Experimental Section

Electrochemical measurements were carried out using a potentiostat/galvanostat Model 273A (EG&G Prinston Applied Research). A three-electrode scheme was used with a working glassy carbon electrode, saturated AgCl/Ag reference electrode, and an auxiliary Pt electrode. GO from *Aspergillus niger* (EC1.1.3.4, 285 U mg^{-1}) was a Serva preparation. Ruthenium(II) complexes were prepared as described.[17]

Modification of GO by Ru^{II}: To a solution of **2** (1 mL, 9.8×10^{-4} M) in 0.01 M phosphate buffer (pH 5.5) a weighed amount of GO (20.5 mg) was added (Ru:GO ratio 7:1) to yield a brownish red solution. The mixture was kept at room temperature for 4 h during which the solution faded, which was attributed to binding to GO and partial oxidation of Ru^{II} to Ru^{III}. The solution was then dialyzed against 0.01 M phosphate buffer (1 L, pH 7.0) for 48 h at 5 °C, and the buffer was changed at least twice. A green solution was finally formed indicative of complete oxidation of Ru^{II} to Ru^{III}. Analysis of the dialyzed solution by differential pulse voltammetry indicated the absence of free ruthenium complex not bound to GO . The amount of protein in the sample as determined according to the Lowry method was 17.1 mg mL^{-1}; the activity determined spectrophotometrically with respect to DCIP was 73.4 % relative to the native GO with 100 % activity. Modification of GO by **1** was carried out in a similar way by using a Ru to GO ratio of 3.5:1. The activity was 82 %.

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Neutral, Cationic, and Anionic Alkyl Derivatives of Tungsten Bonded to a Calix[4]arene Oxo Surface[**]

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Particular attention is focused on those systems which can mimic at the molecular level the chemical behavior of M–C functionalities bonded to an oxo surface.[1] The most common approach employs alkoxo and phenoxo groups as ancillary ligands.[2] However, a quite recent and significant advance in the field was achieved with the preorganized set of oxygen donor atoms from calix[4]arenes,[3] which bear a number of unique peculiarities[4] within this context. We report here the generation of a dimethyl tungsten(VI) derivative bonded to an O_4 set of donor atoms, its conversion into an unsaturated monomethyl cation, and its very peculiar redox behavior.

The alkylation of *cis*-[(Cl)$_2$W{*p*-*t*Bu-calix[4]-(O)$_4$}][5] (**1**) is strongly dependent on the alkylating agent. The use of carbanionic, reducing species, like lithium and magnesium organometallic compounds, led straight to the corresponding anionic alkylidynes,[4b] while the use of $ZnMe_2$ in toluene in a 1:1 ratio led cleanly to *cis*-[(Me)$_2$W{*p*-*t*Bu-calix[4]-(O)$_4$}] (**2**, Scheme 1). The use of smaller amounts of $ZnMe_2$ produced mixtures of **1** and **2**. The monoalkyl derivative [(Cl)(Me)W-{*p*-*t*Bu-calix[4]-(O)$_4$}] (**3**) could be best prepared by photolysis of **1** in CH_2Cl_2 in the presence of an excess of pyridinium hydrochloride (PyHCl). As **1** does not react with PyHCl in the dark and the photolysis of **1** in C_6D_6 led to evolution of methane and ethylene (^{1}H NMR), we believe that PyHCl traps an unstable methylene species generated by photolysis.[6, 7] Compound **3** was also obtained by a ligand exchange reaction of **2** with $SnCl_4$.

The apparent C_{4v} symmetry of the calix[4]arene fragment, as determined from the ^{1}H NMR spectra at 298 and 193 K, is a consequence of the equal availability of d_{xz} and d_{yz} as well as d_{z^2} orbitals for binding of the two methyl groups. This result emphasizes the very high mobility of the alkyl groups between two equivalent positions over the oxo surface and the absence of a significant energy barrier for movement of the methyl groups between them. In the case of **3**, the C_{4v} symmetry at 298 K is modified to C_s in the ^{1}H NMR spectrum measured at 188 K. The difference in the metal-to-ligand bonding mode for Me (σ only) and Cl substituents (σ and π) is a factor in the increased barrier to mobility of the ligands Me and Cl over the oxo surface.

