Dinuclear Molybdenum(III) and Tungsten(III) Calix[4]arene Complexes − Metal-Metal Triple Bonds Supported by Bridging Calix[4]arene Ligands[☆]

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Addition of *p-tert*-butylcalix[4]arene LH_4 to the dinuclear compounds $M_2(NMe_2)_6$ (M = Mo, W) results in the formation of $[NH_2Me_2]_2[L_2M_2]$ **1** (M = Mo) and **2** (M = W). Both compounds have been characterized by spectroscopic methods and single-crystal X-ray diffraction. The metal−metal distances of **1** and **2**, of 2.194(1) Å and 2.293(1) Å, respectively, are consistent with the retention of the M≡M triple bond. Both "ate" complexes contain a $[M≡M]^{6+}$ dimetal core, supported by two bridging μ_2-κ^2O,κ^2O-calix[4]arene ligands in the solid state. These compounds are the first examples of a formally fourfold deprotonated calix[4]arene acting as a μ_2-κ^2O,κ^2O bridging ligand for two transition metal centres. The calix[4]arenes in **1** and **2** are distorted from a *cone* conformation in the uncomplexed ligand, to an *elliptical cone* section. ^{1}H-NMR data at variable temperatures suggest fluxional behaviour of **1** and **2** in solution.

Introduction

Calixarenes and related macrocycles have received considerable attention for their host−guest chemistry, and their ability to bind metals.[1] There is currently much interest in the synthesis and structural characterization of new metallocalixarenes.[2][3][4][5] The simplest of the calixarenes, the calix[4]arene system, usually binds in an tetradentate fashion, and retains its *cone*-like appearance. In recent examples, it has been found that the calix[4]arene is capable of adopting alternative conformations in binding to metal centres, for example in an alkali-metal constrained *elliptical cone* conformation, in which the calixarene oxygen atoms adopt mutually *cis*- and *trans* sites in an octahedral geometry.[2h] There has also been an example of an *elliptical* calixarene arrangement in the absence of alkali-metal ions for mononuclear complexes.[2c]

These terminal ligating forms of the *p-tert*-butylcalix[4]-arene ligand (L) have also been reported for dinuclear complexes, strongly dependant on alkali metal binding sites. C. Floriani and co-workers have recently published studies on the reduction of $LWCl_2$ in the absence of σ-donor/π-acceptor ligands.[2g] Two dinuclear species, [Na(py)-(thf)]$_2$[L$_2$W$_2$(μ-Cl)$_2$] **A** and [μ-Na(py)$_3$][μ-Na(py)$_2$][L$_2$W$_2$] **B** were structurally characterized in the course of this investigation (see Scheme).

In the former molecule (**A**), the calix[4]arene ligand adopts an *elliptical cone* arrangement, in which the sodium ions are ligated within the calixarene cavity. Each alkali-metal ion of this dinuclear ditungsten(IV) complex interacts with two oxygen atoms and two arene entities of the phenoxide groups of the calix[4]arene ligand.

The X-ray structure analysis of the ditungsten(III) species (**B**) reveals a tetragonal prismatic environment for the


A   **B**
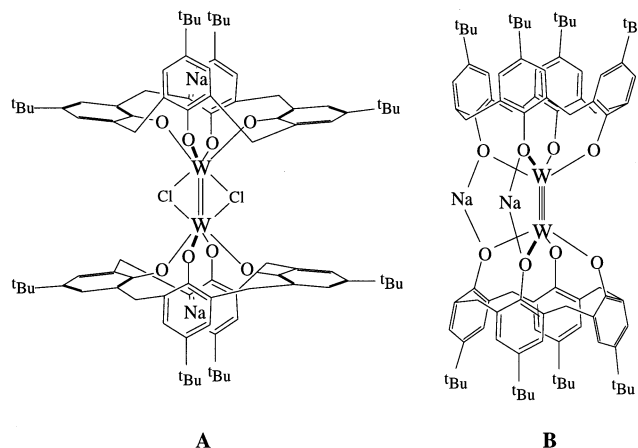
$[W≡W]^{6+}$ metal core, spanned by two terminal calix[4]arene ligands in their *cone* conformations. Each sodium atom bridges two oxygen atoms of the calix[4]arene ligands. The reported tungsten−tungsten bond length at 2.313(1) Å is in range for tungsten−tungsten triple bonds.

