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The Ditungsten Decacarbonyl Dianion

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We report the synthesis and structural authentication of the ditungsten decarbonyl dianion in $[(OC)_5W-W(CO)_5][K(18\text{-crown-6})(THF)_2]_2$ (**1**), completing the group 6 dianion triad over half a century since the area began. The W-W bond is long [3.2419(8) Å] and, surprisingly, in the solid-state the dianion adopts a D_{4h} eclipsed rather than D_{4d} staggered geometry, the latter of which dominates the structural chemistry of binary homobimetallic carbonyls. Computational studies at levels of theory from DFT to CCSD(T) confirm that the D_{4d} geometry is energetically preferred in the gas-phase, being $\sim 18\text{ kJ mol}^{-1}$ more stable than the D_{4h} form, since slight destabilisation of the degenerate W-CO $\pi 5d_{xz}$ and $5d_{yz}$ orbitals is outweighed by greater stabilisation of the W-W σ -bond orbital. The gas-phase D_{4h} structure displays a single imaginary vibrational mode, intrinsic reaction coordinate analysis of which links the D_{4h} isomer directly to the D_{4d} forms, which are produced by rotation around the W-W bond by $\pm 45^\circ$. It is therefore concluded that the gas-phase transition state becomes a minimum on the potential energy surface when subjected to crystal packing in the solid-state.

Introduction

Transition metal-carbonyls constitute a class of molecule that has played a pivotal and fundamental role in the advancement of the theory and application of coordination and organometallic chemistries.¹ Within this family, binary homobimetallic carbonyls with unsupported metal-metal bonds, *i.e.* being free of stabilising bridging ligands, occupy a key place at the intersection of seminal developments in metal-metal bond and organometallic areas.² The solid-state structures of $[(OC)_5M-M(CO)_5]$ ($M = Mn, Tc, Re$), $[(OC)_5M-M(CO)_5]^{2-}$ ($M = Cr, Mo$), $[(OC)_4M-M(CO)_4]^{2-}$ ($M = Fe, Ru, Os$), and $[(OC)_4Co-Co(CO)_4]$ have been determined from the 1950s onwards.³ For $[(OC)_5M-M(CO)_5]^n$ ($n = 0, 2-$) complexes the D_{4d} geometry overwhelmingly dominates their solid-state structures, with only one example of D_{4h} symmetry found for Cr,⁴ but the reason for this and any resulting implications were never investigated further and so have remained unknown.⁵ However, studies on the Mn and Re derivatives have shown that kbar pressures are required to force those complexes to convert from D_{4d} into D_{4h} geometries,⁶ suggesting that the former is lower in energy than the latter. However, considering their fundamental importance, there are remarkably few solid-state structures of homobimetallic carbonyls with unsupported metal-metal bonds. This may reflect difficulties in crystallising them, or that the metal-metal bonds are weak and prone to

cleavage or require stabilising bridging ligands or coordinated counter ions.

Prominent by its absence from the exemplars above is structural authentication of the free $[(OC)_5W-W(CO)_5]^{2-}$ dianion, even though $[Na_2W_2(CO)_{10}]$ was first reported in 1963,⁷ and the Cr and Mo congeners were structurally characterised in 1970.^{3d} Much more commonly, $[W_2(CO)_{10}(\mu-X)]$ ($X =$ formally anionic ligand) moieties are known, and structural authentication of $(OC)_5W-W(CO)_5$ as an unbridged unit is limited to $\{[(THF)_2Sm(N_4Et_8)Sm(THF)]_2\{(\mu-CO)_2W_2(CO)_8\}\}$ (**I**, $N_4Et_8 = \text{meso-octaethylcalix[4]pyrrolide}$) where the $W_2(CO)_{10}$ unit has D_{4d} symmetry and is stabilised,⁸ and thus influenced, by carbonyl-bound cations as is most likely the case in $[Na_2W_2(CO)_{10}]$ itself.⁷ Thus, after almost six decades a structure of free $[(OC)_5W-W(CO)_5]^{2-}$ unperturbed by bridging ligands or stabilising counter cations has remained elusive, with the closest relative being homotrimetallic $[Na(DME)_3][(OC)_5W-W(CO)_4-W(CO)_5]$ (**II**).⁹

