

Preparation and characterization of the kinetic and thermodynamic isomers of dinuclear molybdenum and tungsten complexes with metal–metal triple bonds supported by *p*-*tert*-butylcalix[4]arene anions†

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The reaction between $M_2(NMe_2)_6$ and <2 equiv. of *p*-*tert*-butylcalix[4]arene (H_4L) in hydrocarbon solvents leads to $(H_2NMe_2)_2[M_2(\mu, \eta^2, \eta^2-L)_2]$ **1** ($M = Mo, W$), which isomerizes to the unbridged isomers $(H_2NMe_2)_2[M_2(\eta^4-L)_2]$ **2** upon heating in refluxing pyridine ($L =$ quadruply deprotonated calix[4]arene); related complexes $M_2(\eta^4-HL)_2$ **3** ($M = Mo, W$) are prepared from reactions involving $M_2(OBu^t)_6$ and H_4L , and these react with $HNMe_2$ to give **2** ($M = Mo$ and W) while $[NH_2Me_2][W_2(\eta^4-L)(\eta^4-HL)]$ **4** can be obtained by the reaction between **2** and **3** ($M = W$) in a 1:1 ratio.

The recent communication of the elegant synthesis of $W-W$ bonded complexes supported by the *p*-*tert*-butylcalix[4]arene tetraanion, L , namely $Na_2W_2(\eta^4-L)_2(\mu-Cl)_2$ ($M=M$) and $Na_2W_2(\eta^4-L)_2$ ($M\equiv M$),¹ leads us to report on our related findings concerning $(M\equiv M)^{6+}$ centers.

The reaction between $M_2(NMe_2)_6$ and *p*-*tert*-butylcalix[4]arene, H_4L (1.7 equiv.) in a hydrocarbon solvent leads to the formation of green compounds **1** ($M = Mo, W$).[‡] The 1H NMR spectrum reveals one type of Bu^t group and two CH_2 groups, each being diastereotopic, consistent with the structure found for $M = Mo$ in the solid-state shown in Fig. 1.[§] The μ, η^2, η^2-L bridging of the calix[4]arene ligand is similar to that reported for the $Mo-Mo$ quadruple bonded complex $Mo_2(OAc)_2(\mu, \eta^2, \eta^2-H_2L)^2$ but the $Mo-Mo$ distance in the

$M-M$ triple bonded complex is larger by *ca.* 0.07 Å as is commonly seen in comparing $Mo-Mo$ bonded complexes of bond order 4 and 3.³ Also the $Mo-O$ distances are somewhat shorter in the present structure consistent with the Mo_2^{6+} center. The W complex is isomorphous.[§]

We recently have prepared a number of complexes of the type $Mo_2(NMe_2)_2(\mu-diolate)_2$ and noted that bridged diolates are often formed kinetically. The addition of pyridine and heat causes isomerization to the chelate isomers, $Mo_2(NMe_2)_2(\eta-diolate)_2$, which represent the thermodynamic products.⁴ We thus reasoned that the dumb-bell-like isomer $Mo_2(\eta^4-HL)_2$ might be thermodynamically favored and, indeed, upon refluxing in pyridine the green solutions of $(H_2NMe_2)_2[Mo_2(\mu, \eta^2, \eta^2-L)_2]$ **1** turn amber.[‡] The 1H NMR spectrum becomes simpler revealing again one type of Bu^t group and one CH_aH_b group with a large chemical shift difference (δ 5.3 and 3.3 ppm) as might be expected if one CH bond were proximal and the other distal to the $Mo-Mo$ triple bond.⁵ Amber crystals of $[NH_2Me_2]_2[Mo_2(\eta^4-L)_2]$ **2** were obtained that were suitable for an X-ray study and the molecular structure is shown in Fig. 2.[§]

It is interesting to note that in both structural determinations the calix[4]arene ligands encapsulate or attract molecules of dimethylamine, as $[NH_2Me_2]^+$ cations, and solvent molecules. However, upon heating crystalline samples of the kinetic and thermodynamic isomers in a dynamic vacuum, **1**·4thf ($M = Mo$) loses only thf molecules whereas **2**·4py ($M = Mo$) loses

