

## Quintuple Bonds

## Experimental and Theoretical Studies on Arene-Bridged Metal– Metal-Bonded Dimolybdenum Complexes

Mario Carrasco,<sup>[a]</sup> Natalia Curado,<sup>[a]</sup> Eleuterio Álvarez,<sup>[a]</sup> Celia Maya,<sup>[a]</sup> Riccardo Peloso,<sup>[a]</sup> Manuel L. Poveda,<sup>[a]</sup> Amor Rodríguez,<sup>[a]</sup> Eliseo Ruiz,<sup>[b]</sup> Santiago Álvarez,<sup>\*[b]</sup> and Ernesto Carmona<sup>\*[a]</sup>

**Abstract:** The bis(hydride) dimolybdenum complex,  $[Mo_2(H)_2[HC(N-2,6-iPr_2C_6H_3)_2]_2(thf)_2]$ , **2**, which possesses a quadruply bonded  $Mo_2^{\parallel}$  core, undergoes light-induced (365 nm) reductive elimination of  $H_2$  and arene coordination in benzene and toluene solutions, with formation of the  $Mo_2^{\perp}$  complexes  $[Mo_2[HC(N-2,6-iPr_2C_6H_3)_2]_2(arene)]$ , **3·C<sub>6</sub>H<sub>6</sub>** and **3·C<sub>6</sub>H<sub>5</sub>Me**, respectively. The analogous C<sub>6</sub>H<sub>5</sub>OMe, *p*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>F, and *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> derivatives have also been prepared by thermal or photochemical methods, which

## Introduction

Dimolybdenum complexes containing multiple bonds between metal atoms were first uncovered almost five decades ago.<sup>[1]</sup> Despite the time that has elapsed and the spectacular development experienced by the field,<sup>[2]</sup> interesting discoveries continue to be made. The quadruple Mo-Mo bond has been intensively investigated. ^[2-5] Its dimetal unit with a  $\sigma^2\pi^4\delta^2$  electron configuration is redox active and suitable to study mixed valency.<sup>[4]</sup> However, even if a two-electron reduction is expected to lead to a  $\sigma^2 \pi^4 \delta^4$  electron configuration and hence to fivefold Mo-Mo bonding, this was not experimentally achieved until recently. Following the discovery by the Power group of the first quintuple bond in an isolable molecule, Ar'CrCrAr',  $(Ar' = C_6H_3 - 2,6 - (C_6H_3 - 2,6 - iPr_2)_2)^{[6]}$  and the subsequent burgeoning of the field,  $^{\scriptscriptstyle [7]}$  in 2009 prominent research from the group of Tsai allowed isolation of the first molecules featuring a formal bond order of five between molybdenum atoms,

[a]	Dr. M. Carrasco, N. Curado, Dr. E. Álvarez, Dr. C. Maya, Dr. R. Peloso,
	Prof. Dr. M. L. Poveda, Dr. A. Rodríguez, Prof. Dr. E. Carmona
	Instituto de Investigaciones Químicas
	Departamento de Química Inorgánica Universidad
	de Sevilla-Consejo Superior de Investigaciones Científicas
	Avenida Américo Vespucio 49, 41092 Sevilla (Spain)
	Fax: (+ 34) 954460565
	E-mail: guzman@us.es
[b]	Prof. Dr. E. Ruiz, Prof. Dr. S. Álvarez
	Departament de Química Inorgànica and
	Institut de Química Teòrica i Computacional
	Universitat de Barcelona, Diagonal 647, 08028 Barcelona (Spain)
	E-mail: santiago@qi.ub.es
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nevertheless employ different Mo<sub>2</sub> complex precursors. X-ray crystallography and solution NMR studies demonstrate that the molecule of the arene bridges the molybdenum atoms of the Mo<sup>1</sup><sub>2</sub> core, coordinating to each in an  $\eta^2$  fashion. In solution, the arene rotates fast on the NMR timescale around the Mo<sub>2</sub>-arene axis. For the substituted aromatic hydrocarbons, the NMR data are consistent with the existence of a major rotamer in which the metal atoms are coordinated to the more electron-rich C–C bonds.

namely the bis(amidinate) complexes  $[Mo_2\{RC(N-2,6-iPr_2C_6H_3)_2\}_2]$  (R = H, Ph), which were obtained by reduction with potassium graphite of suitable Mo $\equiv$ Mo precursors.<sup>[8]</sup> Since then, other compounds with Cr–Cr<sup>[9a]</sup> and Mo–Mo<sup>[9b]</sup> quintuple bonds have been characterized. Reactivity studies of the quintuple M–M bond have been reported too.<sup>[7i,9a,10,11]</sup>

Some years ago our group started to study the reactions of the dimolybdenum tetracarboxylates  $[Mo_2(O_2CR)_4]$  (R = H, CH<sub>3</sub>, CF<sub>3</sub>) with the lithium derivatives of bulky terphenyl, amidinate, and aminopyridinate ligands, aiming to obtain suitable precursors for further reduction to the corresponding Mo $\equiv$ Mo complexes. In collaboration with the group of Power, we reported recently the formation of some mono- and bis(terphenyl) dimolybdenum compounds of unusual unsaturated structures.<sup>[12a]</sup> Latterly, our group also communicated that the bis-(hvdride) bis(amidinate) derivative, [Mo<sub>2</sub>(H)<sub>2</sub>{HC(N-2,6 $iPr_2C_6H_3)_2\}_2(thf)_2]$ , **2**, with a Mo<sup>II</sup><sub>2</sub> core, and Tsai's complex,<sup>[8]</sup>  $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2]$ , 4, interconvert readily by formal dinuclear reductive elimination and oxidative addition of H<sub>2</sub>.<sup>[12b]</sup> This work also demonstrated that interesting Mol<sub>2</sub>·arene structures, compounds 3-arene, could be generated starting from either 2 or 4, under suitable conditions. Multiply bonded  $M_2$ compounds with bridging arene ligands are scarce; the first example of a quadruply bonded Mo<sup>II</sup><sub>2</sub> species of this kind was described recently by Masuda and co-workers.<sup>[13,14]</sup> Accordingly, we extended our initial study that was limited to  $C_6H_6$  and  $C_6H_5Me$ , to other arenes, including  $C_6H_5OMe$ ,  $p-C_6H_4Me_2$  and the fluoroarenes  $C_6H_5F$  and  $1,4-C_6H_4F_2$ . Herein, we give a full description of this work that encompasses reactivity, structural (solid-state and solution) and theoretical studies of the Mo<sup>1</sup><sub>2</sub>•arene motif.

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## **Results and Discussion**

#### Bis-(carboxylate) and -(hydride) complexes of the bis(amidinate) fragment $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2]$

The Mol<sub>2</sub> arene complexes described in this paper emanated originally from the bis(acetate) bis(amidinate) dimolybdenum compound, 1a, that exhibits a quadruple Mo-Mo bond. This complex, and the formate analogue 1b, were generated by treatment of the lithium amidinate,  $Li[HC(N-2,6-iPr_2C_6H_3)_2]$  with the corresponding [Mo<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>] precursor, under the conditions shown in Scheme 1. Both are yellow, air-sensitive crystalline solids, of low solubility in common organic solvents (Et<sub>2</sub>O, THF or aromatic hydrocarbons). Solid-state magnetic susceptibility, NMR and other characterization data for the two complexes are given in the Supporting Information. Their solidstate molecular structures were determined by X-ray crystallography (see the Supporting Information, Figure S5 and S6). The two compounds feature a Mo-Mo quadruple bond of length  $\approx$  2.10 Å. Interestingly, the formate derivative **1**b, which was crystallized from a hot, saturated solution in tetrahydrofuran, contains in the axial positions two weakly bound molecules of the solvent, with a Mo-O separation of 2.75 Å. As in other Mo=Mo compounds with axial ligands, the coordination of these extra molecules has a minimal effect on the Mo-Mo bond,<sup>[2]</sup> which at 2.1047(7) Å is only marginally longer than the 2.0892(8) Å value found for 1 a.