We herein report our preliminary findings concerning the reaction of *p-tert*-butylcalix[4]arene LH_4 with dimolybdenum- and ditungstenhexamid $M_2(NMe_2)_6$ (M = Mo, W), which resulted in the isolation and characterization of two complexes $[NH_2Me_2]_2[L_2M_2]$ **1** (M = Mo) and **2** (M = W). The central $[L_2M_2]$ moieties in **1** and **2** are isoelectronic but not isostructural to the formally double negatively charged $[L_2W_2]^{2-}$ entity of **B**. Whereas in **A** and **B**, the macrocycles are terminally coordinated to each tungsten centre, the metal-metal multiple bonds in **1** and **2** are supported by bridging calix[4]arene ligands.

Results and Discussion

The reactions of *p-tert*-butylcalix[4]arene LH₄ with the dimetallahexamides M₂(NMe₂)₆ in toluene at 100 °C gave [NH₂Me₂]₂[L₂M₂] (M = Mo, **1**; M = W, **2**) after work-up in good to excellent yields, although the formation of small quantities of side products was observed. Some of these minor products have been structurally characterized.[6] Dissolution of the main products in acetonitrile on warming up to 80 °C, and then cooling to room temperature afforded a crop of dark green crystals suitable for X-ray analysis. Each compound crystallizes in the monoclinic space group $P2_1/c$, with six non-coordinated molecules of acetonitrile. Figure 1 and Figure 2 show SCHAKAL plots of the solid state structure of the dianions of **1** (Figure 1) and **2** (Figure 2). Selected bond lengths and bond angles are given in the captions.

Figure 1. SCHAKAL drawing of the solid state structure of **1** (only the anion is depicted), showing the atom labeling scheme. Hydrogen atoms are omitted for clarity[a]
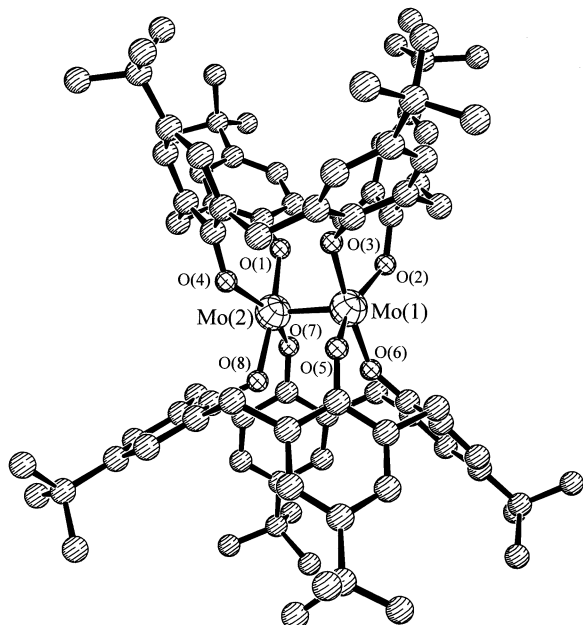
[a] Selected bond lengths [Å] and angles [°]: Mo(1)−Mo(2): 2.1938(7), Mo(1)−O(2): 2.011(2), Mo(1)−O(3): 1.970(2), Mo(1)−O(5): 2.022(2), Mo(1)−O(6): 1.938(2), Mo(2)−O(1): 1.942(2), Mo(2)−O(7): 2.016(2), Mo(2)−O(4): 1.991(2), Mo(2)−O(8): 1.979(2), O(2)−Mo(1)−O(3): 86.42(9), O(2)−Mo(1)−O(5): 155.91(10), O(2)−Mo(1)−O(6): 93.53(10), O(3)−Mo(1)−O(5): 87.53(10), O(3)−Mo(1)−O(6): 173.76(10), O(5)−Mo(1)−O(6): 90.02(10), O(1)−Mo(2)−O(4): 89.75(10), O(1)−Mo(2)−O(7): 91.81(10), O(1)−Mo(2)−O(8): 173.15(10), O(4)−Mo(2)−O(7): 155.39(10), O(4)−Mo(2)−O(8): 89.39(9), O(7)−Mo(2)−O(8): 86.16(9), O(2)−Mo(1)−Mo(2): 102.42(8), O(3)−Mo(1)−Mo(2): 92.53(7), O(5)−Mo(1)−Mo(2): 101.13(7), O(6)−Mo(1)−Mo(2): 93.57(8), O(1)−Mo(2)−Mo(1): 93.60(8), O(4)−Mo(2)−Mo(1): 102.37(8), O(7)−Mo(2)−Mo(1): 102.03(7), O(8)−Mo(2)−Mo(1): 93.23(7).