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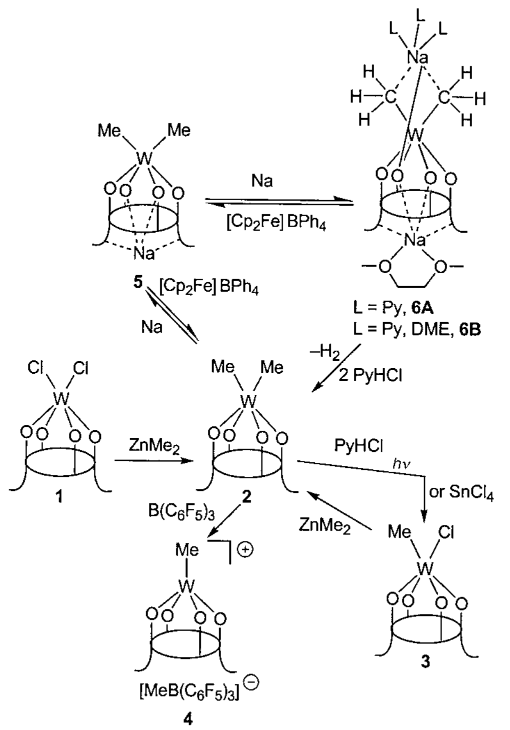

Scheme 1. Synthesis and reactivity of **2**. Py = C_5H_5N.

Complexes **1**–**3** do not undergo any ligand exchange reaction.[4d] The methyl group can be transfered to particularly strong Lewis acids—namely, $[B(C_6F_5)_3]$[8]—to form the cationic monomethyl derivative $[(Me)W\{p\text{-}t\text{Bu-calix[4]-}(O)_4\}]^+[MeB(C_6F_5)_3]^-$ (**4**), whose proposed structure is supported by an X-ray analysis (Figure 1).[9]

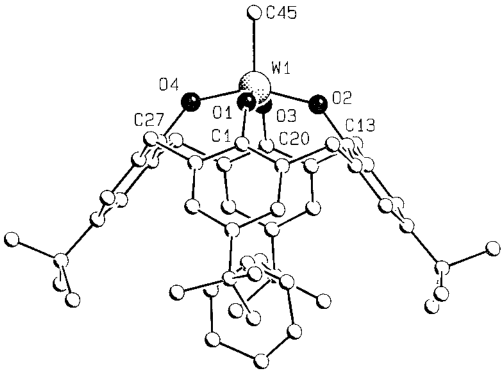

Figure 1. SCHAKAL view of the cation in complex **4**. Selected bond lengths [Å]: W–O 1.837 (av), W1–C45 2.055(8).

The tungsten atom in **4** exhibits a square-pyramidal coordination geometry. The W–C45 bond length (2.055(8) Å) is in agreement with a W–C σ bond.[10] The W–C45 direction is perpendicular to the plane formed by the O_4 core, from which tungsten is displaced by 0.425(1) Å towards the methyl group. The W–O bond lengths, which are not significant different from each other (mean value 1.836(3) Å), are in agreement with a significant metal–oxygen π interaction.[11] The calix[4]arene unit is in a cone conformation, as is usually found in square-pyramidal pentacoordinated metals.[4, 12]

A particularly interesting reaction is the stepwise reduction of **2** with sodium metal (Scheme 1). Such a reaction is related to what occurs in the solid state rather than in molecular organometallic systems. Complex **2** can be reduced[13] to *cis*-$[(Me)_2W\{p\text{-}t\text{Bu-calix[4]-}(O)_4\}Na]$ (**5**) and subsequently to *cis*-$[(Me)_2W\{p\text{-}t\text{Bu-calix[4]-}(O)_4\}Na_2]$ (**6**). The reduction of **2** does not produce any change in connectivity for the overall structure. Compounds **5** and **6** can be oxidized back to **2** with stoichiometric amounts of $[Cp_2Fe]BPh_4$ (Cp = C_5H_5). The diamagnetism of complex **6** is particularly significant in view of the two available d_{xy} and d_{yz} frontier orbitals centered at the metal,[4d, 4e] and supports a significant energy separation between them (d_{xy} is lower in energy). The NMR spectrum of **6** shows peculiar chemical shifts of the calix[4]arene skeleton which are highly affected by the temperature.

