(2)–Li(3') 265.3(1), Li(3)–Li(3') 250.0(2), Li(3)–Li(1') 308.8(1), Li(1)–Li(2) 248.9(1); O(2)–Li(1)–O(4) 101.3(5), O(1)–Li(2)–O(2) 109.0(5), O(1)–Li(2)–O(3') 139.8(6), O(1)–Li(2)–O(4) 111.0(5), O(2)–Li(2)–O(4) 94.4(5), O(3')–Li(2)–O(4) 95.7(5), O(3')–Li(2)–O(2) 97.8(5), O(3')–Li(3)–O(3) 101.2(5), O(3')–Li(3)–O(4') 96.8(4), O(3)–Li(3)–O(4') 91.3(4), O(3')–Li(3)–O(2) 92.1(4), O(3)–Li(3)–O(2) 95.4(4), O(4')–Li(3)–O(2) 167.6(6).

and by the interactions with carbon atoms of the three phenolate entities of the calix[4]arene, which results in a η^3 coordination of the lithium atom with these ring systems. The Li–C bond lengths are (with the exception of Li(1)– C(30) of 232.8 pm) in a range between 262.3 and 269.0 pm and are comparable to bond lengths found in the perlithiated salt of the parent calix[4]arene [{Li₄(Calix)}₂] [22].

The reaction of the lithium salt of the calix[4]arene methyl ether with the vanadium (V) imidoyl chlorides $[\{V(NR)Cl_3\}_n]$ (R = Ph 1, Tol 2, tBu 3) in THF affords the calix[4]arene vanadium imido complexes [V(NR)-(Mecalix)] (R = Ph 7, Tol 8, tBu 9) in good to excellent vields (see Scheme 2) as red-brown powders. These compounds were characterized by elemental analysis, mass spectroscopy, IR as well as proton and carbon NMR spectroscopy. The EI mass spectra of these complexes reveal peaks for the mononuclear molecular ion at m/z = 801(7), m/z = 815 (8), and m/z = 781 (9) with the typical isotope distribution as the basis peak of each spectrum. The results of 1 H as well as 13 C NMR spectroscopy are in accordance with C_s symmetrical complexes as proposed in Scheme 2. Despite all attempts to obtain high quality crystals of these complexes failed so far, a preliminary X ray structure of the tert butyl imido complex 9 confirmed a mononuclear structure in the solid state with a short V-N(imido) bond of 163.5 pm. First investigations on the reactivity of this complex demonstrated that it is less reactive with respect to cycloaddition and protonolysis reactions than the related titanium complex [Ti(NtBu)-(Me₂calix)] [6]. Imido exchange reactions of the tert butyl imido complex 9, for example, with aryl amines ArNH₂ (Ar = Ph, Tol) afforded only traces of the corresponding arylimido complexes 7 or 8 after three days at 80 °C. After 5 days at 120 °C in toluene, a mixture of products in the ratio 1:2.5 was observed, i.e. a conversion of approximately 30%. In the case of the titanium complex, these reactions have been completed after two days at 50 °C. One reason for this reduced reactivity might be the reduced ionic radius of the V⁵⁺ ion in comparison with Ti⁴⁺ associated with a better fit of the metal ion into the O₄ rim of the calix[4]arene ligand and a more efficient shielding of the metal ion.

Although starting material of the type $[M(NR)Cl_3L_2]$ is known in niobium and tantalum chemistry [23], we used a different approach for the synthesis of the higher congeners of vanadium. Contrary to vanadium chemistry, calix[4]arene stabilized imido complexes of niobium and tantalum in their highest oxidation states can be prepared systematically starting from the dichloride complexes $[MCl_2(Mecalix)]$ (M = Nb 10, M = Ta 11). The synthesis of the tantalum complex has been previously described by Floriani et al [11], and the niobium compound can be synthesized in a similar way. The complexes $[MCl_2(Mecalix)]$ are readily prepared starting from calix[4]arene *bis*methylether H₂-Me₂calix and the pentachlorides MCl₅ involving the elimination of two equivalents HCl and one equivalent MeCl, to afford the complexes of the calix[4]arene *mono*alkylether in high yields. The NMR spectrum of **10** reveals a typical signal pattern of a C_s symmetrical metallacalix[4]arene, comprising three resonances at 0.67, 0.73 and 1.34 ppm in an integration ratio of 9:9:18 for the *t*Bu protons, four doublets at 3.14, 3.24, 4.46, and 4.99 ppm (2H each) for the methylene protons and a singlet at 3.96 ppm (3H) for the methoxy group protons. The EI mass spectrum of **10** shows a peak for the mononuclear molecular ion at m/z = 822.2 with the typical isotope distribution as the basis peak of the spectrum. Suitable crystals of [NbCl₂(MeCalix)] were grown from saturated toluene solutions of this compound in toluene. The molecular structure of this compound is depicted in Fig. 4.

