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The Stepwise Four- and Six-Electron Reduction of Carbon Monoxide to Oxyalkylidyne, to Carbide and Oxide, Then to Carbide over an Nb−Oxo Surface Modeled by Calix[4]arene[1]

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The reductive cleavage of carbon monoxide by using organometallic fragments represents a discrete homogeneous analogue to the CO dissociation to carbide and oxide on many metal surfaces.[2] The few existing homogeneous analogues of the CO dissociation, which are mainly due to Wolczanski,[3] Chisholm,[4] and Cummins,[5] often follow convoluted pathways, as is also the case in cluster chemistry.[2d] We report here how the Nb═Nb (d^2-d^2)[6] unit bonded to the *p*-Bu^t-calix[4]arene tetraanion [(Nb═Nb){*p*-Bu^t-calix[4]-$(O)_4$}$_2$Na$_2$],[7] **1** (Scheme 1) assists the stepwise reductive cleavage of carbon monoxide with the formation of two different kinds of carbides. Complex **1**, which is able to perform the four-electron reduction of dinitrogen[8] and ketones,[9] reacts with carbon monoxide (1 atm, −40 °C), leading to the oxyalkylidyne dianion **2**,[10] (Scheme 1 and Figure 1)[11] occurring in a tetranuclear ion-pair form made up by two dianions bridged by four sodium cations.[12]

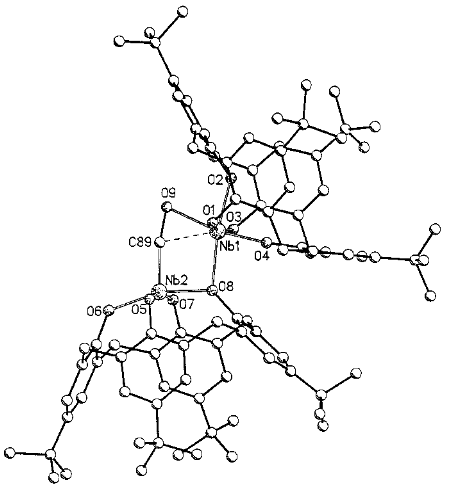
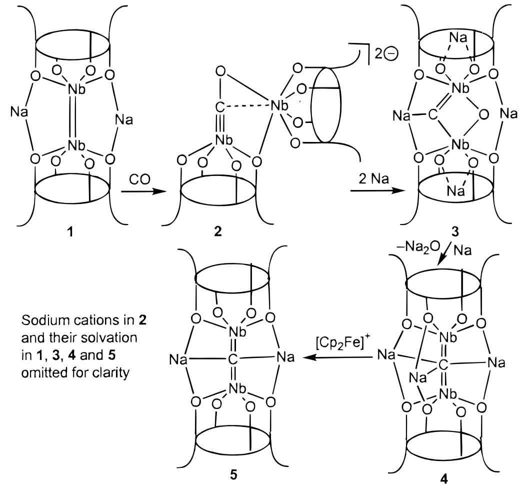


Figure 1. A plot showing one of the two dianionic dimers of compound **2**. Selected bond distances (Å) and angles (deg): Nb2−C89, 1.83(1); C89−O9, 1.32(1); Nb1−C89, 2.22(1); Nb1−O9, 2.154(7); Nb1···Nb2, 3.123(2); Nb2−C89−O9, 169(1).

