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Terphenyl Complexes of Molybdenum and Tungsten with Quadruple Metal-Metal Bonds and Bridging Carboxylate Ligands

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KEYWORDS: molybdenum, tungsten, quadruple bond, carboxylate, terphenyl ligand.

ABSTRACT: Mono- and bis-terphenyl complexes of molybdenum and composition tungsten with general $M_2(Ar')(O_2CR)_3$ and $M_2(Ar')_2(O_2CR)_2$, respectively (Ar' = terphenyl ligand), that contain carboxylate groups bridging the quadruply bonded metal atoms, have been prepared and structurally characterized. The new compounds stem from the reactions of the dimetal tetracarboxylates, $M_2(O_2CR)_4$ $(M = Mo, R = H, Me, CF_3; M = W, R = CF_3)$ with the lithium salts of the appropriate terphenyl groups (Ar' = Ar^{Xyl_2} , Ar^{Mes_2} , Ar^{Dipp_2} and Ar^{Trip_2}). Substitution of one bidentate carboxylate by a monodentate terphenyl forms a M–C σ bond and creates a coordination unsaturation at the other metal atom. Hence in $M_2(Ar')_2(O_2CR)_2$, complexes the two metal



atoms have formally a low coordination number and an also low electron count. However, the unsaturation seems to be compensated by a weak $M-C_{arene}$ bonding interaction that implicates one of the aryl substituents of the terphenyl central aryl ring, as revealed by X-ray studies performed with some of these complexes and by theoretical calculations.

INTRODUCTION

Fifty years after the recognition by Cotton and co-workers of the first metal-metal quadruple bond,¹ the study of compounds with multiple metal-metal bonds has become a mature field of research. However, in many cases intriguing structural and electronic properties of these complexes, their notable applications in inorganic, bioinorganic and organometallic chemistry, along with some fascinating aspects of their bonding characteristics, continue to attract the interest of experimentalists and theoreticians alike.^{2–9} Besides, renewed impetus to the field was provided recently by the remarkable discovery of their quintuply bonded analogues made possible by the use of bulky ligands, and by other interesting developments.^{10–14}

The majority of Mo≡Mo complexes feature a fivecoordinate (considering the metal-metal bond) paddlewheel structure. Nevertheless, in the dichromium complex Ar'CrCrAr' reported by Power and co-workers as the first stable molecule with quintuple metal-metal bonding¹⁰ (Ar' is utilized in this paper as general abbreviation for a terphenyl ligand) the bulkiness of the aryl group, C_6H_3 -2,6- $(C_6H_3$ -2,6- $iPr_2)_2$, allowed the observation of a formally two coordinated geometry, complemented for each chromium atom by a weaker $Cr-C_{arene}$ secondary interaction.^{10,14d} This involves the *ipso* carbon of a flanking aryl ring belonging to the terphenyl ligand bonded to the other metal atom. With a related approach, Tsai and coworkers succeeded in the isolation of a three coordinated Mo \equiv Mo complex using a sterically encumbered silyldiamido ligand.¹⁵

The existence of a multiply M–M bonded Ar'CrCrAr' family of complexes prompted us to investigate related Mo_2 and W_2 complexes stabilized also by terphenyl groups. We envisaged that the use as precursors of some members of the well-known series of $M_2(O_2CR)_4$ complexes with quadruple metal-metal bonds,² could lead to low-coordinate terphenyl derivatives with interesting structural properties, as a result of the replacement of bidentate carboxylate by monodentate terphenyl ligands. We also surmised that some of the new complexes might prove useful as precursors for the $(Mo_2)^{2+}$ and $(W_2)^{2+}$ analogues of the above dichromium molecules. While the latter objective has proved elusive and the targeted $(M_2)^{2+}$

complexes have not been obtained, several mono- and bis-terphenyl complexes of composition $M_2(Ar')(O_2CR)_3$ and $M_2(Ar')_2(O_2CR)_2$ have been isolated and structurally authenticated. Binuclear multiply bonded alkyl or aryl $(Mo_2)^{4+}$ complexes are scarce.^{2–4,16} Moreover, the new compounds reported present unusual four-coordinate geometries with a formal 14-electron count, and are useful precursors for other low-coordinate second and third row diorganometal(II) species that will be reported in due course. Part of this work (the molybdenum complexes 1a and 2a) has been communicated.¹⁷

RESULTS AND DISCUSSION

Bulky terphenyl ligands have been used widely to stabilize new types of metal-metal bonds between main group elements of groups 1, 2 and from group 12 to 15.^{18–21} Related complexes of some 3*d* elements have been studied too,²² and include, among others, the already cited Ar'CrCrAr' molecules.¹⁰ Arguably, use of these and other very bulky ligands^{11–13,23} aims to provide kinetic stabilization to the low coordination number complexes that they generate.

As mentioned briefly, this paper discusses the synthesis and structural characterization of molybdenum and tungsten complexes with quadruple M–M bonds stabilized by coordination to bulky terphenyl ligands and carboxylate groups. As shown in Figure 1, three $Mo_2(O_2CR)_4$ complexes (R = H, Me, CF₃), as well as the ditungsten compound $W_2(O_2CCF_3)_4$, were used as metal precursors and were reacted with the LiAr' reagents that are also presented in Figure 1.



Figure 1. $M_2(O_2CR)_4$ complexes and terphenyl ligands employed in this work.

Terphenyl-acetate and -formate dimolybdenum complexes. Reacting $Mo_2(O_2CMe)_4$ with 1 equiv of LiAr^{X-} y^{l_2} in THF (-40 to 20 °C) yielded a deep red-burgundy solution from which red crystals of the mono-terphenyl complex $Mo_2(Ar^{Xyl_2})(O_2CMe)_3$, 1a, were isolated. As shown in Scheme 1, extension of this reactivity to other LiAr' reagents was straightforward and afforded analogous complexes 1b (Ar^{Mes_2}), 1c (Ar^{Dipp_2}) and 1d (Ar^{Trip_2}), as dark red crystalline solids too. A number of attempts were made to replace the acetate group of complexes 1 *trans* to the terphenyl ligand by a second terphenyl to form the expected $Mo_2(Ar')_2(O_2CMe)_2$ derivatives. Nevertheless, neither the reaction of $Mo_2(O_2CMe)_4$ with an excess of LiAr' (ca. 2.2 equiv) nor the interaction of the isolated monoterphenyl complexes 1 with another equivalent of the corresponding LiAr' gave the desired complexes, even after prolonged refluxing in THF. Most probably, this is due to the high steric protection provided by the incorporated Ar' and the remaining acetate ligands.