Attempts to reduce THF solutions of these compounds with Na, K, KC<sub>8</sub> or KH, either at room temperature or at 60 °C, proved fruitless. However, acetate **1a** reacted cleanly with LiMe with displacement of the two acetate groups and formation of the "ate" complex Li[Mo<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>{HC(*N*-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}<sub>2</sub>-(thf)], which underwent readily loss of LiMe with production of the neutral species [Mo<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>{HC(*N*-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]. These and other related complexes with metal–metal quadruple bonding will be described in a forthcoming publication. Meanwhile, action of H<sub>2</sub> on the latter complex under ambient conditions readily eliminated CH<sub>4</sub> and produced the bis(hydride) [Mo<sub>2</sub>(H)<sub>2</sub>{HC(*N*-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(thf)<sub>2</sub>], **2**, as represented in Scheme 1.

Complex **2** is a rare example of a formally quadruply bonded dimolybdenum hydride species.<sup>[15–17]</sup> Its  $\text{Mol}_2^{II}(H)_2$  core is characterized by a medium intensity IR absorption at

1525 cm<sup>-1</sup> due to  $\nu$ (Mo–H), which disappeared upon deuteration of a solid sample investigated by diffuse reflectance infrared spectroscopy (DRIFT). The corresponding  $\nu$ (Mo–D) band, which would be expected around 1090 cm<sup>-1</sup> on the assumption of a  $\nu$ (Mo–H)/ $\nu$ (Mo–D) ratio of  $\approx$  1.4, could not be assigned with certainty because of the presence in the 1060-1120 cm<sup>-1</sup> region of the spectrum of other bands originated by vibrations of the amidinate ligands. In the <sup>1</sup>H NMR spectrum, a singlet at  $\delta = 5.67$  ppm, with relative intensity corresponding to 2H, can be confidently attributed to the two equivalent hydrides. This signal vanished upon treatment with D<sub>2</sub>, when it became clearly discernable in the <sup>2</sup>H NMR spectrum of the deuterated sample. The chloroform test provided further support for this assignment (see the Supporting Information). In this regard, it should be noted that even if the Mo-H resonance of **2** appears at a higher frequency than is commonly observed for transition-metal hydrides, metal-metal-bonded molybdenum hydrides included,<sup>[17]</sup> our observation is not uncommon for Mo-H compounds, and in general for early transition-metal hydrides.<sup>[18-20]</sup> The structure proposed for 2 was further substantiated by a single-crystal X-ray study (Figure 1). Despite the caveats of defining hydride positions by X-ray diffraction methods, the two hydride ligands were located in the difference Fourier maps and were ascertained to be coplanar with the two Mo atoms. The Mo-H distance of 1.71 Å is in the 1.55–1.75 Å range expected for terminal Mo–H bonds. On the other hand the Mo-Mo bond length of 2.077(1) Å is in accordance with a guadruple Mo–Mo bond formulation.<sup>[21]</sup>

# Synthesis and solid-state structure of arene-bridged adducts $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2(arene)]$ (3·arene)

To induce reductive elimination of dihydrogen from the bis-(hydride) complex **2**, and form the known binuclear species  $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}]$  (**4**), with a Mo–Mo quintuple bond,<sup>[8]</sup> we performed the photolysis of a benzene solution of **2**. After stirring for 24 h at room temperature under UV light (365 nm), clean conversion to a new dark-red complex, identified as  $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2(C_6H_6)]$  (**3**·C<sub>6</sub>H<sub>6</sub>; Scheme 2 **A**) was observed. Spectroscopic and X-ray studies demonstrated that a molecule of C<sub>6</sub>H<sub>6</sub> bridges the Mo atoms of the electronrich, formally Mo<sup>1</sup><sub>2</sub> central unit, coordinating to each in a  $\eta^2$ fashion through the C1–C2 and C4–C5 bonds.



Scheme 1. Syntheses of bis(amidinate) Mo=Mo complexes with carboxylate (1) and hydride ligands (2).

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**Figure 1.** Molecular structure of **2** with anisotropic displacement parameters drawn at the 50% level and all hydrogen atoms omitted for clarity, except H1. This atom was determined by difference Fourier synthesis and refined, along with its isotropic thermal parameters, by least-square procedures.

Transition-metal arenes are a prominent family of organometallic compounds.<sup>[22-24]</sup> However, molecules that possess a multiple metal-metal bond coordinated to an aromatic hydrocarbon that actually bridges the two metal atoms are very rare. As mentioned briefly, in 2009 the group of Masuda<sup>[13]</sup> reported



Scheme 2. Photochemical and thermal generation of complexes 3-arene (arene  $= C_6H_6$ ,  $C_6H_5CH_3$ ,  $C_6H_5OCH_3$ , 1,4- $C_6H_4(CH_3)_2$ ,  $C_6H_5F$ , and 1,4- $C_6H_4F_3$ ).

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the synthesis and structural characterization of a new Mo≣Mo complex supported by 1,4-diazadiene-derived diamido ligands, with a molecule of benzene bound to each metal center in an  $\eta^2$  manner, also through the C1–C2 and C4–C5 bonds. Subsequently, the same group extended these results to the toluene and anisole analogues.<sup>[14]</sup> Nonetheless, despite extensive reactivity studies on the quintuple metal-metal bond,<sup>[7i,9a,10,11]</sup> its interaction with aromatic hydrocarbons has not been investigated. This is surprising, particularly if one considers that in landmark dichromium molecules by the Power group, that is, Ar'CrCrAr',<sup>[6,7a]</sup> each chromium atom exhibits a Cr-C<sub>arene</sub> interaction with the ipso carbon of a flanking aryl ring belonging to the terphenyl ligand bonded to the other. This so-called secondary arene interaction was later shown by quantum mechanical calculations to cause only a slight weakening of the Cr-Cr quintuple bond, whereas for cobalt and iron complexes strong  $\eta^6$ -arene coordination precluded significant metal-metal bonding.[25]

On these grounds, it was thought worthwhile to expand our knowledge of these molecules, and in this vein this study focuses on a range of arenes, which in addition to benzene and toluene,<sup>[12b]</sup> includes anisole,  $1,4-C_6H_4Me_2$ , and the fluoroarenes  $C_6H_5F$  and  $1,4-C_6H_4F_2$ . The complexes **3-arene** were synthesized by one or more of the pathways **A--C** in Scheme 2. Routes **A** and **B** are photolytic (365 nm), whereas **C** involves direct coor-

dination of the arene to the Mo-Mo quintuple bond in Tsai's complex.<sup>[8]</sup> Alternatively, these compounds may be produced thermally by arene exchange reactions (see below), but experimentally this latter procedure is less convenient as prolonged heating at 120°C in the dark is required. Accordingly, the  $C_6H_6$ , C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, and 1,4-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> adducts were quantitatively obtained starting from the bis-(hydride) compound 2 (route A in Scheme 2) and this was also a suitable method to isolate 3-anisole, which was additionally generated through procedure B. However, because of the insolubility of bis(hydride) **2** in  $C_6H_5F$ and  $p-C_6H_4F_2$ corresponding fluoarenes, 3∙C<sub>6</sub>H₅F and 3-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, were best prepared either by route B or C. Unfortunately, we did not succeed in isolating analogous complexes containing hexafluorobenzene, pyridine or anthracene, as bridging aromatic molecules.

All arene complexes **3** are very air-sensitive both in solution and in the solid state. They were iso-

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lated as dark-red diamagnetic crystalline solids. In solution, they exhibit a strong absorption in the higher energy region of the Vis spectrum (ca. 435 nm;  $\varepsilon$  ca. 3000 mol<sup>-1</sup>Lcm<sup>-1</sup>), along with other lower energy and intensity bands in the region 580–600 nm ( $\varepsilon$  ca. 700 mol<sup>-1</sup>Lcm<sup>-1</sup>).