Scheme 1



The structural parameters of the [Nb$_2$CO] fragment in **2**, [{*μ*-*p*-Bu^t-calix[4]-$(O)_4$}Nb≡C−O−Nb{*p*-Bu^t-calix[4]-$(O)_4$}Na$_2$] (Scheme 1), prove the four-electron reduction of carbon monoxide, with the two Nb ions playing completely different roles. Referring to Figure 1, one can observe that Nb2 bears the oxyalkylidyne anion [Nb2−C89, 1.83(1) Å; C89−O9, 1.32(1) Å; Nb2−C89−O9, 169(1)°], which is η^2-C,O bonded to Nb1 functioning as a Lewis acid, binding at a shorter distance the oxygen than the carbon [Nb1−O9, 2.154(7) Å; Nb1−C89, 2.22(1) Å].[13] Both the Nb2−C89 bond length and the ^{13}C chemical shift of the alkylidyne carbon at 238.9 ppm are in agreement with the values reported by Lippard.[14] In the aforementioned reduction of CO, one should not disregard the driving force associated with the strong oxygen−alkali cation interactions. The further reduction of **2** using 2 equiv of sodium metal led to the cleavage of the residual C−O bond and the formation of **3**,[14] [Nb$_2$(*μ*-C)(*μ*-O)-{*p*-Bu^t-calix[4]-$(O)_4$}$_2$Na$_4$], (Figure 2[15]). The two Nb-calix[4]arene

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[6] As far as the M═M reactivity is concerned, the reactivity of **1** has very few analogues, the closest one being the [W$_2$(OR)$_8$], containing a d^2-d^2-W═W unit: Chisholm, M. H.; Folting, K.; Lynn, M. A.; Streib, W. E.; Tiedke, D. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 52 and references therein.

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[10] Synthesis of **2**. A cold (−40 °C) THF (290 mL) solution of **1** (17.71 g, 9.06 mmol), prepared under argon atmosphere in a 500 mL flask was saturated with CO. Stirring at −40 °C was maintained over 12 h, CO was replaced with N_2, and the resulting blue suspension was filtered (keep all glassware cold). Volatiles were removed in vacuo (0 °C), the deep blue residue was suspended in cold *n*-pentane (30 mL) and stored overnight at −23 °C (11.46 g, 64%). Anal. Calcd for **2**·Na$_2$(THF)$_6$: $C_{113}H_{152}Na_2Nb_2O_{15}$, C 68.47, H 7.73. Found: C 68.42, H 7.71. ^{1}H NMR (C_6D_6, 298 K, ppm): δ 7.39 (m, 1H, ArH), 7.32 (m, 1H, ArH), 7.26 (m, 1H, ArH), 7.21−7.01 (m, 10H, ArH), 7.03 (m, 1H, ArH), 6.92 (m, 1H, ArH), 6.90 (m, 1H, ArH), 5.51 (d, J = 12.8 Hz, 1H, *endo*-CH$_2$), 5.37 (d, J = 12.0 Hz, 1H, *endo*-CH$_2$), 5.29 (d, J = 11.6 Hz, 1H, *endo*-CH$_2$), 5.05 (d, J = 12.0 Hz, 1H, *endo*-CH$_2$), 4.87 (d, J = 13.2 Hz, 1H, *endo*-CH$_2$), 4.82 (d, J = 11.2 Hz, 1H, *endo*-CH$_2$), 4.71 (d, J = 12.4 Hz, 1H, *endo*-CH$_2$), 4.24 (d, J = 13.6 Hz, 1H, *endo*-CH$_2$), 4.07 (d, J = 13.6 Hz, 1H, *exo*-CH$_2$), 3.80 (d, J = 13.2 Hz, 1H, *exo*-CH$_2$), 3.56 (d, J = 12.8 Hz, 1H, *exo*-CH$_2$), 3.43−3.33 (m, 4H, *exo*-CH$_2$) overlapping with 3.34 (m, 24H, THF), 3.21 (d, J = 12.4 Hz, 1H, *exo*-CH$_2$), 1.53 (s, 9H, Bu^t), 1.31 (m, 24H, THF), 1.23 (s, 9H, Bu^t), 1.13 (s, 9H, Bu^t), 1.06 (s, 9H, Bu^t), 1.02 (s, 9H, Bu^t), 0.90 (s, 9H, Bu^t), 0.85 (s, 9H, Bu^t), 0.84 (s, 9H, Bu^t). ^{13}C NMR (C_6D_6, 298 K, ppm): 238.9 (^{13}*C*O). Detection of the ^{13}C resonance was much easier when 30% enriched ^{13}CO was employed. Crystals suitable for X-ray analysis were grown at −23 °C in a toluene/hexane solution and contain THF and toluene of crystallization, **2**·Na$_2$·THF·6C_7H_8.