Scheme 1. Synthesis of mono-terphenyl complexes 1a-1d.



(Ar' = Ar^{Xyl}₂, **1a**; Ar^{Mes}₂, **1b**; Ar^{Dipp}₂, **1c**; Ar^{Trip}₂, **1d**)

Compounds 1, show good solubility properties in organic solvents of low polarity like benzene or toluene, are highly sensitive to moisture and oxygen and must be carefully handled under an inert atmosphere of Ar or N₂. Their UV-Vis spectra (Figure 2) show an intense absorption band centred at ca. 530 nm (ϵ_{max} in the range 1080–1260 M⁻¹cm⁻¹) together with a somewhat weaker one in the proximity of 440 nm ($\varepsilon_{max} \sim 540 \text{ M}^{-1}\text{cm}^{-1}$). These absorptions can be attributed to $\delta^2 \rightarrow \delta \delta^*$ transitions. DFT (Mo6, 6-31g(d,p)/SDD) and time-dependent DFT (TD-DFT)²⁴ calculations identify the lower energy excited state of 1a as a singlet related to the excitation of an electron from the HOMO (δ) to the LUMO (δ *). The calculated (gas phase) excitation energy for this transition is 1.97 eV (or 629.71 nm), ca. 0.37 eV lower than the experimental values. According to the calculations, the weaker band centred around 440 nm can be assigned to d-d transitions, but with some metal to terphenyl contribution (see SI).

The new compounds are diamagnetic. In the ¹H NMR spectrum they exhibit similar features that are consistent with the $C_{\rm s}$ symmetry of their molecules. Thus, two signals assigned to the methyl protons of the acetate groups with relative intensity 6H : 3H can be recorded with chemical shifts close to 2.5 and 2.0 ppm, respectively. The flanking aromatic rings of the terphenyl ligand give rise to two sets of signals when the NMR experiment is performed at room temperature, thereby indicating that neither rotation of the central aryl ring around the Mo–C bond (Figure 3 top) nor interchange of Ar' between the two Mo atoms through a terphenyl-bridged structure (Figure 3) occur at the NMR time scale. Nonetheless,

 upon heating at higher temperatures the solutions of **1a** in toluene- d_8 , the two Ar' methyl resonances (2.35 and 2.18 ppm at 25 °C) coalesce (75 °C) and convert at 100 °C into a singlet centred at ca. 2.20 ppm. Room temperature NOESY experiments provide additional evidence for this dynamic behaviour, which in accordance with DFT calculations, can be associated with a 1,2-Ar' shift from one molybdenum atom to the other. The calculations yield an energy barrier for 1,2-Ar' shift of 19.7 kcal·mol⁻¹, whereas a Relaxed Potential Energy Scan of the rotation of the terphenyl ligand (Ar^{Xyl}₂) about the Mo–C bond gives a barrier to kcal·mol⁻¹ higher.



Figure 2. UV-Vis spectra of mono- and bis-terphenyl complexes **1a**, **2a** in Et₂O and **4a**, **5a** in THF solution (ca. 10^{-4} M).

At variance with the above results, the comparable reactions of the formate dimer $Mo_2(O_2CH)_4$ with 2 equiv of LiAr^{Xyl₂} yielded a bis(terphenyl) bis(formate) complex $Mo_2(Ar^{Xyl_2})_2(O_2CH)_2$, **2a**, with the expected *trans* distribution of the terphenyl ligands. No attempts were made to obtain and isolate the mono-terphenyl analogues of the tris-acetates **1**. Compound **2a** features a deep-red colour too (absorption band at 550 nm, with ε_{max} 3100 M⁻¹cm⁻¹) and is also very reactive toward air, both in solution and in the solid state. ¹H and ¹³C[¹H} MNR data¹⁷ are in full agreement with the proposed structure.

Compounds 1a, 1b, 1d, and 2a were characterized by X-ray crystallography and their molecular structures are depicted in Figures 4 and 5 (complexes 1d and 2a) and in Figures S1 and S2 (Supporting Information, compounds 1a and 1b). In the four compounds studied there is a (Mo₂)⁴⁺ core characterized by a Mo–Mo bond length of ca. 2.09 Å. This is a median value of the lower range 2.06–2.13 Å compiled for quadruply bonded Mo–Mo compounds with four bidentate ligands.²⁵ Therefore, replacing one or two bridging carboxylate ligands by monodentate terphenyl groups has no effect in the length of the quadruple Mo–Mo bond. The Mo–C distances to the terphenyl ligand(s) are also identical or nearly identical in the four compounds analysed (2.19–2.21 Å).



Figure 3. Possible fluxionality (top), variable temperature ¹H NMR spectra for compound **1a** (400 MHz, C_7D_8), and calculated geometry of the transition state for 1,2-Ar' shift.



Figure 4. The solid-state molecular structure of $Mo_2(Ar^{Trip_2})(O_2CMe)_3$, **1d**, with thermal ellipsoids set at 30% probability. All hydrogen atoms and the Mo– C_{arene} secondary interaction have been omitted for clarity. Selected bond lengths (Å): Mo(1)-Mo(2), 2.086(1); Mo(1)-C(1), 2.211(4); Mo(1)-O(1), 2.101(3); Mo(1)-O(3), 2.119(4); Mo(1)-O(5), 2.150(3); $Mo(2)\cdots$ C(8), 2.57(1).