Complex **6** was crystallized from pyridine/1,2-dimethoxyethane (DME), and its structure determined (Figure 2).[14] In the asymmetric unit there are two crystallographically independent $[(Me)_2W\{p\text{-}t\text{Bu-calix[4]-}(O)_4\}Na(dme)]^-$ ions interacting through the O4 oxygen atom with a sodium cation, which is bonded to three pyridine molecules in the A anion and to a pyridine and a dme molecule in the B anion.[12] The geometries of the two anions are very similar. As a consequence of the hexacoordination of tungsten,[5] the calixarene ligand assumes a flattened cone conformation. The alkali cation is solvated by oxygen atoms from the calix[4]arene and coordinated dme molecule, and interacts in a η^6 fashion with the arene (C22–C27).[12]

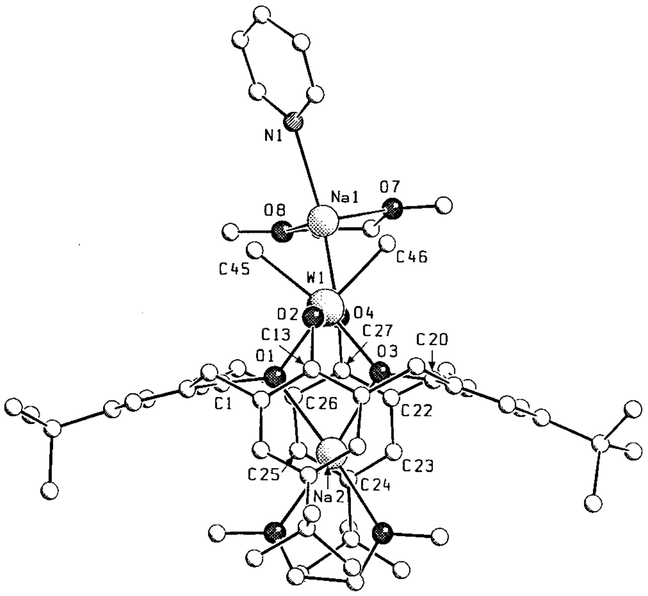

Figure 2. SCHAKAL view of molecule A in complex **6**. Selected bond lengths [Å] and angles [°]: W–O 2.031 (av), W1–C45 2.197(14), W1–C46 2.208(16); C45-W1-C46 96.4(6), O2-W1-O4 167.8(4), O1-W1-O3 77.9(3).

The tungsten atom of **6** exhibits a pseudo-octahedral coordination involving the O_4 core of the calixarene and two methyl groups (C45, C46). Bonds in the coordination sphere of tungsten are lengthened with respect to the corresponding ones in complex **4**; the lengthening (as calculated with the mean values) are 0.206(9) and

0.126(15) Å for the W–O and W–C bonds, respectively. The methyl groups should be considered as bridging tungsten and sodium ions, the contact distances being rather short (Na1 ⋯ C45 2.844(15), Na1 ⋯ C46 3.023(17) Å). The occurrence of **6** in such an ion-pair form with two methyl groups chelating a sodium cation is extremely promising for the chemical reactivity of the alkyl functionality assisted by two metal centers.

Complex **6** might be considered as being formally obtained by the addition of two NaMe units to the d^2 [W(calix[4]-arene)] fragment. However, it does not readily undergo alkyl transfer reactions, which is typical of metalated species,[15] but rather can be oxidized back to **2** without affecting the metal–carbon functionalities. The reaction of **6** with proton source like PyHCl, which leads back to **2** and hydrogen, is emblematic of the peculiarities of the system. Such a redox behavior can be explained by protonation of one of the oxygen atoms (the most basic site of the system) followed by an electron transfer from the metal-centered HOMO to the proton by the intermediacy of the oxygen, which can form a π bond with the metal. Such a behavior is quite reminiscent of a metal–oxo surface, more than a molecular system, and sheds light on the very peculiar role of the calix[4]arene ligand, making the comparison with the metal–oxo surface particularly valuable.[16]

Experimental Section

2: A 2.0 M solution of $ZnMe_2$ (17.2 mL, 34.4 mmol) in toluene was added to a suspension of **1**·$2\,C_7H_8$ (30.4 g, 28.1 mmol) in toluene (800 mL), and the resulting mixture was stirred at room temperature overnight and then at 50 °C for 5 h to give a red suspension. Bu_4NCl (8.14 g, 29.3 mmol) was added, and the suspension was stirred for 1 h at 100 °C. A solid was filtered off the hot mixture, volatile components were evaporated, and the residue was washed with pentane (300 mL) and dried in vacuo to give red **2** (yield: 18.1 g, 73 %). ^1H NMR (200 MHz, CD_2Cl_2, 298 K): $\delta = 7.19$ (s, 8H; ArH), 4.20 (d, $J(H,H) = 12.8$ Hz, 4H; *endo*-CH_2), 3.36 (d, $J(H,H) = 12.8$ Hz, 4H; *exo*-CH_2), 2.62 (s, 6H; Me), 1.24 (s, 36H; *t*Bu); ^1H NMR (400 MHz, CD_2Cl_2, 193 K): $\delta = 7.15$ (s, 8H; ArH), 4.02 (d, $J(H,H) = 13.3$ Hz, 4H; *endo*-CH_2), 3.34 (d, $J(H,H) = 13.3$ Hz, 4H; *exo*-CH_2), 2.47 (s, 6H; Me), 1.16 (s, 36H; *t*Bu); elemental analysis calcd for $C_{46}H_{58}O_4W$ (%): C 64.33, H 6.81; found: C 64.48, H 6.98.