X ray crystallographic studies of some of the arene complexes **3** were accomplished. Their solid-state molecular structures are presented in Figure 2. Despite substantial differences in the donor-acceptor properties of the aromatic molecules investigated, their Mo<sub>2</sub>-arene linkages display similar structural parameters. Thus, the Mo–Mo distances have almost the same value within experimental error, as they range from 2.105(1) Å in **3·C**<sub>6</sub>**H**<sub>5</sub>**Me** to 2.117(1) in **3·C**<sub>6</sub>**H**<sub>4</sub>**F**<sub>2</sub>. This bond length is longer than in Tsai's complex by nearly 0.1 Å, and even if it lies in the upper part of the 2.02–2.12 Å interval calculated theoretically for fivefold Mo–Mo bonding,<sup>[26]</sup> it is clearly signaling that the effective metal–metal bond order in compounds **3** must be substantially lower than five (see below).

Coordination of the C–C bonds to the Mo atoms is symmetric and it is characterized by Mo–C distances of about 2.22 Å in all compounds. Instead, distances between each Mo atom and the two remaining arene carbon atoms are significantly longer (between 2.63 and 2.74 Å, approximately) and may be judged as non-bonding. There is one exception to this trend that appears in  $3 \cdot C_6 H_4 Me_2$ , in which each Mo atom features a Mo–C separation shorter than the other (2.596(2) Å vs. 2.726(2) Å), so that in the solid state *p*-xylene coordination



In addition to these changes, there is some deviation from planarity. For example, for  $3 \cdot C_6 H_4 F_2$  the dihedral angle between the C(2)-C(1)-C(6) and C(3)-C(4)-C(5) planes is of  $3.5^{\circ}$ , whereas for  $3 \cdot C_6 H_4 Me_2$  the corresponding angle is of  $15.5^{\circ}$ . The  $C_6 H_6$  and  $C_6 H_5 Me$  adducts exhibit intermediate values of 8.9 and





6.8°, respectively. Therefore, the aromatic ring is nearly planar in  $3 \cdot C_6 H_4 F_2$  but becomes significantly folded in  $3 \cdot C_6 H_4 Me_2$ . Likewise, arene substituents undergo some bending out of the ring plane (1.4, F; 3.5 and 13.6° for the Me groups in  $3 \cdot C_6 H_5 Me$  and  $3 \cdot C_6 H_4 Me_2$ , respectively).

In all these complexes the aryl groups of the amidinate ligands pair up in a form that minimizes their steric interactions. Interestingly, in complex  $3 \cdot p - C_6 H_4 Me_2$  the para C - Me substituents are not symmetrically oriented relative to the Mo–Mo bond but adopt a distribution that reduces steric strain with the amidinate aryl substituents.

In summary, as a general rule, coordination of arenes to transition metals in low formal oxidation states causes an elongation of the six aromatic C–C bonds, deviation from planarity and a bending of the arene substituents with respect to the ring planarity. These distortions may be induced by charge-transfer from

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the electron-rich metal center to the arene. However, since the distortions ascertained for compounds **3** are comparatively smaller than in  $C_6H_6$  complexes formulated as benzenide dianions,<sup>[29,30]</sup> we conclude that such charge-transfer is modest in the **Mo<sub>2</sub>-arene** derivatives **3**. In accordance with this premise, we formulate complexes **3** as Mo<sup>1</sup><sub>2</sub> species with a coordinated neutral molecule of the arene, a proposal that is supported by the solution behavior of these complexes, in particular by their arene substitution chemistry that will be discussed below.

#### Solution structure and reactivity of complexes 3-arene

To disclose the structural characteristics of the Mol<sub>2</sub>-arene linkage of complexes 3-arene in solution, we inspected their NMR spectroscopic properties. The analysis included variable temperature (-80 to 80°C) <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR experiments, as well as NOESY and other 2D studies. All 3-arene compounds exhibit dynamic behavior in solution due to fast rotation of the arene around the Mo<sub>2</sub>-arene axis. With reference, for the sake of simplicity, first to the benzene complex  $3 \cdot C_6 H_{6}$ , eight doublet and four septet resonances appear in the <sup>1</sup>H NMR spectrum due respectively to the methyl and methine protons of the eight *i*Pr ligand substituents, in accordance with  $C_2$  molecular symmetry. This observation clearly indicates that in solution the amidinate ligands maintain the conformation observed in the solid-state structure and furthermore that rotation of the non-equivalent aryl substituents (A and B in Figure 3) is slow on the NMR timescale (500 MHz, 25 °C). Interestingly, the high-temperature NOESY spectrum of 3.C6H6  $(C_6D_6$ , 500 MHz, 70 °C) revealed the exchange of two of the four pairs of iPr groups. A reasonable explanation is that this results from rotation around the  $N-C_{ar}$  bond of two  $C_2$ -related aryl substituents (either A or B in Figure 3). The six C-H groups of the µ-benzene ring appear as isochronous at room temperature and yield only one resonance in the <sup>1</sup>H ( $\delta$  = 3.87 ppm) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra ( $\delta$  = 71.2 ppm). Cooling at -80 °C causes a significant broadening of the signals but does not permit separation of those corresponding to the four molybdenumbound and the two non-bonded C-H units. These data imply that rotation around the Mo<sup>1</sup><sub>2</sub> core is a low-barrier process that exchanges the C(H)–C(H) bonds fast in the NMR timescale. From the variable temperature NMR data, a crude estimation of  $\Delta G^{\neq} = (7.5 \pm 2.6)$  kcal mol<sup>-1</sup> can be made for this process. This is in contrast with the results reported by the group of Masuda for a  $Mo_{2}^{\parallel}C_{6}H_{6}$  complex, in which signals of the coordinated and non-coordinated C(D)-C(D) bonds were observed in the room temperature <sup>2</sup>H NMR spectrum of the C<sub>6</sub>D<sub>6</sub> isotopologue.<sup>[13]</sup> In  $3 \cdot C_6 H_6$  both the <sup>1</sup>H and <sup>13</sup>C chemical shifts have moved by about  $\delta = 3.3$  and 56 ppm, respectively, to lower frequency relative to uncoordinated benzene (evidently, the observed  $\delta$  values are the average of those corresponding to four coordinated and two non-coordinated C-H units). Such shifts are common in transition-metal olefin, diene, and arene  $\pi$ complexes and are a consequence of the nature of the M–L( $\pi$ ) bonding.<sup>[31]</sup> No significant variation was measured in the value of the averaged  ${}^{1}J_{C-H}$  (ca. 164 Hz) indicating very little change in hybridization upon coordination.





 $3 \cdot C_6 H_6$ 







**Figure 3.** Schematic representations of the solution structures of complexes **3-arene**. In all cases the rotation of the arene around the  $Mo_2^l$  core is fast on the NMR timescale at 25 °C (500 MHz).

In the remaining **3-arene** complexes, fast rotation of the arene engenders effective  $C_2$  symmetry and pairs up the 2,6*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> amidinate substituents. As a consequence, their NMR spectroscopic features are similar to those of the benzene complex analogue. Similarly to **3-C**<sub>6</sub>H<sub>6</sub>, two of the four pairs of *i*Pr groups undergo exchange due to rotation around the N–C<sub>ar</sub> bonds, but the movement is now discernible in the NOESY experiment at 25 °C. Considering the electronic diversity of substituents (Me, OMe, and F) the somewhat more facile rotation around the N–C<sub>ar</sub> bonds may be due to the steric pressure exerted by the coordinated molecule of the arene.