An interesting structural peculiarity of these complexes is the coordinative and electronic unsaturation of one of the Mo atoms in complexes 1 and of both molybdenum atoms in 2a, partly offset by the existence of a Mo– C_{arene} secondary interaction. In complexes 1, Mo1 exhibits coordination number five and a sixteen electron count, similar to the vast majority of complexes with a Mo \equiv Mo bond.² Instead and leaving aside for the time being the Mo– C_{arene} secondary interaction, Mo2 in compounds 1 and the two

metal atoms of 2a are four-coordinate and have an effective valence electron count of fourteen. For the two situations, the basic coordination polyhedron surrounding each Mo atom is a square pyramid, with the other metal atom at the apex of the pyramid. In complexes 1 Mo1 is bound to the terphenyl carbon atom C1 and to the oxygen atoms O1, O3 and O5, each from a bridging acetate group, and it lays slightly above the mean basal plane (ca. 0.17 Å). In turn, Mo2 in complexes of type 1 has only three oxygen atoms within bonding distance, while the two metal atoms of 2a are bound to a terphenyl carbon atom and two oxygen atoms (one from each formate). Hence, one of the basal coordination sites of these polyhedra is empty. However, hovering over the unoccupied position there is a flanking aryl ring of the terphenyl ligand, which suggests that its ipso (or one of the ortho) carbon atom is participating in a secondary interaction alike that found by Power and co-workers in the Ar'CrCrAr' molecules.¹⁰ In complexes 1 the shortest $Mo-C_{arene}$ separation is of ca. 2.58 Å, a value that increases to 2.78 Å in the bis(terphenyl) complex 2a, due possibly to the high trans influence of the aryl ring and also to steric hindrance. While these metrics are too long to support significant electron communication between the implicated Carene carbon atom and the unsaturated molybdenum atom, they nevertheless underpin the existence of a weakly bonding secondary interaction that balances the metal atom unsaturation. This was addressed by means of a computational analysis.¹⁷ The geometry of 2a was optimized in the gas phase by DFT methods. The resulting structural parameters are in good agreement with the Xray data, the shortest calculated Mo-Carene being 2.79 Å. NBO analysis²⁶ of 2a is consistent with a quadruple Mo-Mo bond (comprised of one localized bonding orbital of σ symmetry, two of π and one of δ symmetry). Wiberg Bond Orders (WBOs) indicate that the interactions of the Mo atoms with the flanking aryls are weak. The overall WBO for each set of Mo-Ar^{Xyl} interactions amounts to 0.3, with the largest contribution corresponding to the Mo– C_{ipso} interactions (WBO = 0.08). Interestingly when a model is used in which the Ar^{Xyl} fragments of the terphenyl ligands are replaced by less bulky Ar^{Ph}, the shortest calculated Mo-Carene separation (now Mo-Cortho) is 2.57 Å, which is remarkably similar to that measured by X-ray in complexes 1. This result agrees with steric hindrance having a role in the elongation of the Mo-Aryl separations in the bis(terphenyl) complexes. Nevertheless the overall WBOs for the Mo–Ar^{Ph} interactions in the model remain unchanged (0.31), although the largest contribution, corresponding to the Mo-Cortho, increases to 0.15. In addition the electron density of 2a has been analyzed within Bader's theory of Atoms in Molecules.²⁷ While Bond Critical Points (BCPs) have been found that connect the Mo and the Cipso of the flanking rings, the charge densities $[\rho(r_c)]$ at these points are low (0.025 au vs 0.103 au at the BCPs of the Mo-C sigma bonds). Also, the positive values of the Laplacian of the electron density $[\nabla^2 \rho(r_c)]$ at

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59 60 the Mo– C_{ipso} critical points are indicative of weak, closed shell or ionic interactions.²⁸ To complete the analysis of the secondary interaction, we are presently carrying out a detailed experimental and computational investigation of a series of newly prepared terphenyl complexes of the Mo \equiv Mo core, in which the nature of the ligand in *trans* with respect to the secondary interaction is varied in a systematic manner.



Figure 5. The solid-state molecular structure of $Mo_2(Ar^{Xyl_2})_2(O_2CH)_2$, **2a**, with thermal ellipsoids set at 30% probability. All hydrogen atoms and the Mo– C_{arene} secondary interactions have been omitted for clarity. Selected bond lengths (Å): Mo(1)-Mo(1'), 2.095(1); Mo(1)-C(1), 2.187(3); Mo(1)-O(1), 2.106(3); Mo(1)-O(2), 2.110(3); $Mo(1')\cdots C(15)$, 2.78(1).

Trifluoroacetate complexes. The stronger acidity of HO_2CCF_3 relative to HO_2CMe (difference in pK_a of ca. 5) makes trifluoroacetate much better a leaving group than acetate. This observation and the isolation of the bis(terphenyl) complex **2a**, prompted us to utilize the well-known $Mo_2(O_2CCF_3)_4$ compound as starting material and to extend these investigations to the tungsten analogue $W_2(O_2CCF_3)_4$. For the latter, its reactivity toward LiAr^{Xyl2} was tested while for molybdenum two terphenyl ligands were essayed, namely Ar^{Xyl_2} and Ar^{Dipp_2} .

In agreement with expectations, the reaction of $Mo_2(O_2CCF_3)_4$ and LiAr' proceeded in a step-wise manner to furnish first mono(terphenyl) complexes **3** and subsequently their bis(terphenyl) counterparts **4** (Scheme 2). The reactions were begun at -40 °C in Et₂O as the solvent and were then permitted to reach room temperature over a period of a few hours. They could be followed readily by ¹⁹F NMR spectroscopy, as complexes **3** exhibit two resonances with chemical shift -72.5 and -73.3 ppm (2:1 ratio; data for **3a**) whereas solutions of **4a** give rise to a singlet at -70.8 ppm. Interestingly, the perfluorocarboxylate ligands impart enhanced solubility in non-polar solvents including hexanes. Compounds **3** and **4** were isolated as pink or red crystalline materials.