Here, as part of our ongoing studies into metal-metal bonding,¹⁰ we report the synthesis, structural authentication, and characterisation of $[(OC)_5W-W(CO)_5][K(18\text{-crown-6})(THF)_2]_2$ (**1**), completing the triad of structurally authenticated free group 6 homobimetallic binary metal-carbonyls. Surprisingly, the free $[(OC)_5W-W(CO)_5]^{2-}$ dianion is found to adopt a perfectly D_{4h} eclipsed geometry, instead of the D_{4d} staggered form. Computational analysis reveals that in the gas-phase the D_{4h} isomer is linked directly to the D_{4d} form along the intrinsic reaction coordinate and that the former is a transition state, which leads to the conclusion that crystal packing effects render the D_{4h} form a minimum on the potential energy surface in the solid-state.

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Results and discussion

Synthetic Considerations

Scheme 1. Synthesis of compound **1** from tungsten hexacarbonyl, potassium naphthalenide, and 18-crown-6 ether precursors.

Dropwise treatment of an equimolar THF solution of tungsten hexacarbonyl and 18-crown-6 ether with a freshly prepared solution of potassium naphthalenide in THF results in immediate formation of a bright red solution. After a three day stir, work-up of the resulting brown solution and recrystallization from THF straightforwardly gave yellow $[(OC)_5W-W(CO)_5][K(18\text{-crown-6})(THF)_2]_2$ (**1**) in 58% crystalline yield (Scheme 1).¹¹

Crystallographic Analysis

The solid-state structure of **1** (Figure 1a) confirms (i) the unsupported metal-metal bond formulation with one axial and four equatorial carbonyls per tungsten, (ii) the separated ion pair nature, and (iii) that the $[(OC)_5W-W(CO)_5]^{2-}$ dianion unit surprisingly adopts an exact D_{4h} rather than D_{4d} geometry, since the centre of the W-W bond resides on a crystallographic inversion centre. Point (iii) contrasts to the situation found in **I**,⁸ and for binary homobimetallic carbonyls generally. The W-W distance in **1** is 3.2421(8) Å, which is significantly longer than the values of 2.74 and 2.79(2) Å for the sum of the single bond covalent radii of two tungsten atoms¹² and **II**,⁹ respectively, but it is closer to the W-W bond lengths of 3.1107(6) Å in **I**⁸ and 3.2881(1) Å in $[(\eta^5-C_5Me_5)W(CO)_3]_2$.¹³ The W-C3 distance of 1.906(11) Å is shorter than the W-C2-5 distances (av. 2.033, range 2.025(11)-2.043(11) Å), and the C3-O3 distance of 1.201(13) Å is longer than the other four C-O distances (av. 1.143, range 1.133(13)-1.153(12) Å) suggesting, as anticipated, that there is more W-C back-bonding to the two axial carbonyls than the eight equatorial ones. The two $[K(18\text{-crown-6})(THF)_2]^+$ cations are unremarkable.

Spectroscopic and Electrochemical Analyses

The 1H NMR spectrum of **1** exhibits the anticipated crown and THF resonances, with no resonances in the range -8 to -12 ppm suggesting the absence of bridging hydrides that would present with ^{183}W satellites. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with the formulation of **1**, and it exhibits one very

weak resonance at 222.86 ppm, which is attributed to the equatorial CO groups, with the two axial CO groups not being observable due to the poor solubility of **1** in THF.

The ATR-IR spectrum of **1** (Figure 1b) is characteristic of such a system. Specifically, it features three bands in the carbonyl region centred at 1937 (A_{2u}), 1863 (E_u), and 1772 (A_{2u}) cm^{-1} . The first band is sharp and weaker compared to the other two that are much broader and intense, which is consistent with $[M(CO)_5]$ metal-carbonyls with local metal C_{4v} symmetry and other examples of $[(OC)_5M-M(CO)_5]^n$ complexes.^{7,8,14} The Raman spectrum of **1** (Figure 1b) features the anticipated four bands in the carbonyl region at 2019 (A_{1g}), 1960 (B_{1g}), 1904 (E_g), and 1794 (A_{1g}) cm^{-1} , whilst a strong absorption at 97 cm^{-1} (A_{1g}) can be assigned to the W-W bond stretch, which is lower than the value of 130 cm^{-1} for **I**.⁷ The latter observation is consistent with the respective W-W bond lengths of **1** and **I**, and lower than W-W quadruple bonds that typically are observed at 300 cm^{-1} .¹⁵