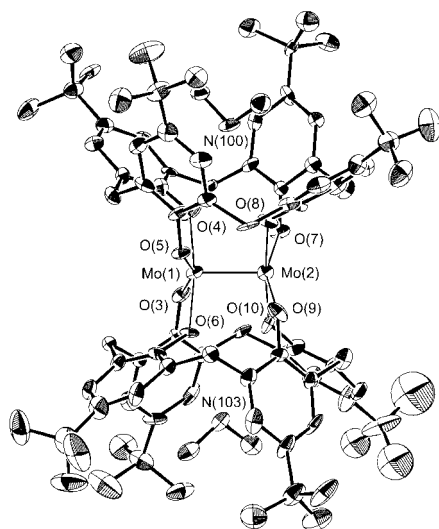


Fig. 1 An ORTEP drawing of **1** ($M = Mo$) showing the atom numbering scheme. Selected bond lengths (Å) and bond angles (°): $Mo(1)-Mo(2)$ 2.194(2), $Mo(1)-O(3)$ 2.033(7), $Mo(1)-O(4)$ 1.959(8), $Mo(1)-O(5)$ 2.009(7), $Mo(1)-O(6)$ 1.968(7), $Mo(2)-O(7)$ 2.035(7), $Mo(2)-O(8)$ 1.989(7), $Mo(2)-O(9)$ 2.025(7), $Mo(2)-O(10)$ 1.954(8); $Mo(2)-Mo(1)-O(3)$ 101.6(2), $Mo(2)-Mo(1)-O(4)$ 94.1(3), $Mo(2)-Mo(1)-O(5)$ 101.9(2), $Mo(2)-Mo(1)-O(6)$ 94.5(2), $Mo(1)-Mo(2)-O(7)$ 102.2(2), $Mo(1)-Mo(2)-O(8)$ 92.1(2), $Mo(1)-Mo(2)-O(9)$ 100.7(2), $Mo(1)-Mo(2)-O(10)$ 92.8(2).

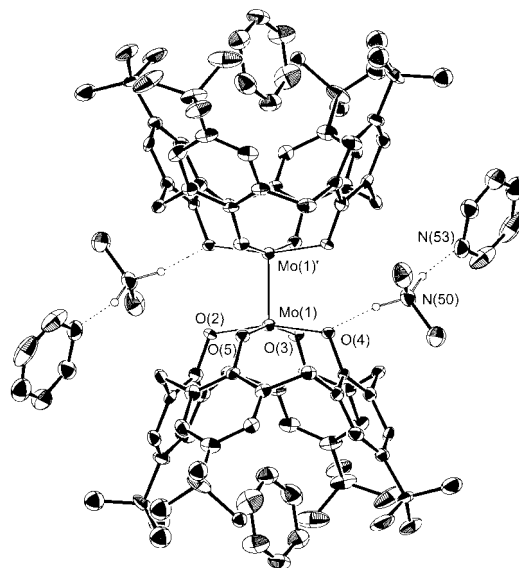


Fig. 2 An ORTEP drawing of **2**·4py ($M = Mo$) showing the atom numbering scheme. Selected bond lengths (Å) and bond angles (°): $Mo(1)-Mo(1')$ 2.226(1), $Mo(1)-O(2)$ 2.009(4), $Mo(1)-O(3)$ 1.975(4), $Mo(1)-O(4)$ 2.028(4), $Mo(1)-O(5)$ 1.973(4); $Mo(1')-Mo(1)-O(2)$ 97.9(1), $Mo(1')-Mo(1)-O(3)$ 98.8(1), $Mo(1')-Mo(1)-O(4)$ 97.1(1), $Mo(1')-Mo(1)-O(5)$ 100.1(1). The molecule has a crystallographically imposed inversion center.