 Scheme 2. Synthesis of mono- and bis-terphenyl complexes 3 and 4, respectively, with bridging tri-fluoroacetate groups ($\overrightarrow{O} = O_2 CCF_3$).



The ¹H and ¹³C{¹H} NMR spectra of complexes **3** and **4** are also very informative. For instance, the ¹H NMR spectrum of **3c** that possesses flanking 2,6-*i*Pr₂C₆H₃ substituents, features two CHMe₂ septets and four doublet resonances, the latter associated with the CHMe₂ protons. This is in agreement with the foreseen non-equivalency of the two lateral aryl rings and with the proposed formulation with Cs symmetry (Scheme 2). Of the bis(terphenyl)bis(trifluoroacetate) derivatives **4**, complex **4c** of the Ar^{Dipp₂} ligand was not obtained with microanalytical purity except for a few crystals used for X-ray studies (see below). This was due to its high reactivity toward oxygen and moisture that causes its partial decomposition under our experimental conditions.

Similarly to $Mo_2(O_2CCF_3)_4$, $W_2(O_2CCF_3)_4$ reacted with 2 equiv of LiAr^{Xyl₂} to form the green complex $W_2(Ar^{Xyl_2})_2(O_2CCF_3)_2$, **5a**, whose solutions are characterized by three bands in the visible region of the spectrum (Figure 2), with maxima at 430, 485 and 600 nm. Its ¹H, ¹³C{¹H} and ¹⁹F NMR spectra are similar to those of **4a** and need no further discussion.

The solid-state molecular structures of compounds **3a**, **3c**, **4a**, **4c** and **5a** have been determined by X-ray crystallography and are presented in Figures 6 and 7. The tris(trifluoroacetate) complexes **3** (Figure 6) are structurally similar to the acetate analogues **1**, and are characterized by a Mo \equiv Mo bond of length ca. **2**.10 Å and by a Mo–C_{aryl} distance of about **2**.16 Å. Also in analogy with compounds **1**, the aryl bonded molybdenum atom Mo1 has coordination number five while Mo2 presents a fourcoordinate structure plus a long, weakly bonding, Mo–C_{arene} interaction of **2**.56 Å (to C ortho).

In the same manner, the $M_2(Ar')_2(O_2CCF_3)_2$, complexes 4 and 5 have structures with coordination properties akin to those of $Mo_2(Ar^{Xyl_2})_2(O_2CH)_2$, **2a**. For example, in compounds of type **4** the Mo–Mo bond has a length of ca. 2.11 Å, the Mo– C_{aryl} sigma bonds exhibit distances close to 2.19 Å and the Mo– C_{arene} secondary interactions are in the range 2.76–2.80 Å and may therefore be viewed as weakly bonding. The separation of 2.21 Å between the tungsten atoms of complex **5a**, while longer than the Mo–Mo distance in **4**, is comparable with values reported for other trifluoroacetate complexes of the $(W_2)^{4+}$ core.² However, both the W– C_{aryl} and W– C_{arene} separation at 2.15 and 2.67 Å, respectively, are slightly shorter than in the molybdenum analogue **4a** (2.18 and 2.76 Å), despite the somewhat larger covalent radius of tungsten²⁹ relative to mo-



Figure 6. The solid-state molecular structures of $Mo_2(Ar^{Xyl_2})(O_2CCF_3)_3$, **3a** (left) and $Mo_2(Ar^{Dipp_2})(O_2CCF_3)_3$, **3c** (right), with thermal ellipsoids set at 30% probability. All hydrogen atoms and the Mo– C_{arene} secondary interactions have been omitted for clarity. Selected bond lengths in Å. **3a**: Mo(1)–Mo(2), 2.103(1); Mo(1)–C(1), 2.164(3); Mo(1)–O(1), 2.112(2); Mo(1)–O(3), 2.200(2); Mo(1)–O(5), 2.126(2); Mo(2)···C(12), 2.55(1). **3c**: Mo(1)–Mo(2), 2.100(1); Mo(1)–C(1), 2.162(4); Mo(1)–O(1), 2.118(2); Mo(1)–O(3), 2.182(3); Mo(1)–O(5), 2.119(3); Mo(2)···C(24), 2.56(1).



Figure 7. The solid-state molecular structures of $Mo_2(Ar^{Xyl_2})_2(O_2CCF_3)_2$, 4a (left), $Mo_2(Ar^{Dipp_2})_2(O_2CCF_3)_2$, 4c (centre) and $W_2(Ar^{Xyl_2})_2(O_2CCF_3)_2$, **5a** (right) with thermal ellipsoids set at 30% probability. All hydrogen atoms and the M-C_{arene} secondary interactions have been omitted for clarity. Selected bond lengths in Å. 4a: Mo(1)-Mo(2), 2.107(3); Mo(1)-C(1), 2.175(10); Mo(1)-O(1), 2.123(8); Mo(1)-O(3), 2.124(8); Mo(2)-O(2), 2.115(8); Mo(2)-O(4), 2.110(8); Mo(2)-··C(12), 2.76(1). 4c: Mo(1)-Mo(1A), 2.112(1); Mo(1)–C(1), 2.200(3); Mo(1)–O(1), 2.119(2); Mo(1)–O(2A), 2.114(2); Mo(1A)···C(20), 2.80(1). **5a**: W(1)–W(2), 2.213(1); W(1)-C(1), 2.157(5); W(1)-O(1), 2.093(4); W(1)-O(3), 2.092(4); W(2)-O(2), 2.092(4); W(1)-O(4), 2.078(4); W(2)-C(15), 2.67(1).

lybdenum (1.62 and 1.54 Å, respectively).