Figure 1. Selected characterisation data for **1**. Top: Molecular structure of the dianion component of crystalline $[(OC)_5W-W(CO)_5][K(18\text{-crown-6})(THF)_2]_2$ (**1**) at 150 K with probability ellipsoids. Selected distances are W1-W1A, 3.2421(8) Å; W1-C1, 2.037(10) Å; W1-C2, 2.026(11) Å; W1-C3, 1.906(11) Å; W1-C4, 2.043(12) Å; W1-C5, 2.025(11) Å; C1-O1, 1.139(12) Å; C2-O2, 1.148(13) Å; C3-O3, 1.201(13) Å; C4-O4, 1.133(14) Å; C5-O5, 1.153(12) Å. Bottom: Solid-state infrared and Raman spectra of **1** emphasising the carbonyl and metal-metal stretching regions.

The UV/Vis spectrum of **1** exhibits absorptions at 232, 350, and 400 nm, which is similar to isoelectronic $[(OC)_5Mn-Mn(CO)_5]$.¹⁶ The first is intense and assigned as $d \rightarrow \pi^*$ MLCT, whereas the other two are weak and assigned as $d \rightarrow d$.

The cyclic voltammogram of **1** in diethyl ether (Figure S2) reveals two well separated and almost irreversible one-

electron oxidation events ($E_{p,ox} = -0.99$ and -0.5 V) assigned as successive $W^{0/I}$ redox couples. The peak separation of 0.49 V equates to a hypothetical (noting their mostly irreversible nature) comproportionation constant of $K_{com} = 10^{8.281}$, which would classify $[(OC)_5W-W(CO)_5]^{1-}$ as a Robin-Day Class III mixed valence species. Consistent with the irreversible nature of these oxidations, we could not isolate any oxidised species by chemical oxidations, presumably due to their instability. On the basis of computational studies (see below) the electrons removed during these two oxidation events should derive from the W-W bond, which is the computed highest occupied molecular orbital (HOMO) of **1**. This nicely accounts for the observed oxidatively-induced decomposition and irreversible electrochemical behaviour, and the negative oxidation potentials are consistent with the dianionic nature of the tungsten component of **1** and that the W-W bond is computed to be diffuse and weak.

Computational Analyses

To further explore the bonding in the $[(OC)_5W-W(CO)_5]^{2-}$ dianion component of **1**, we turned to computational methods, and performed relaxed energy scans at several levels of theory (Figure 2 and Tables S1 and S2).¹¹ In-line with the structural and high pressure literature, at all levels the D_{4d} geometry is preferred; by 16.7–17.2 kJ mol⁻¹ with the B3LYP density functional and 18.4 kJ mol⁻¹ using spin-component scaled second-order Møller–Plesset perturbation theory (SCS-MP2, where singlet excitations are scaled up by 1.2, and triplet excitations down by 1/3). Coupled-cluster with single, double and perturbative triple excitations (CCSD(T)) single point energy calculations at the SCS-MP2 geometries reinforces the DFT and SCS-MP2 energies, with the D_{4h} geometry being 17.4 kJ mol⁻¹ higher than the D_{4d} isomer. The CCSD(T) T_1 diagnostic is 0.021 in both cases, suggesting that single-reference techniques should suffice. Because, for the dianion, DFT calculations compute positive eigenvalues for some Kohn-Sham orbitals, we performed further calculations with two

explicit Na^+ cations set 4 Å away from each of the axial carbonyls, however these explicit cation calculations give very similar results to those of the dianion. SCS-MP2 provides the best overall match to the crystal structure geometry (optimized variables are given in Tables S3–S5). At each level of theory, the W-W bond length shortens by about 0.1 Å going from D_{4h} to D_{4d} geometry. The introduction of the explicit Na^+ cations further reduces the W-W bond length by ~0.05 Å for B3LYP calculations, which is consistent with the situation in **1** where the Sm ions perform the same stabilising role as Na^+ .⁸

Figure 2. Relaxed energy scans of **1**, where the geometry is optimised at each point while preserving (at least) D_4 symmetry and fixing the dihedral angle. Black square: SCS-MP2, blue circle: B3LYP with Na cations, yellow circle: B3LYP, red triangle: CCSD(T) at SCS-MP2 optimised geometry. Blue arrows indicate the motion of the twisting imaginary mode at the eclipsed geometry.