The NMR parameters of the arene ligand are very informative with regard to the nature of the main rotamer present in solution (only one out of the three possible rotameric structures). For instance, in **3**-**C**<sub>6</sub>**H**<sub>5</sub>**F** all the arene C–H units are nonequivalent and feature  $\delta$  values that support the structure represented in Figure 3 (bottom left) for the major rotamer, in which the C–F and its *para* C–H carbon atoms are uncoordinated. Thus, the four Mo-bound C–H groups resonate at considerably lower frequencies relative to free C<sub>6</sub>H<sub>5</sub>F (by ca.  $\delta$ =4 and 77 ppm, for the <sup>1</sup>H and <sup>13</sup>C nuclei, respectively), whereas the <sup>13</sup>C–F signal remains essentially unchanged and those of the *para* C–H nuclei move to lower frequency, but only by about  $\delta$ =1 (<sup>1</sup>H) and 20 ppm (<sup>13</sup>C). Similar NMR patterns and chemical shift variations are found in the NMR spectra of

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 $3 \cdot C_6 H_4 F_2$  and  $3 \cdot C_6 H_5 OMe$ , underpinning analogous solution structures, which for the former complex is coincident with the solid-state structure.

A rotamer with a different disposition of the coordinated arene with respect to the Mo<sup>1</sup><sub>2</sub> linkage predominates in solution for the toluene and *p*-xylene complexes (Figure 3). For the latter, the coordination of the arene is identical to that found in the solid state, as revealed by the following observations: the two coordinated quaternary C(Me) nuclei move to  $\delta =$ 71.4 ppm and the coordinated C–H to  $\delta =$  52.9 ppm (more than  $\delta = 60$  and 75 ppm respectively, to lower frequency relative to the uncoordinated arene), whereas the non-bonded C-H carbon nuclei resonate with  $\delta$  = 103.5 ppm (a variation of about  $\delta = 25$  ppm). Comparable features are observed in the <sup>1</sup>H NMR spectrum. With regards to  $3 \cdot C_6 H_5 Me$ , NMR chemical shifts of the coordinated arene are in accordance with a similar structure, with a C(Me)-C(H) bond bound to one of the Mo atoms, and therefore dissimilar to the solid-state structure. Thus, in the  ${}^{13}C{}^{1}H$  NMR spectrum the C(Me) nucleus has a chemical shift of  $\delta =$  70.1 ppm; then, there are three, comparatively low frequency, C–H signals in the interval  $\delta\!=\!59$ -65 ppm, and two higher frequency ones around  $\delta = 92$  ppm. In summary, the NMR data recorded for the Mo2·arene linkage of complexes 3-arene evidence that in all cases studied the most favorable coordination of the molecule of the arene in solution is that in which the best C-donor atoms are bonded to the Mo atoms of the central Mo<sub>2</sub> core. Inductive and resonance effects offer a simple explanation to this observation. Under this assumption, the coordination of the molecule of toluene through four CH carbon atoms found in the solid-state structure of  $3 \cdot C_6 H_5 Me$  may be due to crystal-packing effects.

Solutions of complexes **3-arene** are light-sensitive with regard to substitution of the coordinated aromatic hydrocarbon. Thus, under sunlight, solutions of **3-C**<sub>6</sub>**H**<sub>6</sub> in toluene, or of **3-C**<sub>6</sub>**H**<sub>5</sub>**Me** in benzene, underwent complete arene exchange after only  $\approx$  0.5 h. This contrasts with the inertness that these complexes exhibit in the dark. Heating **3-C**<sub>6</sub>**H**<sub>6</sub> in C<sub>6</sub>D<sub>6</sub> at 80 °C for 24 h in the absence of light resulted in scarcely any substitution; in reality, formation of the isotopologue **3-C**<sub>6</sub>**D**<sub>6</sub> required prolonged heating at 120 °C (ca. 24 h) for completion.

To complement these studies we developed some competition experiments that clarified both the kinetic and the thermodynamic preferences of the aromatic molecules, toward the  $Mo_2^{1}$  core. With reference to the latter, complex  $3 \cdot C_6 H_6$  was dissolved in about 0.6 mL of an equimolar mixture of two arene solvents (**arene-1** and **arene-2** in Scheme 3) and the resulting solution heated at 120 °C for 24 h in the dark. The outcome of the reaction was disclosed by <sup>1</sup>H NMR spectroscopic studies (C<sub>6</sub>D<sub>6</sub>) of the crude product obtained after evaporation of the arene solvent mixture (see the Supporting Information, Table S1). For experiments in which C<sub>6</sub>H<sub>6</sub> was one of the components, **3·C<sub>6</sub>H<sub>6</sub>** was the exclusive reaction product (**arene-2**: toluene, anisole, C<sub>6</sub>H<sub>5</sub>F and C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>). Similarly the *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>/*p*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> mixture resulted in **3·C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>** as the only detectable arene complex. Interestingly, the pairs C<sub>6</sub>H<sub>5</sub>Me/*p*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>F/*p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> yielded about a 3:1 ratio in favor of the monosubstituted arene, whereas closer ratios of  $\approx$  3:2 were ascertained for the C<sub>6</sub>H<sub>5</sub>Me/C<sub>6</sub>H<sub>5</sub>F and C<sub>6</sub>H<sub>5</sub>Me/*p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> couples. As indicated below, these results reveal the importance of steric effects.

An analogous approach to that summarized in Scheme 3 was employed for the kinetic competition experiments, although now Tsai's complex  $[Mo_2\{HC(N-2,6-iPr_2C_6H_3)_2\}_2]$ , **4**, was treated with the same large excess of the 1:1 arene solvent mixture indicated above. Reactions were carried out at room temperature in the dark for 24 h, since under these conditions arene-exchange reactions are negligible. The results (see the Supporting Information for details, Table S2) were strikingly similar to those described above for the experiments performed under conditions of thermodynamic control. Therefore, in comparative terms the less bulky arenes not only furnish thermodynamically more stable complexes 3-arene but they also feature faster reaction rates toward the guintuple Mo-Mo bond of 4. A good correlation exists between our experimental observations and the van der Waals radii<sup>[32]</sup> of the arene substituents: 1.0 and 1.47 Å for aromatic H and F, respectively;[32b] 1.50 Å for oxygen;<sup>[32b]</sup> and 2.0 Å for  $CH_3$ .<sup>[32a]</sup>

## **Computational studies**

The computational studies developed in our earlier communication<sup>[12b]</sup> for the benzene complex **3-C<sub>6</sub>H**<sub>6</sub> have now been extended to other **3-arene** adducts (arene = C<sub>6</sub>H<sub>5</sub>Me, *p*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, and *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>) and their rotameric preferences. Geometry optimization yields in all cases structures that are in excellent agreement with the experimental ones in the Mo–Mo and Mo–C distances, in the C–C distance distribution pattern of the aromatic ring, and in the N-Mo-Mo-N hinge angles, as well as in the orientation of the substituted arene rings. The Mo– Mo bond seems to be practically unaffected by the nature of the coordinated arene, with all four complexes showing the same distance (2.134 Å) in the calculations within 0.001 Å, similar to the experimental results (2.110±0.007 Å). The four short Mo–C distances vary also in less than 0.02 Å from one complex



Scheme 3. Arene competition experiments performed under thermodynamic control. Dipp = 2,6- $iPr_2C_6H_3$ .

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cupied, ensuing in a weakening

of the C–C bonds. From the valence-bond point of view one

could construct several Lewis structures with different occupations of these fragment orbitals that imply two-electron excita-

tions of either fragment and cross-donation of two electron pairs between  $Mo_2$  and  $C_6H_6$ , or two-electron transfer from one

fragment to the other (the Supporting Information, Scheme S1). Such a symmetry-imposed electronic rearrangement<sup>[12b]</sup> results

in a weakening of both the Mo-Mo and benzene C-C bonds, which is neatly reflected in the

lengthening of the Mo–Mo bond is indeed appreciated when comparing the structures

of the quintuply bonded Mo<sub>2</sub>L<sub>2</sub> compound and its benzene adduct, whereas a ring expan-

sion due to the weakening of

the C–C bonds can be appreciated by increases in the sum of

experimental

structures.