As mentioned in the introductory paragraphs of this paper, one of the objectives of this work was the use of the mixed $M_2(Ar')_2(O_2CR)_2$, complexes with an $(M_2)^{+2}$ central unit as precursors for the synthesis of the corresponding Ar'MMAr' molecules with a quintuple metalmetal bond. Many trials were realized to reduce the newly prepared complexes $M_2(Ar')_2(O_2CR)_2$, i.e. 2, 4 and 5, either at room temperature or above (boiling THF), by action of a variety of reducing agents: Na, Na-Hg, K, KC₈, KH and others. However, all of these endeavours proved fruitless, the corresponding reactions leading either to decomposition products or to unreacted starting materials. In a similar fashion, the reduction of the complexes $Mo_2(Ar')(O_2CMe)_3$, 1a-1d with the above reductants in the presence of a second equivalent of the appropriate LiAr' were unsuccessful too. It is possible that the reluctance of these terphenyl-carboxylate complexes to undergo reduction to Ar'MMAr' be due to kinetic reasons (rather than thermodynamic) associated with the high steric hindrance, and the consequent metal protection, exerted by the terphenyl and carboxylate ligands of these complexes.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried and degassed prior to use. Toluene, n-hexane, and n-pentane were distilled over sodium. Diethylether and tetrahydrofuran were distilled under nitrogen over sodium/benzophenone. Quadruply bonded dimolybdenum and ditungsten complexes $M_2(O_2CR)_4$ (M = Mo, R = H, Me, CF₃; M = W, R = CF_3),^{30–33} terphenyl iodides Ar'I (Ar' = Ar^{Xyl₂}, Ar^{Mes₂}, Ar^{Dipp₂}, and Ar^{Trip₂}),³⁴ and the corresponding lithium salts, LiAr',³⁵ were prepared according to literature methods. All other compounds were commercially available and were used as received. Benzene- d_6 was distilled under argon over sodium/benzophenone and toluene-d₈ was distilled under argon over sodium. Both were then degassed and dried over 4 Å molecular sieves. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400, 400R, and DRX-500 spectrometers. The resonances of the solvents were used as the internal standard and the chemical shifts are reported relative to TMS. UV-Visible spectra were recorded on a PerkinElmer Lambda 750 spectrometer and elemental analysis was carried out with a LECO TruSpec CHN elementary analyzer. Synthetic details and characterization data for complexes 1a and 2a can be found in the SI of reference 17.

General of preparation mono(terphenyl) tris(acetate) complexes $Mo_2(Ar')(O_2CMe)_{2}$ (1b-d). Solid samples of Mo₂(O₂CCH₃)₄ (1.46 g, 3.42 mmol) and the appropriate LiAr' (3.42 mmol) were mixed in a glovebox and cooled to -40 °C. Tetrahydrofuran (20 mL) was added and the resulting suspension was stirred for 12 hours, while reaching slowly the room temperature. The solvent was then removed under reduced pressure and the solid residue was extracted with toluene (20 mL). The resulting red-wine-coloured suspension was centrifuged and the solution was transferred to a Schlenk tube, concentrated to ca. 10 mL, and stored in a refrigerator at -23°C overnight. A bright red crystalline solid separated out,

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58 59 60 which was isolated by filtration and dried under vacuum for 3 hours.

 $Mo_{2}(Ar^{Mes_{2}})(O_{2}CMe)_{2}$, (1b). Yield: 66%. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ = 1.40 (s, 3H, p-Me_{Mes}), 1.93 (s, 3H, p-Me_{Mes}), 2.00 (s, 3H, trans-Me_{OAc}), 2.21 (s, 6H, o-Me_{Mes}), 2.37 (s, 6H, o-Me_{Mes}), 2.53 (s, 6H, Me_{OAc}), 6.36 (s, 2H, m-Mes'), 6.66 (s, 2H, m-Mes), 6.95 (d, 1H, ³J_{HH} = 7.6 Hz, m'- C_6H_3), 7.12 (d, 1H, ${}^{3}J_{HH}$ = 7.6 Hz, m- C_6H_3), 7.34 (t, 1H, ${}^{3}J_{HH}$ = 7.6 Hz, $p-C_6H_3$) ppm. ¹³C{¹H} NMR (100 MHz, C_6D_6 , 25 °C): δ = 20.2 (*p*-Me_{Mes}), 20.9 (*p*-Me_{Mes}), 21.2 (o-Me_{Mes}), 22.4 (o-Me_{Mes}), 23.0 (trans-Me_{OAc}), 23.8 (Me_{OAc}), 123.6 (m-C₆H₃), 125.7 ($m'-C_6H_3$), 126.4 ($p-C_6H_3$), 128.1 (m-Mes), 129.8 (m-Mes'), 135.6 (p-Mes), 135.9, 136.0 (o-Mes' and o-Mes), 138.7 (p-Mes'), 140.3 (ipso-Mes), 141.3 (ipso-Mes'), 147.4 (o-C₆H₃), 147.9 (0-C₆H₃), 181.5 (Mo-C_{ar}), 183.4 (O₂CMe), 183.5 (*trans*-O₂*C*Me) ppm. UV-Visible (10⁻⁴ M in benzene): λ = 530 nm (ε = 1080 mol⁻¹ L cm⁻¹); (10⁻⁴ M in diethylether): λ = 280, 445, 530 nm (ϵ = 17400, 700, 1400 mol⁻¹ L cm⁻¹, respectively). Anal. Calcd. for $C_{30}H_{34}Mo_2O_6$: C, 52.8; H, 5.0; Found: C, 53.1; H, 5.3.