The frontier Kohn-Sham orbitals of the B3LYP calculation, with explicit Na^+ cations, for the D_{4h} geometry are shown in Figure 3. The a_{1g} HOMO is the W-W σ -bond, consistent with the cyclic voltammogram, and the remaining frontier orbitals are W-CO π -bonding orbitals.

Figure 3. The frontier molecular orbitals of eclipsed (a) and staggered (b) $[(OC)_5W-W(CO)_5]^{2-}$; the W-W σ HOMO and the W-CO π bonding orbitals are shown, at the B3LYP level of theory with explicit Na cations. Only one of the doubly degenerate orbitals is shown. The isosurfaces enclose 60% of the orbital. Green: W, grey: C, red: O. Na omitted for clarity. The energy of these frontier MOs as a function of OC-W-W-CO dihedral angle is plotted (centre).

Topological analysis of the SCS-MP2 density using the quantum theory of atoms in molecules further supports the orbital-based bonding picture. The ellipticity parameter ϵ of the W-W bond critical point (BCP) is zero, as expected given the cylindrical symmetry of the a_{1g} HOMO. Whilst the delocalization index δ is essentially unchanged from D_{4h} (0.271) to D_{4d} (0.270) geometries, the increase in the BCP electron density ρ (0.029 vs 0.033 au), and the more negative energy density H (−0.007 vs −0.009 au), reflects the increase in covalency due to the shorter bond length, which is consistent with experimental structural and spectroscopic data. The low delocalisation index reflects the weakness of the bond.

To explore the gas-phase preference for the D_{4d} geometry, we analysed the energies of the frontier Kohn-Sham molecular orbitals. Key frontier orbitals, and their energies as a function of the OC-W-W-CO dihedral angle, are shown in Figure 3. Defining the W-W bond as the z-axis, as the OC-W-W-CO dihedral angle moves from D_{4h} (0°) to D_{4d} (45°) geometry, the W-CO π $5d_{xy}$ orbitals are largely unaffected; degenerate at D_{4d} (e_2), with the in- and out-of-phase combinations energetically split for D_{4h} (b_{2u} and b_{1g}) (Figure 3). The four $5d_{xz}$ and $5d_{yz}$ orbitals are slightly destabilized from D_{4h} (0°) to D_{4d} (45°), in contrast to the stabilization of the W-W σ -bond, favouring the D_{4d} geometry. With stabilization of the W-W σ -bond comes a shorter and stronger W-W bond, however the W-W σ -bond remains weak and diffuse, as reflected in the QTAIM analysis, and that the W-W σ -bond HOMO is only 32.9% and 33.6% tungsten-based for D_{4h} (0°) and D_{4d} (45°) respectively.

Frequency analysis of the gas-phase D_{4d} and D_{4h} geometries, using both B3LYP and SCS-MP2, confirms that the D_{4d} geometry is a true minimum structure, with the D_{4h} geometry corresponding to a transition state between two D_{4d} conformations; the imaginary mode of the D_{4h} structure (26.6i

cm^{-1} at SCS-MP2, Figure 2) is characterised by an intrinsic reaction coordinate (IRC) to the two D_{4d} conformations that are $\pm 45^\circ$ of it. Notably, the intensities of the carbonyl absorptions match the experimental pattern (Tables S6 and S7), and the computed W-W stretch is 117.5 cm^{-1} at the D_{4d} geometry vs 100.2 cm^{-1} when D_{4h} (and 97 cm^{-1} experimentally), again reflecting the weakened W-W bond at the D_{4h} geometry.