Both dimethyl ammonium counterions of the molybdenum compound **1** are located inside the calix[4]arene cavities. In the tungsten compound **2**, one cation is replaced by an acetonitrile molecule, thus leaving one dimethylammonium counterion in the cavity of one of the calix[4]arene

Figure 2. SCHAKAL drawing of the solid state structure of **2** (only the anion is depicted), showing the atom labeling scheme. Hydrogen atoms are omitted for clarity[a]
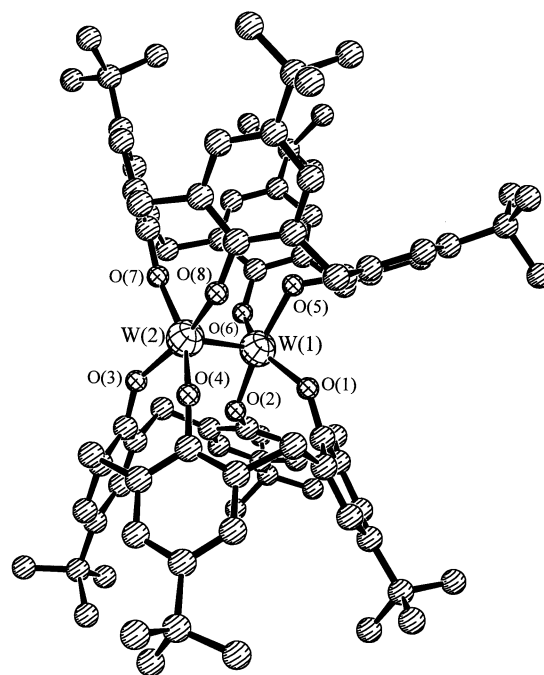
[a] Selected bond lengths [Å] and angles [°]: W(1)−W(2): 2.2926(9), W(1)−O(1): 1.976(5), W(1)−O(2): 1.958(4), W(1)−O(5): 1.998(4), W(1)−O(6): 1.985(5), W(2)−O(3): 1.973(4), W(2)−O(4): 1.989(5), W(2)−O(7): 1.949(5), W(2)−O(8): 2.051(4), O(1)−W(1)−O(2): 88.57(18), O(1)−W(1)−O(6): 149.09(19), O(1)−W(1)−O(5): 87.64(18), O(2)−W(1)−O(5): 169.56(18), O(2)−W(1)−O(6): 91.93(18), O(5)−W(1)−O(6): 86.36(18), O(3)−W(2)−O(4): 89.74(18), O(3)−W(2)−O(7): 91.53(19), O(3)−W(2)−O(8): 158.82(19), O(4)−W(2)−O(7): 153.3(2), O(4)−W(2)−O(8): 79.71(17), O(7)−W(2)−O(8): 89.92(18), O(1)−W(1)−W(2): 106.31(13), O(2)−W(1)−W(2): 94.65(14), O(5)−W(1)−W(2): 95.76(13), O(6)−W(1)−W(2): 104.46(14), O(3)−W(2)−W(1): 101.58(14), O(4)−W(2)−W(1): 105.02(13), O(7)−W(2)−W(1): 100.85(15), O(8)−W(2)−W(1): 98.89(13).

ligands [O(1)−O(4)] and leaving the other one uncoordinated (not shown in Figure 1 and 2). The C−N vector of the acetonitrile molecule is pointing out of the calix[4]arene pocket [O(5)−O(8)]. This orientation is similar to that of a previously studied inclusion complex of acetonitrile by a calix[4]arene macrocycle, tetraethyl *p-tert*-butylcalix[4]arenetetracarbonate]·MeCN.[7] The C−N−C planes of the dimethylammonium ions inside the calix[4]arene cavities of **1** are almost parallel to the planes defined by the oxygen and C$_{ipso}$ carbon atoms of the O(3),O(1) [3.4(5)°], and O(6),O(8) [2.4(5)°] phenoxide moieties. The acute angle between the C−N−C plane, and the corresponding planes of the O(5),O(7) phenoxide entities of **2** is 14.7(9)°. The smallest (calculated) distances of a calix[4]arene oxygen atom to a hydrogen atom of the ammonium counterion are 2.67 Å to O(8) in **1**, and 2.34 Å to O(3) in **2**.[8]