Compound **10** crystallizes in the space group $P2_1/c$ with one formula unit and two solvent molecules of toluene in the asymmetric unit. One of the toluene molecules is hosted inside the calix[4]arene cavity, the other one occupies a general position in the lattice. The octahedral coordination around niobium involves the four oxygen atoms of the methoxycalix[4]arene ligand and two in *cis* position coordinated chlorine atoms. The equatorial plane is defined by the donor atoms O(2), O(4), Cl(1), and Cl(2), and the axial sites are occupied by O(1) and O(3) (angle O(1)–Nb– O(3) = 164.97(9)°). The Nb–Cl bond lengths (Nb–Cl(1) 235.9(1) pm, Nb–Cl(2) 239.6(1) pm) are in accordance with other niobium chloro alkoxides or phenolates such as [{NbCl₃(ODIP)₂}] (237.9, 237.3, and 240.3 pm) or [NbCl₃(ODIP)₂(py)] (234.7 and 235.9 pm) [24].

Compared to the Nb–O distances of the latter two complexes, which are found to be in a range between 181.6 and 185.2 pm, the Nb–O distances to the phenolate groups of the calix[4]arene ligand are slightly longer in complex **10**, 184.1(3) pm for Nb–O(2), 186.2(2) pm for Nb–O(4), and 191.7(2) pm for Nb–O(3). The distances Nb–O(2) and Nb–O(4), however, as well as the bond angles C(20)– O(2)–Nb (170.9(2)°) and C(40)–O(4)–Nb (153.2(2)°), which



Fig. 4. Schakal plot of $[NbCl_2(Mecalix)]$ (10). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): Nb–O(2) 184.1(3), Nb–O(4) 186.2(2), Nb–O(3) 191.7(2), Nb–O(1) 225.9(2), Nb–Cl(1) 235.9(1), Nb–Cl(2) 239.6(1); Cl(1)–Nb–Cl(2) 85.83(4), O(1)–Nb–O(2) 79.58(10), O(1)–Nb–O(3) 164.97(9), O(1)–Nb–O(4) 80.43(10), O(2)–Nb–O(3) 90.84(11), O(2)–Nb–O(4) 96.38(11), O(3)–Nb–O(4) 89.25(10), O(1)–Nb–Cl(1) 92.48(7), O(2)–Nb–Cl(1) 90.93(9), O(4)–Nb–Cl(1) 168.70(8), O(3)–Nb–Cl(1) 99.28(8), O(2)–Nb–Cl(2) 167.98(8), O(4)–Nb–Cl(2) 85.25(8), O(3)–Nb–Cl(2) 101.10(8), O(1)–Nb-Cl(2) 88.99(7), C(10)–O(1)–Nb 117.88(19), C(5)–O(1)–Nb 153.2(2).

are considerably larger than the bond angle C(30)–O(3)– Nb (120.8(2)°) are in accordance with some Nb–O π interaction between the niobium atom and the oxygen atoms O(2) and O(4). Expectably, the Nb–O(1) distance to the anisole methoxy oxygen atom of the calix[4]arene ligand is significantly longer (225.9(2) pm).

The reaction of $[MCl_2(Mecalix)]$ (M = Nb 10, M = Ta 11) with lithium or potassium amides of primary amines afforded the imido complexes [M(NR)(Mecalix)] (M = Nb: R = *t*Bu, 12, R = Tol 13, R = Mes 14, R = Dipp 15; M = Ta: R = *t*Bu 16, R = Tol 17) (Tol = 4-C₆H₄Me, Mes = 2,6-C₆H₃Me₂; Dipp = 2,6-C₆H₃*i*Pr₂), usually in



Fig. 5. Schakal plot of [Nb(NTol)(Mecalix)] (13). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): Nb–N 178.1(5), Nb–O(1) 230.1(4), Nb–O(2) 192.9(6), Nb–O(3) 195.8(5), Nb–O(4) 192.4(5); C(50)–N–Nb 170.1(6), N–Nb–O(1) 93.2(2), N–Nb–O(2) 110.3(3), N–Nb–O(3) 102.9(2), N–Nb–O(4) 106.8(3), O(1)–Nb–O(2) 79.8(2), O(1)–Nb–O(3) 163.85(19), O(1)–Nb–O(4) 81.53(19), O(2)–Nb–O(3) 92.9(2), O(2)–Nb–O(4) 139.1(2), O(3)–Nb–O(4) 95.2(2), C(5)–O(1)–Nb 123.6(5), C(10)–O(1)–Nb 120.9(4), C(20)–O(2)–Nb 150.7(4), C(30)–O(3)–Nb 119.6(4), C(40)–O(4)–Nb 141.9(5).