Α

to another. The interaction energies between the arene and the  $Mo_2L_2$  fragment are around 60 kcal mol<sup>-1</sup>. The difluoro derivative is somewhat more strongly bound (-62 kcal mol<sup>-1</sup>) and the benzene, toluene and xylene adducts have similar interaction energies (-57, -56, and -55 kcal mol<sup>-1</sup>, respectively).

The orbitals of the dimolybdenum and arene fragments that are responsible for the bonding between the quintuple bond and the aromatic hydrocarbon are shown in Figure 4, in which the two B<sub>2</sub> orbitals are occupied and the two A<sub>2</sub> ones are empty (the Supporting Information, Figure S13), in the Mo<sub>2</sub>– C<sub>6</sub>H<sub>6</sub> adduct the antibonding B<sub>2</sub> combination is empty whereas the bonding orbital with A<sub>2</sub> symmetry is occupied. As a consequence, the Mo–Mo bonding  $\delta(B_2)$  orbital is partially depopulated and its antibonding counterpart  $\delta^*(A_2)$  is partially occupied, resulting in a decreased Mo–Mo bond order.<sup>[12b]</sup> Similarly, the C–C bonding  $\pi(B_2)$  orbital is in part depopulated and the antibonding  $\pi^*(A_2)$  is partly oc-



**Figure 4.** Occupied (lower three rows) and empty (upper three rows) orbitals that participate in bonding between the Mo<sub>2</sub> and benzene fragments, classified according to their symmetry representations in the  $C_{2\nu}$  point group.

they have been classified in accordance with their symmetry in the idealized  $C_{2\nu}$  symmetry point group. These comprise the  $\pi$ system of the arene (represented in Figure 4 by  $C_6H_6$ ), the inphase and out-of-phase combinations of the acceptor sp<sup>2</sup> hybrid orbitals of the  $Mo_2$  unit, and one of the two pairs of  $\delta$ and  $\delta^*$  orbitals (with symmetry representations  $B_2$  and  $A_2\text{, re-}$ spectively). The other  $\delta/\delta^*$  orbital pair is not shown because these orbitals have the same symmetry as the combinations of the sp<sup>2</sup> hybrids (see the Supporting Information, Figure S12) and play a minor role in the Mo<sub>2</sub>-arene interaction. Disregarding in a first approximation the high lying  $\pi$  orbitals of benzene of the A<sub>1</sub> and B<sub>2</sub> symmetry representations (depicted in gray in Figure 4), we are left with a pair of orbitals for each symmetry representation to build up four Mo<sub>2</sub>-benzene bonding orbitals and their four antibonding counterparts. The six electrons of benzene and the two  $\delta$  electrons therefore occupy fully the four bonding MOs.

Focusing the discussion on the orbitals with  $A_2$  and  $B_2$  symmetries that are responsible for the back-bonding interactions,<sup>[12b]</sup> despite the fact that in the independent fragments

the six experimental bond distances of 0.22 Å or higher upon coordination (0.24 Å computationally).

As a consequence of the back donation from the  $\delta(B_2)$  orbital to the  $\pi$  system, the coordinated arene becomes negatively charged, according to a natural population analysis (NPA). Whereas the differences between benzene, toluene, and xylene are minimal (-0.21, -0.20, and -0.19, respectively), difluorobenzene bears a significantly higher negative charge (-0.30). This differential behavior is due to the interaction of the  $\boldsymbol{\pi}$  orbitals of the fluorine atoms with those of the phenyl ring. In the uncoordinated difluorobenzene molecule there is a three-orbital interaction of the in-phase combination of the fluorine  $\pi$  lone pair orbital with one occupied and one empty  $\pi$  orbitals of the phenyl ring, all belonging to the A<sub>1</sub> symmetry species (the Supporting Information, Figure S14). The result is a localization of the occupied  $\pi$  orbital at the unsubstituted carbon atoms of the phenyl ring, which may explain the preference of difluorobenzene for an orientation that is not the most favorable one from a steric point of view (see the Supporting Information for a more detailed discussion of steric ef-



fects). This orientation is, however, consistent with a high positive charge at the substituted carbon atoms (+0.32 and +0.45 in the uncoordinated and coordinated molecule, respectively), which contrasts with practically neutral carbon atoms in toluene and xylene, and with a negative charge in benzene (-0.21). The above observations are also in agreement with the marked NMR shieldings observed for the CH units involved in the coordination to the  $Mo_2$  core that was considered before.

To complete this investigation we carried out a computational study of the rotational isomers and the rotational barriers for the benzene, *p*-xylene, *p*-difluorobenzene, and toluene adducts, with the results summarized in Figure 5 (see the Sup-



**Figure 5.** The experimentally found rotamers in the solid state and in solution (first column), and calculated free energies for different energy minima and transition states found computationally. The dashed line indicates the relative position of the  $Mo_2$  unit.

porting Information for additional information details). It can be seen that in the first three cases the lowest energy minimum has the same geometry as found experimentally both in the solid state and in solution. With reference once more to **3-C<sub>6</sub>H<sub>6</sub>** as model complex, the exchange of the coordinated and non-coordinated C–C bonds, which explains the already discussed solution dynamic behavior of these complexes, occurs through a  $\mu$ - $\eta^3$ : $\eta^3$  transition state that lies about 9.9 kcal mol<sup>-1</sup> above the ground state. This energy barrier is in good agreement with the  $\Delta G^{\neq}$  value of  $\approx$  (7.5±2.6) kcal mol<sup>-1</sup>, which can be estimated from variable temperature <sup>1</sup>H NMR data (see above). For toluene the predominant rotamer in solution is different from the one found in the crystal structure, but those two structures are coincident with the calculated minima, which differ by only 2.5 kcalmol<sup>-1</sup> and are separated by a barrier of 14 kcalmol<sup>-1</sup>. The existence of only two minima for the **3-arene** complexes (Figure 5) can be understood by analyzing the topology of the cavity in which the  $\pi$ -coordinated arene sits surrounded by the aryl groups of the bidentate amidinate ligands. This is shown in Figure S15 (left, in the Supporting Information); additional details for this structural problem are provided in the Supporting Information.

#### Conclusion

We have demonstrated that the bis(hydride) complex  $[Mo_2(H)_2[HC(N-2,6-iPr_2C_6H_3)_2]_2(thf)_2]$ , **2**, which features a Mo–Mo quadruple bond, experiences photolytic reductive elimination of dihydrogen in different reaction solvents to form bis(amidinate) derivatives of the Mo<sup>1</sup><sub>2</sub> core. The use of cyclohexane permits isolation of quintuply bonded molecules of  $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2]$ , **4**, known since 2009 thanks to the pioneering work of Tsai and co-workers,<sup>[8]</sup> whereas employing benzene or other arene solvents, corresponding adducts of the Mo<sup>1</sup><sub>2</sub> central unit are obtained instead. These **3-arene** complexes can also be accessed by the direct reaction of **4** with the arene.

The experimental and computational studies reported herein support the formulation of the arene complexes as Mo<sup>1</sup><sub>2</sub> species resulting from a Lewis acid/base interaction between the quintuple Mo-Mo bond of 4 and the aromatic hydrocarbon. This proposal finds reinforcement in the reversibility of the reactions of 4 with the investigated arenes and is additionally underpinned by the arene substitution chemistry discussed above. In accordance with these arguments, throughout this paper compounds 3-arene have been represented as Mo<sup>1</sup><sub>2</sub> derivatives, thereby exhibiting a "formal" Mo-Mo bond order of five. However, the strong electronic interaction that exists between a pair of  $\delta/\delta^*$  orbitals of the dimolybdenum unit and the  $\pi$  system of the arene results in the partial depopulation of the bonding  $\delta(B_2)$  orbital and the partial occupation of the antibonding  $\delta^*(A_2)$  orbital. Hence, despite the formal quintuple bond representation, the calculated Meyer bond order is of about 3<sup>[12b]</sup> (ca. 3.6 in Power's Ar'CrCrAr' complexes)<sup>[6]</sup>, which makes a quadruple Mo-Mo bond a more realistic description of the electronic structure of the Mol<sub>2</sub> central unit of 3-arene complexes.