 $Mo_{3}(Ar^{Dipp_{2}})(O_{2}CMe)_{3}$, (1c). Yield: 50%. ¹H RMN (500 MHz, C_6D_6 , 25 °C): δ = 1.07, 1.12, 1.31, 1.55 (d, 6H each, Me_{Dipp}), 1.96 (s, 3H, trans-Me_{OAc}), 2.56 (s, 6H, Me_{OAc}), 3.13, 3.21 (sept, 4H each, CHMe_{2Dipp}), 6.48 (t, 1H, p-Dipp'), 6.58 (d, 2H, m-Dipp'), 7.02 (m, 3H, m-Dipp and p-Dipp), 7.10 $(d, 1H, m-C_6H_3)$, 7.20 $(t, 1H, p-C_6H_3)$, 7.36 $(d, 1H, m'-C_6H_3)$ ppm. All ³J_{HH} constants are about 7.0 Hz. ¹³C{¹H} NMR (125 MHz, C_6D_6 , 25 °C): δ = 21.7, 22.6 (Me_{Dipp}), 22.7 (trans-Me_{OAc}), 23.6 (Me_{OAc}), 26.7, 26.8 (Me_{Dipp}), 30.3, 31.3 $(CHMe_{2Dipp})$, 121.9 (*m*-Dipp), 122.5 (*m*-C₆H₃ or *m*'-C₆H₃), 123.7 $(m-C_6H_3 \text{ or } m'-C_6H_3)$, 123.7 (m-Dipp), 126.0 $(p-C_6H_3)$, 127.0 (p-Dipp), 129.4 (p-Dipp'), 140.2 (ipso-Dipp), 144.8 (o-Dipp'), 145.1 ($o-C_6H_3$ or $o'-C_6H_3$), 145.2 ($o-C_6H_3$ or $o'-C_6H_3$), 146.5 (ipso-Dipp'), 146.6 (o-Dipp), 182.3 (Mo-C_{ar}), 182.7 (O2CMe), 183.4 (trans-O2CMe) ppm. UV-Visible (10⁻⁴ M in benzene): $\lambda = 535$ nm ($\varepsilon = 1300$ mol⁻¹ L cm⁻¹). Anal. Calcd. For C₃₆H₄₆Mo₂O₆: C, 56.40; H, 6.05; Found: C, 56.0; H, 6.3.

 $Mo_2(Ar^{Trip_2})(O_2CMe)_{3}$, (1d). Yield: 48%. ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ = 0.84 (d, 6H, *p*-Me_{Trip}), 1.16 (m, 12H, o-Me_{Trip} and *p*-Me_{Trip}), 1.20 (d, 6H, o-Me_{Trip}), 1.42 (d, 6H, o-Me_{Trip}), 1.64 (d, 6H, o-Me_{Trip}), 1.98 (s, 3H, trans-Me_{OAc}), 2.23 (sept, 1H, p-CHMe_{2Trip}), 2.55 (s, 6H, Me_{OAc}), 2.68 (sept, 1H, *p*-CHMe_{2Trip}), 3.18 (sept, 2H, o-CHMe_{2Trip}), 3.23 (sept, 2H, o-CHMe_{2Trip}), 6.76 (s, 2H, m-Trip'), 7.04 (s, 2H, *m*-Trip), 7.29 (m, 2H, *p*-C₆H₃ and *m*'-C₆H₃), 7.38 (d, 1H, *m*- C_6H_3) ppm. All ${}^{3}J_{HH}$ constants are about 7.0 Hz. ${}^{13}C{}^{1}H$ NMR (125 MHz, C_6D_6 , 25 °C): δ = 21.8 (o-Me_{Trip}), 22.4 (o-Me_{Trip}), 22.7 (trans-Me_{OAc}), 23.5 (p-Me_{Trip}), 23.6 (p-Me_{Trip}), 24.0 (Me_{OAc}), 26.8 (o-Me_{Trip}), 26.9 (o-Me_{Trip}), 30.4 (o-CHMe_{2Trip}), 31.6 (o-CHMe_{2Trip}), 33.9 (p-CHMe_{2Trip}), 34.3 (p-CHMe_{2Trip}), 119.7 (*m*-Trip), 121.6 (*m*-Trip), 123.4 (*p*-C₆H₃), 125.9 $(m-C_6H_3)$, 128.3 $(m-C_6H_3)$, 137.9 (ipso-Trip), 144.2 (*ipso*-Trip), 145.1 (o-Trip), 145.2 (o- C_6H_3), 145.4 (o- C_6H_3), 146.6 (o-Trip), 147.3 (p-Trip), 150.5 (p-Trip), 182.5 (O₂CMe), 183.1 (Mo-C_{ar}), 183.3 (trans-O₂CMe) ppm. UV- Visible (10⁻⁴ M in benzene): λ = 530 nm (ϵ = 1260 mol⁻¹ L cm⁻¹). Anal. Calcd. For C₄₂H₅₈Mo₂O₆: C, 59.3; H, 6.9; Found: C, 58.6; H, 6.2.

General preparation of mono(terphenyl) tris(trifluoroacetate) complexes $Mo_2(Ar')(O_2CF_2)_2$, (3a, **3c**). Solid samples of $Mo_2(O_2CCF_3)_4$ (0.50 g, 0.77 mmol) and 1 equiv of the appropriate LiAr' were mixed in a glovebox and cooled to -40 °C. Diethylether (15 mL, for 3a) or pentane (15 mL, for 3c) was added and the resulting suspension was stirred for 24 hours, while reaching slowly the room temperature. The solvent was then removed under reduced pressure and the solid residue was extracted with hexane (15 mL). The resulting red-wine-coloured suspension was centrifuged and the solution was transferred to a Schlenk tube, concentrated to ca. 5 mL, and stored in a refrigerator at -23 °C overnight. A pink crystalline solid separated out, which was isolated by filtration and dried under vacuum for 3 hours.