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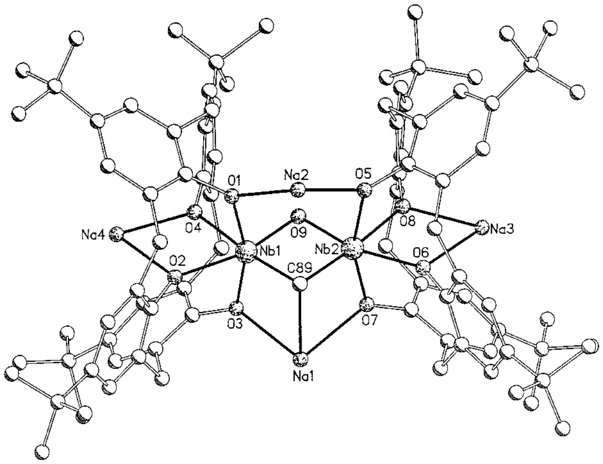

Figure 2. A view of compound **3** (solvent molecules omitted). Selected bond distances (Å) and angles (deg): Nb1−C89, 1.966(5); Nb2−C89, 1.968(5); Nb1−O9, 1.945(3); Nb2−O9, 1.939(3); C89···O9, 2.696(6); Nb1···Nb2, 2.8302(8); Na1−C89, 2.625(5); Nb1−C89−Nb2, 92.0(2).

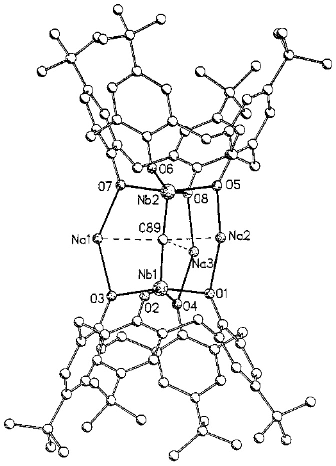

Figure 3. A view of compound **4** (solvent molecules omitted). Selected bond distances (Å) and angles (deg): Nb1−C89, 1.925(4); Nb2−C89, 1.919(3); Na1−C89, 2.698(4); Na2−C89, 2.745(4); Na3−C89, 2.876(4); Nb1−C89−Nb2, 173.9(2).

moieties are joined by a μ-carbido and a μ-oxo ligand [Nb−O9$_{av}$, 1.942(3) Å; Nb−C$_{av}$, 1.967(5) Å], the latter distance being rather close to that found in a series of Nb-alkylidene functionalities.[9] The bent bonding mode of a carbido bridging two transition metal ions in dinuclear complexes is unique.[16] The quite short interaction of C89 with one of the sodium cations [Na1···C89, 2.625(5) Å][17] exemplifies the attack at the nucleophilic carbide by an electrophile. Such an interaction, observed in a metalated alkylidyne,[5] accounts for the ^{13}C NMR (C_6D_6) chemical shift of the carbido ligand at 268.9 ppm, which does not differ very much from that of a bridging alkylidyne.[9]