## **Experimental Section**

#### **General considerations**

All manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried and degassed prior to use, and stored over 4 Å molecular sieves. Cyclohexane  $(C_6H_{12})$ , toluene  $(C_7H_8)$ , *n*-pentane  $(C_5H_{12})$ , and anisole  $(C_6H_5OMe)$  were distilled under nitrogen over sodium. Tetrahydrofuran (THF) was distilled under nitrogen over sodium/benzophenone.  $[D_6]$ Benzene and  $[D_8]$ THF were distilled under argon over sodium/



benzophenone; [D<sub>8</sub>]toluene and [D<sub>12</sub>]cyclohexane were distilled under argon over sodium. Fluorobenzene and 1,4-difluorobenzene were dried over sodium during 4 and 12 h, respectively. The quadruply bonded dimolybdenum complexes  $[Mo_2(O_2CR)_4]$  (R = H, Me)<sup>[33]</sup> as well as the formamidinate ligand H{HC(N-2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>},<sup>[34]</sup> and its lithium salt  $[Li{HC}(N-2,6-iPr_2C_6H_3)_2][THF]_2$ ,<sup>[35]</sup> were prepared according to literature methods. [Mo2(O2CMe)4] was washed with toluene at 100  $^{\circ}\text{C}$  to remove any acidic residue. [Mo\_2(O\_2CR)\_2{HC(N- $2,6-iPr_2C_6H_3)_2$  (R=Me, **1a** and R=H, **1b**), bis(hydride) complex  $[Mo_2(H)_2\{HC(\textit{N-2,6-i}Pr_2C_6H_3)_2\}_2(thf)_2]$  (2) and the quintuply bonded dimolybdenum complex  $[Mo_2{HC(N-2,6-iPr_2C_6H_3)_2}_2]$  (4)<sup>[8]</sup> were prepared by the synthetic methods communicated recently by our research group.<sup>[12b]</sup> All other compounds were commercially available and were used as received. Photochemical reactions were carried out using a medium pressure mercury lamp, model 3010 (Photochemical Reactors Ltd). Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. The resonance of the solvent was used as the internal standard, chemical shifts are reported relative to TMS and the NMR signals of fluorinated derivatives are reported relative to CFCl<sub>3</sub>. UV/Visible spectra were recorded on a PerkinElmer Lambda 750 spectrometer. For elemental analyses a LECO TruSpec CHN elementary analyzer was utilized and infrared experiments were carried out on a Bruker Vector 22 and Tensor 27 spectrometer. For details on the computational study see ref. 12b.

#### Syntheses

#### $[Mo_{2}(H)_{2}\{HC(N-2,6-iPr_{2}C_{6}H_{3})_{2}\}_{2}(thf)_{2}] (2)$

This synthesis involves compound **1a** and LiMe and produces initially a trimethyl dimolybdate lithium derivative, by substitution of the two acetate ligands of **1a**. Loss of LiMe from the "ate" complex occurs upon heating in a mixture of hydrocarbon solvents, yielding a neutral dimethyl bis(amidinate) dimolybdenum species, which upon reaction with  $H_2$  affords the title compound. Details of this three-step, one-flask procedure are given below.

A suspension of 1a (4.0 g, 3.86 mmol) in THF (80 mL) was cooled at -10°C and LiMe (8.3 mL, 1.6 M solution in Et<sub>2</sub>O) was added slowly with a syringe. The reaction mixture was stirred overnight, allowing it to reach slowly to room temperature, to give a red suspension that was centrifuged and taken to dryness. A mixture of toluene/hexane (45/15 mL) was added and the solution was heated at 100 °C for 5 h, after which time it was cooled to 25 °C and centrifuged. The solvent was removed under vacuum and the residue dissolved in toluene (20 mL) and treated with dihydrogen for one day (1 bar, 20 °C, with stirring). Removal of the solvent under vacuum, washing of the crude product with cold pentane (0 °C) and crystallization from THF at -20 °C for 2 days, provided yellow crystals of the desired product that were dried under vacuum for 2 h (yield: 1.85 g, 45%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C):  $\delta = 1.02$ , 1.09 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 12H each; 2 CHMe<sub>2</sub>), 1.27 (m, 8H; O- $CH_2CH_2$ ), 1.35, 1.48 (d,  ${}^{3}J_{HH} = 6.8$  Hz, 12H each; 2CHMe<sub>2</sub>), 3.40 (m, 8H; O-CH<sub>2</sub>CH<sub>2</sub>), 3.80, 4.46 (sept,  ${}^{3}J_{HH}$  = 6.8 Hz, 4H each; 4CHMe<sub>2</sub>), 5.67 (s, 2H; Mo-H), 7.01-7.07 (m, 12H; aromatics), 8.45 ppm (s, 2H; NC(H)N);  ${}^{13}C{}^{1}H$  NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 24.9, 25.0 (CH*Me*<sub>2</sub>), 25.6 (O-CH2CH2), 25.7, 27.1 (CHMe2), 28.3, 28.5 (CHMe2), 69.2 (O-CH<sub>2</sub>CH<sub>2</sub>), 123.7, 123.9 (m-Dipp), 126.0 (p-Dipp), 144.9, 143.9 (o-Dipp), 145.9 (ipso-Dipp), 161.6 ppm (NC(H)N); UV/Vis (benzene solution  $10^{-4}$  M):  $\lambda$  ( $\epsilon$ ) = 348 (5300), 425 (2000), 548 nm (1200  $M^{-1}$  cm<sup>-1</sup>); magnetic susceptibility:  $\chi = -12.7 \times 10^{-4}$  cm<sup>3</sup> mol<sup>-1</sup>; elemental analysis calcd (%) for  $C_{58}H_{88}Mo_2N_4O_2\colon$  C 65.40; H 8.33; N 5.26; found: C 65.1; H 7.9; N 5.0.

## $3 \cdot C_6 H_6$ and $3 \cdot C_6 H_5 Me$ (Method A)<sup>[12b]</sup>

The two compounds were obtained by UV irradiation (365 nm) of stirred solutions of complex 2 (ca. 0.40–0.50 g) in benzene or toluene (10 mL) for 24 h. Green/yellow solutions resulted from these transformations that were evaporated to dryness. Solids were washed with pentane at 0 °C giving products sufficiently pure for reactivity studies in yields of about 70%. Crystallization of the crude solids from light-protected solutions in hexane with small amounts of benzene and ether (in the case of  $3 \cdot C_6 H_6$ ), or toluene plus pentane (for  $3 \cdot C_6 H_5 Me$ ), provided microanalytically pure compounds.