The metal-metal bond lengths of 2.194(1) Å (Mo−Mo) in **1**, and of 2.293 (1) Å (W−W) in **2** are in the range expected for molybdenum−molybdenum or tungsten−tungsten triple bonds.[9] The coordination sphere of the [M≡M]

unit is a distorted tetragonal prismatic (partly staggered). The smallest angles of intersection between the planes defined by O−M(1)−M(2) and O−M(2)−M(1) come to approximately 30° in **1**, and 20° to 30° in **2**. A similar $[M_2O_8]$ structural type was reported for d^3-d^3 dimers in the "ate" complexes $K_2[M_2(OCH_2tBu)_8]$ (M = Mo, W) by M. H. Chisholm and co-workers.[10]

The X-ray single crystal structure determinations show that **1** and **2** contain a $[M≡M]^{6+}$ dimetal core, supported by two bridging μ_2-κ^2O,κ^2O-calix[4]arene ligands. The complexes **1** and **2** are, to the best of our knowledge, the first examples of a formally fourfold deprotonated calix[4]arene acting as a μ_2-κ^2O,κ^2O bridging ligand for two transition metal centres. These compounds are probably best compared to $LH_2Mo_2(OAc)_2$,[3b] where a similar bridging mode was reported for the doubly deprotonated calix[4]arene ligand. In this compound, the hydrogen atoms form bonds to the phenoxide oxygen atoms of the calix[4]arene ligand, which retains the *cone* conformation and bridges two metal-metal quadruple bonded molybdenum atoms.

Both macrocyclic ligands of the molybdenum complex (**1**) are symmetrically distorted from the *cone* conformation. Each bridging calix[4]arene shows two opposing phenoxide rings − those of the oxygen atoms O_{inside} [O(1), O(3), O(6), and O(8)] − pushed away from the macrocycle and two − those of the oxygen atoms $O_{outside}$ [O(2), O(4), O(5), and O(7)] − towards the macrocycle. Thus, they define an *elliptical cone* section, along the O(1)−O(3) and O(6)−O(8) axis. As a result of this distortion, the bond distances M−O_{inside} are slightly shorter, e. g. 1.942(2) Å for Mo(2)−O(1) vs. 2.016(2) Å for Mo(2)−O(7), and the bond angles O_{inside}−M−M' are close to 90°. Consequently, the O_{inside}−M−O_{inside} angles of approximately 175.5° are much larger than the corresponding $O_{outside}$−M−$O_{outside}$ angles of approximately 155.5°.

The angle of intersection between the least square planes through the carbon atoms of the methylene bridges and the least square planes through a phenoxide moiety, defined by the oxygen atom and the C_{ipso} and C_{ortho} carbon atoms, can serve as a good measurement for the tilting of the phenoxide entities of the calix[4]arene ligand. We calculated these angles for the $O_{outside}$ phenoxide moieties to be in a range between 74.3(2)° and 76.5(2)°, and for the O_{inside} phenoxide entities between 26.9(2)° and 37.9(2)°. The appropriate angles of the mononuclear calix[4]arene complex LMoNMes (Mes = mesityl),[11] in which the calix[4]arene ligand retains the *cone*-like shape might be a good reference. We calculated for this compound an angle of 59.0(1)° on average, with values ranging from 56.7(1)° to 61.4(1)°.