 $Mo_{,}(Ar^{Xyl_{2}})(O_{2}CF_{,})_{,,}$ (3*a*). Yield: 63%. ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ = 1.99 (s, 6H, Me_{Xyl}), 2.11 (s, 6H, $Me_{Xyl'}$), 5.96 (t, 1H, ${}^{3}J_{HH}$ = 7.6 Hz, p-Xyl), 6.24 (d, 2H, ${}^{3}J_{HH}$ = 7.6 Hz, m-Xyl), 6.67 (m, 3H, m-Xyl' and p-Xyl'), 6.73 (d, ${}^{1}H, {}^{3}J_{HH} = 7.6 \text{ Hz}, m-C_{6}H_{3}$, 6.92 (d, 1H, ${}^{3}J_{HH} = 7.5 \text{ Hz}, m' C_6H_3$), 7.21 (t, 1H, ${}^{3}J_{HH}$ = 7.6 Hz, *p*- C_6H_3) ppm. ${}^{13}C{}^{1}H$ NMR (125 MHz, C_6D_6 , 25 °C): δ = 20.6 (Me_{Xyl}), 21.9 (Me_{Xyl}), 124.0 $(m-C_6H_3)$, 126.6 $(m'-C_6H_3)$, 127.7 (m-Xyl'), 127.9 (p-Xyl'), $128.4 (p-C_6H_3)$, 129.9 (p-Xyl), 130.3 (m-Xyl), 135.5 (o-Xyl), 135.8 (o-Xyl), 140.1 (ipso-Xyl'), 145.6 (ipso-Xyl'), 146.2 (o-C₆H₃), 146.7 (o-C₆H₃), 178.1 (Mo-C_{ar}) ppm. Resonances due to the trifluoroacetate groups were not detected. ¹⁹F NMR (100 MHz, 25 °C): $\delta = -72.2$ (s, 6F, *cis*-O₂CCF₃), -72.9 (s, 3F, trans-O2CCF3) ppm. UV-Visible (10⁻⁵ M in diethylether): $\lambda = 525$ nm ($\varepsilon = 2160$ mol⁻¹ L cm⁻¹, respectively). Anal. Calcd. for C₂₈H₂₁F₉Mo₂O₆: C, 41.20; H, 2.59. Found: C, 41.0; H, 2.8.

 $Mo_2(Ar^{Dipp_2})(O_2CF_3)_{y}$ (3c). Yield: 33%. ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ = 0.91 (d, 6H, Me_{Dipp}), 1.00 (d, 6H, Me_{Dipp}), 1.14 (d, 6H, Me_{Dipp}), 1.48 (d, 6H, Me_{Dipp}), 2.86 (sept, 2H, CHMe_{2Dipp}'), 3.06 (sept, 2H, CHMe_{2Dipp}), 6.30 (t, 1H, p-Dipp'), 6.39 (d, 2H, m-Dipp'), 6.92 (m, 3H, m-Dipp and p-Dipp), 7.20-7.26 (m, 3H, m-C₆H₃, m'-C₆H₃ and p- C_6H_3) ppm. All ${}^{3}J_{HH}$ constants are about 7.0 Hz. ${}^{13}C{}^{1}H{}$ NMR (125 MHz, C_6D_6 , 25 °C): $\delta = 21.6$ (Me_{Dipp}), 21.9 (Me_{Dipp}), 26.6 (Me_{Dipp}), 27.0 (Me_{Dipp}), 30.7 (CHMe_{2Dipp}), 31.6 (CHMe_{2Dipp}'), 122.8 (m-Dipp), 125.5 (m-Dipp'), 125.7 $(m-C_6H_3 \text{ or } m'-C_6H_3)$, 126.8 $(m-C_6H_3 \text{ or } m'-C_6H_3)$, 129.1 $(p-C_6H_3)$ C₆H₃), 129.2 (*p*-Dipp), 131.1 (*p*-Dipp'), 137.7 (*ipso*-Dipp), 144.4 ($o-C_6H_3$ or $o'-C_6H_3$), 144.5 ($o-C_6H_3$ or $o'-C_6H_3$), 145.4 (o-Dipp'), 146.7 (o-Dipp), 148.0 (ipso-Dipp'), 180.1 (Mo-C_{ar}) ppm. Resonances due to the trifluoroacetate groups were not detected. ¹⁹F NMR (100 MHz, 25 °C): δ = -72.2 (s, 6F, *cis*-O₂CCF₃), -74.1 (s, 3F, *trans*-O₂CCF₃) ppm. UV-Visible (10⁻⁴ M in diethylether): $\lambda = 535$ nm ($\varepsilon = 1300$ mol⁻¹ L cm⁻¹). Anal. Calcd. for $C_{36}H_{37}F_{0}Mo_{2}O_{6}$: C, 46.57; H, 4.02. Found: C, 46.4; H, 4.4.

General preparation of bis(terphenyl) bis(trifluoroacetate) complexes M₂(Ar')₂(O₂CF₃)₂, (4a, 5a). Solid samples of LiAr' (2 equiv) and $Mo_2(O_2CCF_3)_4$ (1.00 g, 1.55 mmol) (in the case of 4) and $W_2(O_2CCF_3)_4$ (0.40 g, 0.49 mmol) (for 5) were mixed in a glovebox and cooled to -40 °C. Diethylether (20 mL) was added and the resulting suspension was stirred for 12 hours, while reaching slowly the room temperature. A pink (for compound 4a) or green (for compound 5a) crystalline solid separated out, which was isolated by filtration and dried in vacuum. The mother liquor was concentrated under reduced pressure to ca. 5 mL and stored in a refrigerator overnight to induce further precipitation of the product.

 $Mo_2(Ar^{Xyl_2})_2(O_2CCF_3)_2$, (4a). Yield: 62%. ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ = 1.95 (s, 12H, Me_{Xyl}), 2.13 (s, 12H, Me_{Xvl}), 6.07 (d, 4H, ${}^{3}J_{HH}$ = 7.5 Hz, m-Xvl'), 6.16 (t, 2H, ${}^{3}J_{HH}$ = 7.5 Hz, *p*-Xyl'), 6.52 (d, 2H, ${}^{3}J_{HH}$ = 7.5 Hz, *m*'-C₆H₃), 6.69 (d, 2H, ${}^{3}J_{HH}$ = 7.5 Hz, m-C₆H₃), 6.82 (m, 6H, m-Xyl and p-Xyl, AB₂ system), 7.10 (t, 2H, ${}^{3}J_{HH} = 7.5$ Hz, p-C₆H₃) ppm. ¹³C{¹H} NMR (125 MHz, C₆D₆, 25 °C): δ = 20.8 (Me_{Xvl}), 22.3 (Me_{Xvl}), 125.1 (*m*'-C₆H₂), 127.2 (*m*-Xyl, *p*-Xyl and *m*-C₆H₂), 127.5 (*m*-Xyl and *p*-C₆H₃), 128.6 (*m*-Xyl'), 129.7 (*p*-Xyl'), 135.5 (o-Xyl'), 137.8 (o-Xyl), 142.6 (ipso-Xyl), 144.4 (ipso-Xyl'), 146.0 (0-C₆H₃), 146.5 (0-C₆H₃), 172.5 (Mo-C_{ar}) ppm. Resonances due to the trifluoroacetate groups were not detected. ¹⁹F NMR (100 MHz, 25 °C): $\delta = -70.8$ ppm. UV-Visible (10⁻⁵ M in diethylether): λ = 555, 404 nm (ϵ = 1660, 1500 mol⁻¹ L cm⁻¹, respectively). Anal. Calcd. for C₄₈H₄₂F₆Mo₂O₄: C, 58.31; H, 4.28. Found: C, 57.9; H, 4.2.