#### Compound 3.C6H6

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.04, 0.76, 0.98, 1.05, 1.06, 1.12, 1.19, 1.51 (d, 6 H each, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz; CHMe<sub>2</sub>), 2.54, 2.89, 3.39, 3.59 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2 H each; 2 CHMe<sub>2</sub>), 3.87 (s, 6 H, Mo<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>), 6.92 (dd, <sup>2</sup>J<sub>HH</sub> = 2.7 Hz, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2 H; *m*-Dipp<sup>B</sup>), 6.95–7.00 (m, 6 H; *m*-Dipp<sup>B</sup>, *p*-Dipp<sup>B</sup>, *m*-Dipp<sup>A</sup>), 7.09 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H; *p*-Dipp<sup>A</sup>), 7.20 (dd, <sup>2</sup>J<sub>HH</sub> = 1.4 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H; *m*-Dipp<sup>A</sup>), 7.56 ppm (s, 2 H; NC(H)N); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 23.3, 24.3, 24.4, 24.7, 25.3, 25.6 (CHMe<sub>2</sub>), 27.1 (CHMe<sub>2</sub> and CHMe<sub>2</sub>), 27.6, 27.8 (CHMe<sub>2</sub>), 27.9 (CHMe<sub>2</sub>), 28.3 (CHMe<sub>2</sub>), 71.7 (Mo<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>), 123.0, 123.4, 124.7, 124.9 (*m*-Dipp), 125.0, 125.1 (*p*-Dipp), 141.7, 143.4, 143.9, 144.3 (*o*-Dipp), 144.8, 147.4 (*ipso*-Dipp), 161.1 ppm (NC(H)N); Magnetic susceptibility:  $\chi$  = -15.6 × 10<sup>-4</sup> cm<sup>3</sup> mol<sup>-1</sup>. UV/Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\varepsilon$ ) 435 (3050), 595 nm (545 M<sup>-1</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>56</sub>H<sub>76</sub>Mo<sub>2</sub>N<sub>4</sub>: C 67.45; H 7.68; N 5.62; found: C 67.8; H 8.0; N 5.9.

#### Compound 3.C<sub>6</sub>H<sub>5</sub>Me

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 0.05$ , 0.85 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H each; CHMe<sub>2</sub>), 0.99-1.02 (m, 12H; 2CHMe<sub>2</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 6H; CHMe<sub>2</sub>), 1.17, 1.20 (d,  ${}^{3}J_{HH} = 6.8$  Hz; 6H each, CHMe<sub>2</sub>), 1.50 (d,  ${}^{3}J_{HH} = 6.8$  Hz; 6 H, CHMe<sub>2</sub>), 1.60 (s, 3 H; C<sub>6</sub>H<sub>5</sub>Me), 2.64 (sept,  ${}^{3}J_{HH} =$ 6.8 Hz, 2H; 2CHMe<sub>2</sub>), 3.10 (sept, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 2H; 2CHMe<sub>2</sub>), 3.31-3.37 (m, 4H; C<sup>3</sup>H, C<sup>4</sup>H and 2C*H*Me<sub>2</sub>), 3.40 (br. d,  ${}^{3}J_{HH} = 5.6$  Hz, 1H; C<sup>6</sup>H), 3.58 (sept, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 2H; 2C*H*Me<sub>2</sub>), 4.88 (m, 1H; C<sup>2</sup>H), 5.14 (t,  ${}^{3}J_{HH} = 5.6$  Hz, 1 H; C<sup>5</sup>H), 6.91 (br. d,  ${}^{3}J_{HH} = 7.4$  Hz, 2 H; *m*-Dipp<sup>A</sup>), 6.96 (t, <sup>3</sup>J<sub>HH</sub>=7.4 Hz, 2H; *p*-Dipp<sup>A</sup>), 7.00 (m, 2H; *m*-Dipp<sup>B</sup>), 7.06 (m, 2H; m-Dipp<sup>A</sup>), 7.11 (t,  ${}^{3}J_{HH} = 7.6$  Hz, 1H, p-Dipp<sup>B</sup>), 7.21 (br. d,  ${}^{3}J_{HH} =$ 7.6 Hz, 2 H; *m*-Dipp<sup>B</sup>), 7.57 ppm (s, 2 H; NC(H)N); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 17.3 (C<sub>6</sub>H<sub>5</sub>Me), 23.5, 24.3, 24.7, 24.8, 25.5, 25.7, 27.3 (CHMe2), 27.4, 27.6, 27.8 (CHMe2), 27.9 (CHMe2), 28.3 (CHMe2), 59.4 (C4), 62.3 (C3), 65.1 (C6), 70.1 (C1), 91.6 (C2), 92.5 (C5), 123.1, 123.6, 124.8, 124.9, 125.0, 125.1 (metha and para aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 142.0, 143.1, 144.4, 144.7 (o-Dipp), 144.9, 147.6 (*ipso*-Dipp<sup>A</sup>, *ipso*-Dipp<sup>B</sup>), 161.3 ppm (NC(H)N); UV/Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\varepsilon$ ) 430 (2160), 595 nm (680  $M^{-1}$  cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>57</sub>H<sub>78</sub>Mo<sub>2</sub>N<sub>4</sub>: C 67.71; H 7.78; N 5.54; found: C 68.0; H 8.1; N 5.7.

#### $3 \cdot C_6 H_4 Me_2$ (Method A)

This complex was prepared following the procedure described above. Dark-red crystals were obtained from a *p*-xylene solution of this complex stored at 5 °C for 48 h and were dried under vacuum (yield: 70%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>12</sub>, 25 °C):  $\delta = -0.18$ , 0.80, 0.98, 1.02, 1.12, 1.14, 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H each; CHMe<sub>2</sub>), 1.31 (s, 6H; *p*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>), 1.46 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H; CHMe<sub>2</sub>), 2.60 (dd, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 2H; C<sup>3,6</sup>H, AA'BB' system), 2.65, 3.02, 3.42, 3.55 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H each; 2CHMe<sub>2</sub>), 5.49 (dd, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 2H; C<sup>2,5</sup>H, AA'BB' system), 6.77 (brd, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H; *m*-

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Dipp<sup>A</sup>), 6.86 (t,  ${}^{3}J_{HH} = 7.6$  Hz, 2 H; *p*-Dipp<sup>A</sup>), 6.97 (d,  ${}^{3}J_{HH} = 7.6$  Hz, 2 H; *m*-Dipp<sup>A</sup>), 7.01 (br. d,  ${}^{3}J_{HH} = 7.6$  Hz, 2 H; *m*-Dipp<sup>B</sup>), 7.08 (t,  ${}^{3}J_{HH} = 7.6$  Hz, 2 H; *p*-Dipp<sup>B</sup>), 7.21 (brd,  ${}^{3}J_{HH} = 7.6$  Hz, 2 H; *m*-Dipp<sup>B</sup>), 7.38 ppm (s, 2 H; NC(H)N);  ${}^{13}C{}^{1}H$  NMR (125 MHz, C<sub>6</sub>D<sub>12</sub>, 25 °C):  $\delta = 15.8$  (*p*-C<sub>6</sub>H<sub>4</sub>*Me*<sub>2</sub>), 24.4, 24.7, 25.4, 26.0, 26.1, 26.7 (CH*Me*<sub>2</sub>), 27.8, 27.9, 28.5, 28.6 (CHMe<sub>2</sub>), 28.9, 29.0 (CH*Me*<sub>2</sub>), 52.9 (C<sup>3.6</sup> H), 71.4 (C<sub>q</sub><sup>1.4</sup>), 103.5 (C<sup>2.5</sup> H), 123.5 (*m*-Dipp<sup>A</sup>), 124.4 (*m*-Dipp<sup>B</sup>), 125.2 (*m*-Dipp<sup>A</sup>, *p*-Dipp<sup>A</sup>, *m*-Dipp<sup>B</sup>), 125.7 (*p*-Dipp<sup>B</sup>), 143.0, 143.1, 144.1 (*o*-Dipp), 145.2 (*ipso*-Dipp), 145.4 (*o*-Dipp), 148.4 (*ipso*-Dipp), 161.6 ppm (NC(H)N); UV/Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\varepsilon$ ) 435 (3280), 595 nm (500 m<sup>-1</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>58</sub>H<sub>80</sub>Mo<sub>2</sub>N<sub>4</sub>: C 67.95; H 7.87; N 5.47; found: C 68.3; H 8.4; N 5.9.