The reductive cleavage of C−O from **2** to **3** was followed by the reductive deoxygenation of **3** and the formation of a linear bridging carbido compound, **4**,[15] [{p-Bu^t-calix[4]-(O)$_4$}$_2$Nb$_2$-(μ-C)(μ-Na)$_3$], with the loss of the μ-oxo ligand (Scheme 1). Complex **4** is paramagnetic with a $\mu_{eff} = 1.65\ \mu_B$ at 300 K and displays a 19 lines EPR spectrum (^{93}Nb, 100%, $I = {}^9/_2$) at 153 K in the solid state, with $g_{iso} = 1.96$ and $A_{iso} = 119.4$ G. These features are entirely consistent with a d^1 Nb(V)−Nb(IV), in which the single electron is delocalized. Some serendipity is associated with the formation of **4**, which is a quite reproducible species, and for which a better synthesis is underway.[15] The formation of **4**, even when the correct **2**/Na stoichiometry is used, can be explained by the sodium reduction of **3**[15] being of comparable rate to that of **2**. The structure of **4** is in Figure 3.[18] The Nb−C−Nb fragment is almost linear [Nb1−C89−Nb2, 173.9(2)°], while the Nb−C$_{av}$ distance [1.922(4) Å] is well in agreement with the Nb=C(alkylidene).[9] The carbido anion interacts with the three sodium cations at distances varying from 2.698(4) to 2.876(4) Å. The oxidation of **4** with 1 equiv of Cp$_2$FeBPh$_4$ led to the diamagnetic complex **5**, which shows a typical ^{13}C NMR resonance for the bridging carbide at 257 ppm.[19]

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, bond distances and angles, and supplementary drawings for **2**, **3**, and **4** (PDF). This material is available free of charge via the Internet at htpp://pubs.acs.org.

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(11) Crystal data for {**2**·Na$_2$·THF}$_2$·12C$_7$H$_8$: C$_{186}$H$_{224}$Na$_4$Nb$_4$O$_{20}$.12C$_7$H$_8$, $M = 4348.86$, monoclinic, space group $P2_1/n$, $a = 33.616(7)$ Å, $b = 20.224(4)$ Å, $c = 39.946(8)$ Å, $\beta = 106.77(3)°$, $V = 26002(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.111$ g/cm^3, $F(000) = 9232$, λ(Mo Kα) = 0.71070 Å, μ(Mo$_{K\alpha}$) = 0.236 mm^{-1}; crystal dimensions 0.20 × 0.15 × 0.11. For 14 131 observed reflections [$I > 2\sigma(I)$] and 2136 parameters, the conventional R is 0.1179 (wR2 = 0.3589 for 22411 independent reflections). Data were collected on a mar345 Imaging Plate at 143 K.

(12) The overall structure and the polynuclear skeleton is given in the Supporting Information.

(13) Such a bonding mode has been found for one of the CO bonds in (η^5-C$_5$H$_5$)$_3$Nb$_3$(CO)$_7$, see ref 2k.

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(15) Synthesis of **3** and **4**: Sodium metal (0.26 g, 11.18 mmol) was added to a deep blue THF (100 mL) solution of **2** (11.08 g, 5.59 mmol). Stirring was maintained over 2 d, resulting in a brown suspension. The solvent was concentrated (30 mL), and **3** was collected as a light brown powder (7.5 g, 60%). Anal. Calcd for **3**·12THF, C$_{137}$H$_{200}$Na$_4$Nb$_2$O$_{21}$: C 66.87, H 8.19. Found: C 66.94, H 7.96. ^{1}H NMR (py, 298 K, ppm): δ 7.03 (br, 16H, ArH), 5.04 (d, $J = 13.2$ Hz, 8H, *endo*-CH$_2$), 3.63 (m, 48H, THF), 3.16 (br, 8H, *exo*-CH$_2$),, 1.59 (m, 48H, THF), 1.37 (br, 36H, Bu^t), 0.81 (br, 36H, Bu^t). ^{1}H NMR (py-D$_5$, 354 K, ppm): δ 7.10 (s, 16H, ArH), 5.01 (d, $J = 13.2$ Hz, 8H, *endo*-CH$_2$), 3.71 (m, 48H, THF), 3.23 (d, $J = 13.2$ Hz, 8H, *exo*-CH$_2$), 1.73 (m, 48H, THF), 1.22 (s, 72H, Bu^t). ^{13}C NMR (C$_6$D$_6$, 298 K, ppm): δ 268.9 (μ-C) [^{13}CO 30% enriched was used]. Crystals suitable for X-ray analysis were grown at −23 °C in a benzene/TMEDA solution, as **3**·4TMEDA·2C$_6$H$_6$. The product is very soluble in hydrocarbons, poorly soluble in THF, and soluble in hot pyridine (80 °C). From the mother liquor, evaporating the THF under reduced pressure and washing the residue with n-pentane (30 mL), **4** was isolated as a brown paramagnetic powder (2.02 g, 17%). A selective synthesis of **4** has been subsequently performed, reducing **3** with 1 equiv of sodium metal (35%). Anal. Calcd for **4**·9THF, C$_{125}$H$_{176}$Na$_3$Nb$_2$O$_{17}$: C 68.07, H 8.04. Found: C 68.33, H 7.82. $\mu_{eff} = 1.65\ \mu_B$ at 300 K. Crystals suitable for X-ray analysis were grown in a pentane solution.