3: A mixture of PyHCl (0.96 g, 8.30 mmol) and **2** (4.22 g, 4.92 mmol) in CH_2Cl_2 (200 mL) was irradiated under stirring for 48 h with a Xe lamp (540 $W\,m^{-2}$ at 340 nm). Volatile components were evaporated in vacuo, Et_2O (150 mL) was added, and the mixture was stirred overnight and then filtered. Volatile components were evaporated, and dark brown **3** was washed with pentane (100 mL), collected, and dried in vacuo (yield: 1.90 g, 43 %). ^1H NMR (200 MHz, $CDCl_3$, 298 K): $\delta = 7.14$ (s, 8H; ArH), 4.70 (d, $J(H,H) = 13.2$ Hz, 4H; *endo*-CH_2), 3.37 (d, $J(H,H) = 13.2$ Hz, 4H; *exo*-CH_2), 2.82 (s, 3H; Me), 1.25 (s, 36H; *t*Bu); ^1H NMR (400 MHz, CD_2Cl_2, 188 K): $\delta = 7.32$ (s, 2H; ArH), 7.18 (s, 2H; ArH), 7.10 (s, 2H; ArH), 7.06 (s, 2H; ArH), 4.67 (d, $J(H,H) = 12.8$ Hz, 2H; *endo*-CH_2), 4.22 (d, $J(H,H) = 12.8$ Hz, 2H; *endo*-CH_2), 3.46 (d, $J(H,H) = 12.8$ Hz, 2H; *exo*-CH_2), 3.34 (d, $J(H,H) = 12.8$ Hz, 2H; *exo*-CH_2), 2.68 (s, 3H; Me), 1.35 (s, 9H; *t*Bu), 1.28 (s, 9H; *t*Bu); elemental analysis calcd for $C_{45}H_{55}ClO_4W$ (%): C 61.47, H 6.31; found: C 61.48, H 6.26.

4·$1.5\,C_5H_{12}$: $B(C_6F_5)_3$ (1.47 g, 2.87 mmol) was stirred overnight with **2** (2.47 g, 2.87 mmol) in toluene (200 mL). Volatile components were removed in vacuo. The residue was washed with pentane (100 mL), collected, and dried in vacuo to give brick red **4**·$1.5\,C_5H_{12}$ (yield: 3.38 g, 80 %). ^1H NMR (200 MHz, CD_2Cl_2, 298 K): $\delta = 7.36$ (s, 8H; ArH), 4.77 (d, $J(H,H) = 13.2$ Hz, 4H; *endo*-CH_2), 3.74 (d, $J(H,H) = 13.2$ Hz, 4H; exo-CH_2) overlapping with 3.67 (s, 3H; Me), 1.23 (s, 36H; *t*Bu), 0.90 (m, 9H; pentane), 0.48 (s, 3H; Me); elemental analysis calcd for $C_{71.5}H_{76}BF_{15}O_4W$ (%): C 58.06, H 5.17; found: C 58.14, H 5.12. Crystals suitable for X-ray diffraction study were grown from a solution in C_6D_6.

5·$3\,C_4H_8O$: Compound **2** (2.34 g, 2.72 mmol) was stirred with Na (0.0625 g, 2.72 mmol) in THF (120 mL) overnight. The resulting brown solution was filtered, volatile components were evaporated, and pentane (100 mL) was added. Yellow **5**·$3\,C_4H_8O$ was then collected and dried in vacuo (yield: 0.89 g, 30 %). Elemental analysis calcd for $C_{58}H_{82}NaO_7W$ (%): C 63.44, H 7.53; found: C 63.54, H 7.57.