#### $3 \cdot C_6 H_5 OMe$ (Method B)

This compound was obtained by UV irradiation (365 nm) of stirred solutions of complex  $3 \cdot C_6 H_6$  (ca. 0.35 g) in anisole (5 mL) for 12 h. A dark-red solution was evaporated to dryness. The solid was washed with pentane at 0°C giving a product sufficiently pure for reactivity studies in yields of about 60%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = -0.17$  (brs, 6H; CHMe<sub>2</sub>), 0.65, 1.01, 1.05 (d,  ${}^{3}J_{HH} = 6.7$  Hz, 6H each; CHMe<sub>2</sub>), 1.18 (m, 12H; 2CHMe<sub>2</sub>), 1.21, 143 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H each; CHMe<sub>2</sub>), 2.91 (d,  ${}^{3}J_{HH} = 5.4$  Hz, 1H; C<sup>2</sup>H or C<sup>6</sup>H), 3.08–3.15 (m, 4H; C<sup>2</sup>H or C<sup>6</sup>H, C<sup>3</sup>H or C<sup>5</sup>H, CHMe<sub>2</sub>), 3.22 (m, 4H;  $C_6H_5OMe$ , C<sup>3</sup>H or C<sup>5</sup>H), 3.37 (m, 4H; 4CHMe<sub>2</sub>), 3.51 (sept,  ${}^3J_{HH} =$ 6.7 Hz, 2 H; 2 CHMe\_2), 6.05 (t,  ${}^{3}J_{HH} = 5.4$  Hz, 1 H; C<sup>4</sup>H), 6.94–7.22 (m, 12H; aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 7.57 (s, 2H; NC(H)N); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 23.5–28.4 (12C; CHMe<sub>2</sub> and CHMe<sub>2</sub>), 42.8, 46.4 (C<sup>2</sup> or C<sup>6</sup>), 52.1 (C<sup>3</sup> or C<sup>5</sup>), 54.8 (C<sub>6</sub>H<sub>5</sub>OMe), 56.8 (C<sup>3</sup> or C<sup>5</sup>), 100.0 (C<sup>4</sup>), 123.1–125.4 (6 C; meta and para aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 141.7–147.7 (6C; ortho and ipso aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 161.5 ppm (NC(H)N); UV/Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\epsilon$ ) 430 (2745), 560 nm (870 m<sup>-1</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>57</sub>H<sub>78</sub>Mo<sub>2</sub>N<sub>4</sub>O: C, 66.25; H 7.65; N 5.45; found: C 66.3; H 7.9; N 5.4.

#### $3 \cdot C_6 H_5 F$ and $3 \cdot C_6 H_4 F_2$ (Method C)

The compounds  $3 \cdot C_6 H_5 F$  and  $3 \cdot C_6 H_4 F_2$  were obtained by stirring a solution of complex 4 (ca. 0.20–0.25 g) in fluorobenzene or 1,4difluorobenzene (5–8 mL) of at room temperature for 24 h in the dark. The red filtered solution was concentrated and stored at 5 °C for 48 h. For  $3 \cdot C_6 H_4 F_2$ , dark-red crystals were separated from the solution and dried under vacuum (yield: 55%). In the case of  $3 \cdot C_6 H_4 F$ , the solid was separated from the red solution and dried in vacuo (yield: 50%).

#### Compound 3.C<sub>6</sub>H<sub>5</sub>F

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.04, 0.80, 0.99, 1.03, 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H each; CH*M*e<sub>2</sub>), 1.17 (m, 12H; 2CH*M*e<sub>2</sub>), 1.48 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H; CH*M*e<sub>2</sub>), 2.85 (m, 3 H; 2*CH*Me<sub>2</sub>, C<sup>3</sup>H or C<sup>5</sup>H), 3.02 (m, 2 H; C<sup>2</sup>H or C<sup>6</sup>H, C<sup>3</sup>H or C<sup>5</sup>H), 3.11 (m, 3 H; C*H*Me<sub>2</sub>, C<sup>2</sup>H or C<sup>6</sup>H), 3.26, 3.52 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H each; 2*CH*Me<sub>2</sub>), 5.77 (m, 1H; C<sup>4</sup>H), 6.93–7.21 (12H; aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 7.58 ppm (s, 2H; NC(H)N); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 23.8, 24.5, 25.2, 25.9, 26.0, 27.5 (CH*M*e<sub>2</sub>), 27.7 (CHMe<sub>2</sub>), 27.9 (br. s, CHMe<sub>2</sub>), 28.2 (br. s, CH*M*e<sub>2</sub>), 28.7 (CHMe<sub>2</sub>), 39.2 (d, <sup>2</sup>J<sub>CF</sub> = 21.1 Hz; C<sup>2</sup>H or C<sup>6</sup>H), 48.2 (d, <sup>2</sup>J<sub>CF</sub> = 19.5 Hz; C<sup>2</sup>H or C<sup>6</sup>H), 48.4 (d, <sup>3</sup>J<sub>CF</sub> = 7.3 Hz; C<sup>3</sup>H or C<sup>5</sup>H), 58.1 (d, <sup>3</sup>J<sub>CF</sub> = 10.3 Hz, C<sup>3</sup>H or C<sup>5</sup>H), 102.7 (C<sup>4</sup>H), 123.2, 123.9, 125.3, 125.4 (*m*-Dipp), 125.5, 125.6 (*p*-Dipp), 142.5, 143.7, 144.1, 144.6 (*o*-Dipp), 145.0, 147.7 (*ipso*-Dipp), 161.8 (NC(H)N), 162.3 ppm (d, <sup>1</sup>J<sub>CF</sub> = 274 Hz; C<sup>1</sup>-F); <sup>19</sup>F NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -105.4 ppm; UV/ Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\varepsilon$ ) 430 (1900), 580 nm (410 M<sup>-1</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for  $C_{56}H_{75}FMo_2N_4\colon C$  66.26; H 7.45; N 5.52; found: C 65.9; H 7.9; N 5.7.

#### Compound 3.C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.07, 0.85, 0.99, 1.12 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 6H each; CH*M*e<sub>2</sub>), 1.21 (m, 12 H; 2CH*M*e<sub>2</sub>), 1.27, 1.49 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 6H each; CH*M*e<sub>2</sub>), 2.98 (m, 2H; C<sup>2.5</sup>H or C<sup>3.6</sup>H), 3.21 (m, 6H; CH*M*e<sub>2</sub>), 6.95–7.25 (m, 12 H; aromatics Dipp<sup>A</sup> and Dipp<sup>B</sup>), 7.67 (s, 2H; NC(H)N); <sup>13</sup>C(<sup>1</sup>H) NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 23.9, 24.5, 25.5, 25.9, 26.3, 26.4 (CH*M*e<sub>2</sub>), 27.5 (CH*M*e<sub>2</sub>), 27.7 (CH*M*e<sub>2</sub>), 28.2, 28.3 (CH*M*e<sub>2</sub>), 28.4 (CH*M*e<sub>2</sub>), 28.8 (CHMe<sub>2</sub>), 37.9, 46.2 (dd, <sup>3</sup>J<sub>CF</sub> = 20 Hz, <sup>4</sup>J<sub>CF</sub> = 13 Hz, C<sup>2.5</sup>H or C<sup>3.6</sup>H), 123.2, 124.1 (*m*-Dipp<sup>A</sup> each), 125.5 (*p*-Dipp<sup>A</sup>), 125.7 (*p*-Dipp<sup>B</sup>), 125.8, 125.9 (*m*-Dipp<sup>B</sup> each), 142.9, 143.8, 144.0, 144.5 (*o*-Dipp), 145.1, 147.7 (*ipso*-Dipp), 159.5 (d, <sup>1</sup>J<sub>CF</sub> = 270 Hz; C<sup>1.4</sup>-F), 162.2 (NC(H)N); <sup>19</sup>F NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -114.3 ppm. UV/Vis (C<sub>6</sub>H<sub>6</sub>);  $\lambda_{max}$  ( $\varepsilon$ ) 445 (1900), 560 nm (620 m<sup>-1</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>56</sub>H<sub>74</sub>F<sub>2</sub>Mo<sub>2</sub>N<sub>4</sub>: C 65.10; H 7.22; N 5.42; found: C 65.17; H 7.16; N 5.02.

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