The bridging calix[4]arene ligands of the tungsten compound **2** are also heavily distorted from the *cone* conformation of the parent calix[4]arene LH_4. In contrast to the symmetrical tilting in **1**, only one phenoxide group per ligand − those of O(2) and O(5) − is pushed away from the macrocycle. The angles between the planes of these moieties and the corresponding reference plane through the methylene carbon atoms are 27.0(3)° and 28.8(3)°, respectively. We attribute this difference between the ligand systems in **1** and

2 in the solid state structure to steric reasons, resulting from the slightly longer bonding distance of the tungsten−tungsten triple bond. However, in solution we could observe signals due to two different types of phenoxide groups in the low temperature ^{1}H-NMR spectrum for **1** and **2**. Both compounds show a splitting of the signals of the *tert*-butyl hydrogen atoms and aromatic protons of the *p-tert*-butylcalix-[4]arene ligand at low temperatures. At room temperature, we observe, for example, a sharp signal for the *tert*-butyl protons of **2**, and a broadened singlett in the case of **1**. These signals split on cooling to two sharp singletts at low temperatures. The coalescence temperature for this process is 252 K for the ditungsten compound **2**, and 282 K for the dimolybdenum compound **1**. These NMR data suggest fluxional behaviour of the μ_2-κ^2O,κ^2O bridging calix[4]arene ligand in solution, i.e. an interconversion of the O_{inside} and $O_{outside}$ phenoxide rings of the dinuclear compounds **1** and **2**. We calculated free activation enthalpies of 59.0 kJ/mol (**1**) and 52.2 kJ/mol (**2**) for this process. Details on the ^{1}H-NMR investigations at variable temperatures, on the characterization of side products, and on the reactivity of **1** and **2** will be given elsewhere.[6]

Experimental Section

General: All reactions and subsequent manipulations involving organometallic reagents were performed under argon atmosphere using standard Schlenk techniques. The preparation of samples for spectroscopy was accomplished by using a glove box Braun MB 150 BG-I. Solvents were dried according to standard procedures, stored over activated 4 Å molecular sieve and degassed prior use. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom% D), dried according to standard procedures and stored over activated 4 Å molecular sieves. − NMR spectra were recorded on a Bruker AC 250. ^{13}C-NMR spectra are broad-band proton decoupled (^{13}C{^{1}H}). Standard DEPT-135 experiments were recorded to distinguish -CH$_3$ and -CH type carbons from -C or -CH$_2$ type carbons in the ^{13}C-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: CDCl$_3$, δ = 7.24 (^{1}H) or natural-abundance carbon signal at δ = 77.0; C$_7$D$_8$, δ = 2.09 (^{1}H). − EI-MS spectra were recorded on a Varian MAT 3830 (70 eV). − Elemental analyses were performed by the microanalytical laboratory of the author's department. − Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 and are reported in cm^{-1}. − *p-tert*-butyl-calix[4]arene,[12] Mo$_2$(NMe$_2$)$_6$,[13] and W$_2$(NMe$_2$)$_6$,[14] were prepared as described in the literature. All other reagents were purchased from commercial sources and purified by standard techniques.

Preparation of Bis(dimethylammonium) Di-μ_2-κ^2O,κ^2O-p-tert-butylcalix[4]arenedimolybdate(III) (**1**): A solution of 250 mg (0.55 mmol) of Mo$_2$(NMe$_2$)$_6$ and 812 mg (1.10 mmol) of *p-tert*-butylcalix-[4]arene−toluene adduct in 40 ml of toluene, was stirred for 8 h at