6·$3\,C_4H_8O$: Compound **2** (5.74 g, 6.68 mmol) was stirred with Na (0.31 g, 13.6 mmol) in THF (150 mL) overnight. The resulting brown solution was filtered and evaporated to dryness. Yellow **6**·$3\,C_4H_8O$ was washed with pentane (100 mL), collected, and dried in vacuo (yield: 5.07 g, 68 %) ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta = 9.01$ (s, 4H; ArH), 8.95 (s, 4H; ArH), 5.91 (d, $J(H,H) = 14.2$ Hz, 4H; *endo*-CH_2), 3.66 (m, 12H; THF), 2.55 (d, $J(H,H) = 14.2$ Hz, 4H; *exo*-CH_2), 1.92 (s, 18H; *t*Bu), 1.82 (m, 12H; thf), 1.41 (s, 6H; WMe), −0,28 (s, 18H; *t*Bu); ^1H NMR (400 MHz, CD_3CN, 233 K): $\delta = 9.82$ (s, 4H; ArH), 7.90 (s, 4H; ArH), 5.14 (d, $J(H,H) = 14.2$ Hz, 4H; *endo*-CH_2), 3.63 (m, 12H; thf), 2.38 (s, 18H; *t*Bu), 2.28 (d, $J(H,H) = 14.2$ Hz, 4H; *exo*-CH_2), 1.80 (m, 12H; THF), 1.44 (br s, 6H; WMe), −1.26 (s, 18H; *t*Bu); elemental analysis calcd for $C_{58}H_{82}Na_2O_7W$ (%): C 62.14, H 7.37; found: C 61.84, H, 7.42. Crystals suitable for X-ray analysis were grown in a solution in pyridine/DME.

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[12] See the deposited crystallographic data.[14b]

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[14] a) Crystal data for **6** ($C_{65}H_{83}N_3Na_2O_6W \cdot C_{59}H_{83}NNa_2O_8W \cdot C_5H_5N$): $M_r = 2475.4$, orthorhombic, space group $Pca2_1$, $a = 21.4495(9)$, $b = 14.0773(6)$, $c = 42.0251(18)$ Å, $V = 12689.5(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.296\,g\,cm^{-3}$, $F(000) = 5136$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $\mu(Mo_{K\alpha}) = 19.21\,cm^{-1}$; crystal dimensions $0.20 \times 0.29 \times 0.35$ mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-hydrogen atoms except for the disordered atoms. For 18635 unique observed reflections $[I > 2\sigma(I)]$ collected at $T = 295$ K on a Siemens SMART CCD ($5 < 2\theta < 52^\circ$) and corrected for absorption, $R = 0.082$ ($wR2 = 0.166$ for 20409 unique total data having $I > 0$). Since the space group is polar, the crystal chirality was tested by inverting all the coordinates ($x, y, z \rightarrow x, -y, -z$) and refining to convergence again. The resulting values $R = 0.095$ and $wR2 = 0.191$ indicated that the original choice should be considered the correct one. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111535 (**4**) and CCDC-111536 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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BDH-TTP as a Structural Isomer of BEDT-TTF, and Its Two-Dimensional Hexafluorophosphate Salt

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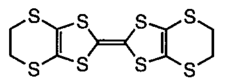
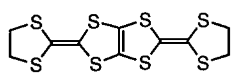
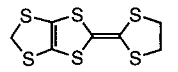
Tetrathiafulvalenes (TTFs) are highly promising π-electron donors for the exploration of new, molecular-based organic metals and superconductors.[1] Of the TTFs synthesized thus far, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is known to yield the largest number of two-dimensional superconducting salts.[2] One structural isomer of BEDT-TTF,[3] the bis-fused dihydrotetrathiafulvalene (DHTTF) compound 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (**1**, BDH-TTP), is very attractive because it contains no TTF moiety, yet it would be expected to produce organic metals that retain the metallic state down to low temperatures. This supposition is based on the results of our recent investigations which showed that a) methylenedithiodihydrotetrathiafulvalene (**2**, MDHT) forms a metallic $(MDHT)_2AuI_2$ salt which is stable down to 1.4 K, although its π-electron system is less extended than that of TTF,[4a] and b) various organic metals are obtained from the fused TTF-DHTTF donors **3a–c** which have more extended π-electron systems than TTF.[4b] Here we report the synthesis, electrochemical properties, and molecular structure of BDH-TTP as well as the conducting behavior of its charge transfer (CT) complexes and salts.



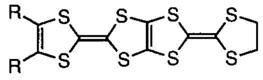
BEDT-TTF



BDH-TTP **1**



MDHT **2**



3a : R = H
3b : R = SMe
3c : R-R = $S(CH_2)_2S$

Our synthetic route to BDH-TTP (**1**) is outlined in Scheme 1. Ketone **5**, a precursor of **6**, was readily available from ketone **4** in 95 % yield.[5] Reaction of **5** with MeMgBr in THF followed by trapping with Cl_2SnBu_2 gave tin dithiolate **6**, which in a key step underwent Me_3Al-promoted coupling[6]

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