Fig. 6. Schakal plot of [Nb(NDipp)(Mecalix)] (15). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): Nb–N 176.8(3), Nb–O(1) 235.9(3), Nb–O(2) 192.9(3), Nb–O(3) 195.2(3), Nb–O(4) 191.2(3); C(50)–N–Nb 177.1(3), C(5)–O(1)–Nb 132.1(3), C(10)–O(1)–Nb 112.5(2), C(20)–O(2)–Nb 149.2(3), C(30)–O(3)–Nb 111.4(2), C(40)–O(4)–Nb 157.4(3), N–Nb–O(1) 94.49(12), N–Nb–O(2) 106.22(15), N–Nb–O(3) 100.23(13), N–Nb–O(4) 110.67(15), O(1)–Nb–O(2) 80.80(11), O(1)–Nb–O(3) 165.25(10), O(1)–Nb–O(4) 79.25(11), O(2)–Nb–O(3) 95.92(12), O(2)–Nb–O(4) 139.06(12), O(3)–Nb–O(4) 94.48(11).



Scheme 3. Synthesis of calix[4]arene methyl ether stabilized niobium and tantalum imido complexes.

moderate isolated yields (50-60%) as white to orange solids, depending on the metal atom and the organic rest R (see Scheme 3). Since earlier studies revealed that in tert butyl imido complexes, the [M=NtBu] linkage is more basic and reactive compared to aryl imido complexes, we put special emphasis on the synthesis of the complexes [M(NtBu)(Mecalix)] (M = Nb 12, M = Ta 16). In both cases the reaction proceeds rather smoothly, but due to the good solubility of the compounds in non polar solvents yields drop during purification. Proton and carbon NMR spectra of these complexes are in accordance with a C_s symmetrical structure, which indicate either a monomeric or a dimeric, imido or calixarene bridged structure. During investigations on the reactivity of [Nb₂(calix)₂]²⁻, Floriani et al. achieved the synthesis of a phenyl imido calix[4]arene complex $[{Nb(NPh)(calix)}_2]^-$ [25], which adopts – in contrast to the isoelectronic molybdenum complex - a dinuclear, calixarene-bridged structure in the solid state. The complex [{Ta(NPh)(Mecalix)}₂], prepared by reacting $[Ta(\eta^4-C_4H_6)(Mecalix)]$ and phenyl azide [11b], is an imido bridged dimeric molecule in the solid state. According to mass spectroscopy, however, the complexes prepared here are monomeric under EI/MS conditions showing the molar peak for a mononuclear species in both cases. Unfortunately, we were not able to obtain crystals suitable for an X-ray analysis of the complexes 12 and 16, but we succeeded with crystal growth of the complexes 13 and 15 (see Figs. 5 and 6). In both cases the molecular structure of these compounds reveal monomeric complexes. The coordination polyhedron around the niobium centers resemble a distorted trigonal bipyramid with the atoms O(2), O(4) and N defining the equatorial plane and O(1)and O(3) atoms in the axial positions. The distances Nb-N of 178.1(5) and 176.8(3) pm indicate triple bond character of the Nb-N linkage [19]. First investigations on the reactivity of 12 and 16 demonstrated that these tert butyl imido complexes do not undergo tert butyl/arylamine exchange reactions. Further investigations concerning the reactivity of these compounds are currently in progress.

4. Conclusion

Calix[4]arene-stabilized imido complexes of group 5 metals are rare and have not been explored systematically. We are reporting here the synthesis and characterization of calix[4]arene methyl ether stabilized group 5 imido complexes. The reaction of imidovl chlorides $[V(NR)Cl_3]$ (R = Ph 1, Tol 2, tBu 3) and calix[4]arene methyl ether H₃Mecalix unexpectedly led to formation of the structurally characterized vanadium (IV) complex [VCl(Mecalix)] (4). Calix[4]arene methyl ether stabilized imido complexes of the type [V(NR)(Mecalix)] (R = Ph 7, Tol 8, tBu 9) have been obtained from the reaction of $[V(NR)Cl_3]$ (R = Ph 1, Tol 2, tBu 3) and the tris(lithium) or tris(sodium) salt of the calix[4]arene ether. The lithium salt 5 is a dimer in the solid state, in which two monomeric trianions are bridged by lithium cations. Imido complexes [M(NR)(Mecalix)] (M = Nb; R = tBu, 12, R = Tol 13, R = Mes 14, R = Dipp15; M = Ta: R = tBu 16, R = Tol 17) have been prepared from structurally characterized [NbCl₂(Mecalix)] (10) or previously known [TaCl₂(Mecalix)] (11) via reaction of the dichlorides with the lithium or potassium amides of the corresponding primary amines. The molecular structures of 13 and 15 confirm the mononuclear nature of these complexes comprising short Nb-N distances, which are in accordance with triple bond character of the niobium nitrogen linkage.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC-608832 to CCDC-608837. Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223 336 033 or deposit@ccdc.cam.uk or via www.ccdc.cam.ac. uk/conts/retrieving.html).

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