100 °C. All volatiles were removed in vacuo, the yellow-greenish residue was washed with 20 ml of hexane and collected. Yield: 737 mg, 85%. Crystals suitable for X-ray analysis were grown in a saturated acetonitrile solution. m.p. 368 °C (dec.). − IR (KBr): $\tilde{v}$ = 3129 vs, 2959 vs, 1743 w, 1597 m, 1552 m, 1449 vs, 1391 m, 1361 m, 1290 vs, 1206 s, 1121 m, 910 s, 873 m, 828 s, 801 m, 763 m, 745 s, 730 m, 694 m, 542 vs, 467 m, 430 m, 404 m. − ^1H NMR (CDCl$_3$, 298 K) δ = 7.15 (s, br, 4 H, aromatic H), 6.87 (s, 4 H, aromatic H), 5.85 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.37 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 2.94 (s, 4 H, CH_2), 2.57 [br, 2 H, H_2N(CH$_3$)$_2^+$], 1.19 [s, br, 36 H, C(CH_3)$_3$], 0.75 [t, 6 H, $^3J_{HH}$ = 5.2 Hz, H$_2$N(CH_3)$_2^+$].− ^1H NMR (C$_7$D$_8$, 333 K): δ = 7.26 (d, 4 H, $^4J_{HH}$ = 2.6 Hz, aromatic H), 6.94 (d, 4 H, $^4J_{HH}$ = 2.6 Hz, aromatic H), 6.30 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.51 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.17 (d, 2 H, $^2J_{HH}$ = 13.4 Hz, CH_2), 2.90 [br, 2 H, H_2N(CH$_3$)$_2^+$], 2.88 (d, 2 H, $^2J_{HH}$ = 13.4 Hz, CH_2), 1.20 [s, 36 H, C(CH_3)$_3$], 0.86 [t, 6 H, $^3J_{HH}$ = 5.5 Hz, H$_2$N(CH_3)$_2^+$]. − ^1H NMR (C$_7$D$_8$, 233K): δ = 7.36 (d, 2 H, $^4J_{HH}$ = 2.0 Hz, aromatic H), 7.23 (d, 2 H, $^4J_{HH}$ = 2.3 Hz, aromatic H), 6.94 (d, 2 H, $^4J_{HH}$ = 2.0 Hz, aromatic H), 6.91 (d, 2 H, $^4J_{HH}$ = 2.3 Hz, aromatic H), 6.44 (d, 2 H, $^2J_{HH}$ = 12.4 Hz, CH_2), 3.63 (d, 2 H, $^2J_{HH}$ = 12.4 Hz, CH_2), 3.24 (d, 2 H, $^2J_{HH}$ = 13.9 Hz, CH_2), 2.88 (d, 2 H, $^2J_{HH}$ = 13.9 Hz, CH_2), 2.70 [br, 2 H, H_2N(CH$_3$)$_2^+$], 1.29 [s, 18 H, C(CH_3)$_3$], 1.17 [s, 18 H, C(CH_3)$_3$], 0.76 [br, 6 H, H$_2$N(CH_3)$_2^+$]. − ^{13}C NMR (CDCl$_3$, 298 K): δ = 31.79 [s, C(CH_3)$_3$], 33.31 (s, CH_2), 33.87 [s, C(CH$_3$)$_3$], 34.84 (s, CH_2), 37.99 [s, N(CH_3)$_2$], 123.85, 125.12 (s, aromatic CH), 128.97, 131.66 (s, aromatic C), 139.46 (s, aromatic C^{t}Bu), 164.55 (s, aromatic CO). − EI/MS (70 eV) m/z (%): 1481(63) ([L$_2$Mo$_2$ − H]$^+$), 1426(36) ([L$_2$Mo$_2$ − C$_4$H$_8$]$^+$). − C$_{92}$H$_{120}$O$_8$Mo$_2$N$_2$ (1576.7) calcd.: C 70.02, H 7.67, N 1.78; found: C 69,55, H 7.92, N 1.80.