(16) Crystal data for {**3**·TMEDA$_4$}·2C$_6$H$_6$: C$_{113}$H$_{168}$N$_8$Na$_4$Nb$_2$O$_9$.2C$_6$H$_6$, $M = 2216.55$, monoclinic, space group $P2_1/c$, $a = 12.982(2)$ Å, $b = 36.694(7)$ Å, $c = 26.359(5)$ Å, $\beta = 91.23(2)°$, $V = 12554(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.173$ g/cm^3, $F(000) = 4736$, λ(Mo Kα) = 0.71070 Å, μ(Mo$_{K\alpha}$) = 0.252 mm^{-1}; crystal dimensions 0.32 × 0.26 × 0.16. For 9928 observed reflections [$I > 2\sigma(I)$] and 1310 parameters, the conventional R is 0.0622 (wR2 = 0.1819 for 17 835 independent reflections). Data were collected on a mar345 Imaging Plate at 143 K.

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(19) Crystal data for {**4**·THF$_6$}·6THF: C$_{113}$H$_{152}$Na$_3$Nb$_2$O$_{14}$.6C$_4$H$_8$O, $M = 2421.76$, monoclinic, space group $P2_1/c$, $a = 33.504(4)$ Å, $b = 13.289(2)$ Å, $c = 31.235(4)$ Å, $\beta = 108.08(2)°$, $V = 13220(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.217$ g/cm^3, $F(000) = 5188$, λ(Mo Kα) = 0.71070 Å, μ(Mo$_{K\alpha}$) = 0.247 mm^{-1}; crystal dimensions 0.33 × 0.27 × 0.20. For 14 902 observed reflections [$I > 2\sigma(I)$] and 1488 parameters, the conventional R is 0.0590 (wR2 = 0.1796 for 20 855 independent reflections). Data were collected on a mar345 Imaging Plate at 143 K.

(20) Synthesis of **5**: Cp$_2$FeBPh$_4$ (0.386 g, 0.764 mmol) was added to a cold (0 °C) solution of **4** (1.710 g, 0.775 mmol). The reaction mixture was allowed to reach room temperature under stirring, it was filtered, volatiles were removed in vacuo, the yellow residue washed with n-pentane (30 mL), and collected (0.324 g, 21%). Anal. Calcd for **5**·6THF, C$_{113}$H$_{152}$Na$_2$Nb$_2$O$_{14}$: C, 69.03; H, 7.80. Found: C, 68.85; H, 7.95. ^{1}H NMR (C$_5$D$_5$N, 298 K, ppm): δ 7.14 (s, 16H, ArH), 5.15 (d, $J = 11.6$ Hz, 8H, *endo*-CH$_2$), 3.64 (m, 24H, THF), 3.20 (d, $J = 11.6$ Hz, 8H, *exo*-CH$_2$), 1.59 (m, 24H, THF), 1.14 (s, 72H, Bu^t). ^{13}C NMR (C$_5$H$_5$D, 298 K, ppm): δ 257 (μ-C) [30% enriched ^{13}CO was used in the reaction sequence].