 $W_2(Ar^{Xyl_2})_2(O_2CCF_3)_{2^*}$ (**5a**). Yield: 70%. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.84 (s, 12H, Me_{Xyl}), 2.19 (s, 12H, Me_{Xyl}), 5.93 (d, 4H, ³*J*_{HH} = 7.6 Hz, *m*-Xyl), 6.35 (m, 4H, *p*-Xyl and *m*-C₆H₃), 6.64 (dd, 2H, ³*J*_{HH} = 7.5 Hz, ⁴*J*_{HH} = 1.4 Hz, *m*'-C₆H₃), 6.82–6.92 (m, 6H, *m*-Xyl' and *p*-Xyl', AB2 system), 6.99 (t, 2H, ³*J*_{HH} = 7.5 Hz, *p*-C₆H₃) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆, 25 °C): δ = 21.0 (Me_{Xyl}), 22.2 (Me_{Xyl}), 126.2 (*m*-C₆H₃), 126.7 (*p*-C₆H₃), 127.4 (*m*-Xyl'), 127.5 (*p*-Xyl'), 127.7 (*m*'-C₆H₃, under signal C₆D₆), 128.7 (*m*-Xyl), 130.1 (*p*-Xyl), 134.4 (o-Xyl), 138.4 (o-Xyl'), 141.1 (*ipso*-Xyl'), 145.1 (o-C₆H₃), 145.9 (*ipso*-Xyl), 147.5 (o-C₆H₃), 172.3 (Mo-C_{ar}). ¹⁹F NMR (100 MHz, 25 °C): δ = -67.20 ppm. UV-Visible (10⁻⁴ M in diethylether): λ = 600, 485, 430 nm (ε = 5100, 4500, 2300 mol⁻¹ L cm⁻¹, respectively). Anal. Calcd. for C₄₈H₄₂F₆W₂O₄: C, 49.51; H, 3.64. Found: C, 49.6; H, 3.7.

Computational details. DFT calculations were performed with the Gaussian o9 package³⁶ using the hybrid meta-GGA functional Mo6³⁷. The Mo atoms were represented by the Stuttgart/Dresden Effective Core Potential and the associated basis set³⁸ as implemented in Gaussian o9 (SDD). The remaining H, C and O atoms were represented by means of the 6-31G(d,p) basis set.^{39–41} The geometry of 1a was optimized in the gas phase without symmetry restrictions, and was characterized as a minimum in the potential energy surface by the absence of imaginary frequencies in a harmonic frequency calculation at the same level of theory. TD-DFT calculations were performed with the same functional and basis set as the geometry optimization. The solution for the 10 first singlet and the 10 first triplet excited states was requested in one calculation, which yielded zero oscillator strength for all triplet excited states.

X-ray diffraction analyses. A single crystal of suitable size, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K for compounds 1b, 1d, 3a, 3c, 4a, 4c and 5a] to the goniometer head. Data collection was performed on Bruker-Nonius X8APEX-II CCD diffractometer, using monochromatic radiation λ (Mo K α I) = 0.71073 Å, by means of ω and φ scans. The data were reduced (SAINT)⁴² and corrected for Lorentz polarisation effects and absorption by multiscan method applied by SADABS.43 The structures were solved by direct methods (SIR-2002)⁴⁴ and refined against all F2 data by full-matrix least-squares techniques (SHELXTL-6.12).45 All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

CONCLUSION

In conclusion, incorporation of one or two terphenyl groups to the coordination sphere of the quadruple Mo-Mo and W-W bonds of the well-known Mo₂(O₂CR)₄ family of compounds is possible, which adds extra value to this versatile family of ligands.^{10,18-22} Since the carboxylate groups of the binuclear precursors bridge the two metal atoms, their replacement by the monodentate terphenyls creates a vacant coordination site and generates an uncommon four-coordinate geometry that derives from a square pyramid with an empty basal site. In the mono(terphenyl) complexes 1 and 3 there is one such an unsaturated, metal centre and the other exhibits the fivecoordinate, 16-electron structure commonly found in complexes of this type.² For the bis(terphenyl) complexes 2, 4 and 5, the two metal atoms feature a low-coordinate structure. However, it is noteworthy that in all compounds studied there exists a weak M-Carene bonding interaction that implicates either the ipso or an ortho carbon atom of a flanking aryl ring. The corresponding M–C_{arene} distance (in the range ca. 2.58–2.80 Å) is significantly longer than the existing σ M–C_{aryl} bond (2.16–2.21 Å) but the interaction counterbalances in some degree the electronic unsaturation and offers at the same time steric protection to the unsaturated metal centre.

ASSOCIATED CONTENT

Supporting Information

Electronic supplementary information (ESI) available: Experimental procedures and characterization data for other new compounds described herein, additional computational details along with CIF files for **1b**, **1d**, **3a**, **3c**, **4a**,

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58 59 60 **4c**, and **5a** CCDC 997253–997259. This information is available free of charge via the Internet at <u>http://pubs.acs.org/</u>.

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Mono- and bis-terphenyl carboxylate dimetal complexes (M = Mo, W; $\overrightarrow{OO} = O_2CR$, R = H, Me, CF₃)