Preparation of Bis(dimethylammonium) Di-μ_2-κ^2O,κ^2O-p-tert-butylcalix[4]areneditungstate(III) (**2**): A solution of 250 mg (0.40 mmol) of W$_2$(NMe)$_6$ and 590 mg (0.80 mmol) of *p-tert*-butylcalix[4]arene−toluene adduct in 40 ml of toluene was stirred for 8 h at 100 °C. All volatiles were removed in vacuo, the green residue was washed with 20 ml of hexane and collected. Yield: 630 mg, 90%. Crystals suitable for X-ray analysis were grown from a saturated acetonitrile solution. m.p. 446 °C (dec.). − IR (KBr): $\tilde{v}$ = 3132 vs, 2967 vs, 1742 w, 1598 s, 1553 s, 1480 vs, 1361 vs, 1312 s, 1210 s, 1120 s, 1026 m, 1008 w, 912 vs, 874 s, 829 vs, 800 s, 763 s, 729 s, 694 m, 538 vs, 463 m, 425 m, 396 m. − ^1H NMR (CDCl$_3$, 298 K) δ = 7.21 (d, 4 H, $^4J_{HH}$ = 2.2 Hz, aromatic H), 6.95 (d, 4 H, $^4J_{HH}$ = 2.2 Hz, aromatic H), 5.95 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.40 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.27 (d, 2 H, $^2J_{HH}$ = 13.4 Hz, CH_2), 3.08 (d, 2 H, $^2J_{HH}$ = 13.4 Hz, CH_2), 2.33 [s, br, 2 H, H_2N(CH$_3$)$_2^+$], 1.23 [s, 36 H, C(CH_3)$_3$], 0.66 [t, 6 H, $^3J_{HH}$ = 5.3 Hz, HN(CH_3)$_2^+$]. − ^1H NMR (C$_7$D$_8$, 298 K): δ = 7.28 (d, 4 H, $^4J_{HH}$ = 2.5 Hz, aromatic H), 6.95 (d, 4 H, $^4J_{HH}$ = 2.5 Hz, aromatic H), 6.41 (d, 2 H, $^2J_{HH}$ = 12.1 Hz, CH_2), 3.56 (d, 2 H, $^2J_{HH}$ = 12.1 Hz, CH_2), 3.48 (d, 2 H, $^2J_{HH}$ = 13.5 Hz, CH_2), 3.03 (d, 2 H, $^2J_{HH}$ = 13.5 Hz, CH_2), 2.58 [br, 2 H, H_2N(CH$_3$)$_2^+$], 1.21 [s, 36 H, C(CH_3)$_3$], 0.69 [t, 6 H, $^3J_{HH}$ = 5.2 Hz, H$_2$N(CH_3)$_2^+$]. − ^1H NMR (C$_7$D$_8$, 213 K): δ = 7.36 (s, 2 H, aromatic H), 7.23 (s, 2 H, aromatic H), 6.96 (s, 2 H, aromatic H), 6.93 (s, 2 H, aromatic H), 6.53 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.67 (d, 2 H, $^2J_{HH}$ = 12.2 Hz, CH_2), 3.54 (d, 2 H, $^2J_{HH}$ = 13.1 Hz, CH_2), 3.02 (d, 2 H, $^2J_{HH}$ = 13.1 Hz, CH_2), 2.45 [br, 2 H, H_2N(CH$_3$)$_2^+$], 1.31 [s, 18 H, C(CH_3)$_3$], 1.17 [s, 18 H, C(CH_3)$_3$], 0.62 [br, 6 H, H$_2$N(CH_3)$_2^+$]. − ^{13}C NMR (CDCl$_3$, 298 K): δ = 31.60 [s, C(CH_3)$_3$], 32.77 (s, CH_2), 33.63 [s, C(CH$_3$)$_3$], 35.44 (s, CH_2), 37.65 [s, N(CH_3)$_2$], 123.65, 125.13 (s, aromatic CH), 129.14, 131,77 (s, aromatic C), 138,95 (s, aromatic C^{t}Bu), 162.39 (s, aromatic CO). − C$_{92}$H$_{120}$O$_8$N$_2$W$_2$ (1748.8) calcd.: C 63.16, H 6.91, N 1.60, found: C 62.98, H 7.01, N 1.42.

Crystal Structure Analysis of **1**: Stoe-IPDS diffractometer (Mo-K_a radiation), T = 200(2) K; data collection and refinement: SHELXS-90[15] and SHELXL-96[16]; monoclinic, space group $P2_1/c$; lattice constants a = 26.393(5), b = 17.607(4), c = 23.468(5) Å, β = 114.59(3), V = 9917(3) Å^3, Z = 4, μ(Mo-K_α) = 0.31 mm^{-1}, $2\Theta_{max}$ = 52°; 18104 independent reflections measured, of which 14857 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 2.172 and −1.439 e/Å^3. 1088 parameters (C, O, N, Mo anisotropic, the positions of the H atoms were calculated for idealized positions); R_1 = 0.0659, wR_2 = 0.1798.

Crystal Structure Analysis of **2**: Stoe-STADI IV diffractometer (Mo-K_a radiation), T = 203(2) K; data collection and refinement: SHELXS-90[15] and SHELXL-96[16]; monoclinic, space group $P2_1/c$; lattice constants a = 23.840(8), b = 15.500(7), c = 21.935(8) Å, β = 100.85(3), V = 10015(6) Å^3, Z = 4, μ(Mo-K_α) = 2.35 mm^{-1}, $2\Theta_{max}$ = 50°; 17236 independent reflections measured, of which 13273 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 3.046 and −2.061 e/Å^3. 1118 parameters (C, O, N, W anisotropic, the positions of the H atoms were calculated for idealized positions); R_1 = 0.048; wR_2 = 0.1203. − Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-407859 and CSD-407860, the names of the authors and the journal citation.

☆ Dedicated to Professor *Hartmut Bärnighausen* on the occasion of his 65th birthday.
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