The majority of binary homobimetallic carbonyls adopt D_{4d} geometries in crystalline phases. For example, of the five reports of $[(\text{OC})_5\text{Cr-Cr}(\text{CO})_5]^{2-}$ four are D_{4d} whilst the fifth is D_{4h} ; with two $[\text{K}(2,2,2\text{-cryptand})]^+$ cations a D_{4h} geometry is adopted,⁴ however replacing K with Na in $[(\text{OC})_5\text{Cr-Cr}(\text{CO})_5][\text{Na}(2,2,2\text{-cryptand})]_2$ results in a D_{4d} geometry,¹⁷ but until now the reason for this was unknown. Our gas-phase calculations on $[(\text{OC})_5\text{W-W}(\text{CO})_5]^{2-}$ from DFT to CCSD(T) levels of theory consistently and decisively give a preference for the D_{4d} geometry over the D_{4h} . However, experimentally we isolate $[(\text{OC})_5\text{W-W}(\text{CO})_5]^{2-}$ in its D_{4h} form. On the basis of our structural and computational data, we conclude that crystal packing is responsible for the adoption of a D_{4h} geometry in **1**, since the predicted preference for the D_{4d} geometry is at most 20 kJ mol^{-1} , and this is certainly in the range of crystal packing forces. This implies that the gas-phase transition state becomes a minimum on the potential energy surface when subject to crystal packing forces. Inspection of the crystal packing diagram of **1** supports this view, Figure 4, since this demonstrates how the D_{4h} geometry of the dianion of **1** packs efficiently with two $[\text{K}(\text{18C6})(\text{THF})_2]^+$ cations, where each channel of $[(\text{OC})_5\text{W-W}(\text{CO})_5]^{2-}$ dianions is surrounded by four symmetrically disposed channels of $[\text{K}(\text{18C6})(\text{THF})_2]^+$ cations when viewed down the plane defined by the crystallographic a axis in between the b and c axes.

Figure 4. Crystal packing diagram for **1**.

Conclusions

To conclude, we have developed a straightforward synthesis of **1**, which contains the free ditungsten decacarbonyl dianion, completing the triad of structurally authenticated group 6 binary homobimetallic metal-carbonyls first established over half a century ago. Surprisingly, in **1** the $[(OC)_5W-W(CO)_5]^{2-}$ dianion adopts a D_{4h} (eclipsed) geometry in the solid-state and not the anticipated D_{4d} (staggered) isomer; quantum chemical calculations at several levels of theory all point to the latter geometry being intrinsically favoured in the gas-phase, with the D_{4h} structure being a rotational transition state linking D_{4d} minima. It is therefore concluded that the gas-phase transition state becomes a minimum on the potential energy surface when subjected to crystal packing in the solid-state.

Experimental

Preparation of $[(OC)_5W-W(CO)_5][K(18\text{-crown-6})(THF)_2]_2$ (**1**)

THF (20 ml) was added to a mixture of $W(CO)_6$ (0.704 g, 2.0 mmol) and 18-crown-6 (0.53 g, 2.0 mmol). THF (20 ml) was then added to a separate mixture of potassium metal (0.08 g, 2.0 mmol) and naphthalene (0.26 g, 2.0 mmol), and the mixture agitated until all the potassium was consumed. The completed potassium naphthalenide solution was added dropwise to the $W(CO)_6$ solution, instantaneously forming a red solution which was allowed to stir over 3 days, resulting in a brown solution. Volatiles were removed *in vacuo* and the resulting brown solid was washed with pentane (2×10 ml), then extracted into THF (5 ml) and filtered away from the remaining solid. Volatiles were removed *in vacuo* to afford **1** as a yellow powder. Crystals of **1** suitable for X-ray diffraction were grown from a concentrated THF solution at ambient temperature. Yield: 0.728 g, 58%. Extended drying under vacuum removes the THF as evidenced by the elemental analyses. Anal. Calc'd for $C_{34}H_{48}K_2O_{22}W_2$: C 32.55; H 3.86%. Found: C 32.80; H 3.90%. 1H NMR (500 MHz, d_8 -THF) δ : 3.64 (48H, s, CH_2), 3.62 (16H, m, $THF(O-CH_2)$), 1.78 (16H, m, $THF(CH_2-CH_2)$). $^{13}C\{^1H\}$ NMR (d_8 -THF) δ : 222.86 (s, W-CO) 70.21 (s, O- CH_2), 66.63 ($THF(O-CH_2)$), 23.33 ($THF(CH_2-CH_2)$). FTIR ν/cm^{-1} (ATR): 2905 (w), 1938 (m), 1863 (s), 1772 (s), 1467 (w), 1351 (w), 1095 (s), 959 (s), 833 (m), 576 (s). Raman ν/cm^{-1} (Neat, ≤ 15 mW): 2019 (w), 1960 (br), 1904 (m), 1794 (w), 595 (w), 447 (s), 405 (m), 97 (vs).

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Notes and references

‡ CCDC 1953958 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. All other data are available from the corresponding authors on request.

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ToC Entry

The D_{4h} isomer of $[(OC)_5W-W(CO)_5]^{2-}$ is a transition state in the gas-phase but isolated in the solid-state.