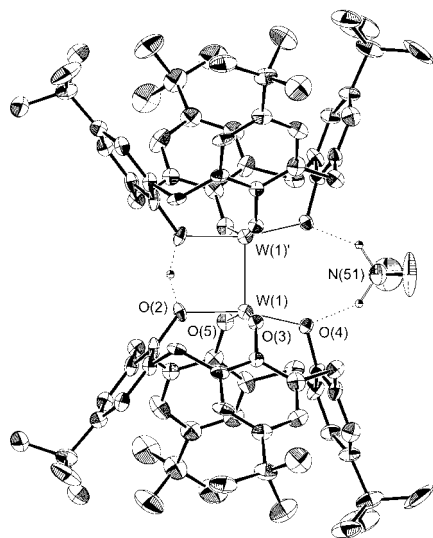
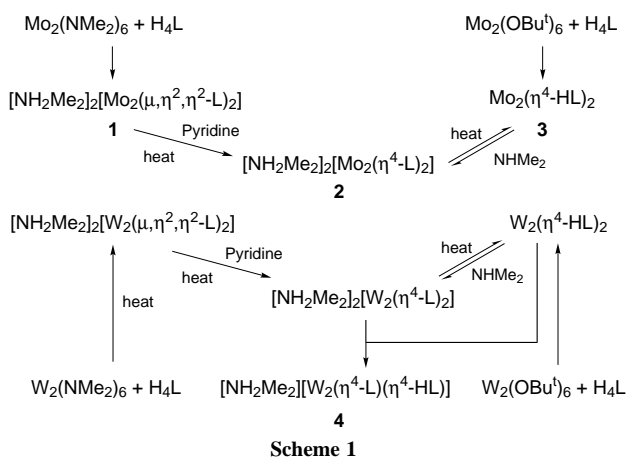


Fig. 3 An ORTEP drawing of **4** ($M = W$) showing the atom numbering scheme. Selected bond lengths (\AA) and bond angles ($^\circ$): $W(1)-W(1')$ 2.3039(8), $W(1)-O(2)$ 2.066(6), $W(1)-O(3)$ 1.947(6), $W(1)-O(4)$ 1.973(6), $W(1)-O(5)$ 1.959(6); $W(1')-W(1)-O(2)$ 90.5(2), $W(1')-W(1)-O(3)$ 99.6(2), $W(1')-W(1)-O(4)$ 102.8(2), $W(1')-W(1)-O(5)$ 98.8(2). The molecule has a crystallographically imposed mirror plane.



pyridine as well as NHMe_2 leaving behind the complex $M_2(\eta^4\text{-HL})_2$ **3** ($M = \text{Mo}$) as evidenced by NMR spectroscopy. Complex **3**, as well as its tungsten analogue $W_2(\eta^4\text{-HL})_2$, can also be prepared from the reaction of $M_2(\text{OBu}^t)_6$ ($M = \text{Mo}, W$) with H_4L .[†]

The addition of NHMe_2 to **3** ($M = \text{Mo}, W$) in benzene leads to **2** ($M = \text{Mo}, W$).[‡] In the case of $M = W$, the reaction between **2** and **3** in a 1:1 ratio gives the pale green compound $[\text{NH}_2\text{Me}_2]_2[\text{W}_2(\eta^4\text{-L})(\eta^4\text{-HL})]$ **4**, which has the structure shown in Fig. 3.[§] These reactions are summarized in Scheme 1 and reveal the fascinating substitution chemistry resulting from reactions involving $(M\equiv M)^{6+}$ complexes ($M = \text{Mo}, W$) and the *p-tert*-butylcalix[4]arene ligand.

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Notes and References

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‡ *Syntheses and spectroscopic data*: **1** ($M = \text{Mo}$): the reaction mixture of $\text{Mo}_2(\text{NMe}_2)_6$ (280 mg, 0.60 mmol) and H_4L (650 mg, 1.00 mmol) in 15 ml of benzene was stirred at room temp. overnight. The volatile components

were removed *in vacuo* and the residue was suspended in hexanes to give a green precipitate **1**, which was collected and dried *in vacuo* (685 mg, yield: 90%). Crystals of 1-4thf ($M = \text{Mo}$) suitable for X-ray analysis were obtained by slow evaporation of a thf solution. Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.29 (br, 8 H), 6.93 (br, 8 H), 6.46 (d, 4 H), 3.59 (d, 4 H), 3.27 (d, 4 H), 2.89 (d, 4 H), 1.22 (br, 72 H), 0.79 (t, 12 H).

1 ($M = W$): the same procedure as **1** ($M = \text{Mo}$) except stirring the mixture with refluxing (yield: 63%). Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.30 (d, 8 H), 6.96 (d, 8 H), 6.51 (d, 4 H), 3.61 (d, 4 H), 3.57 (d, 4 H), 3.03 (d, 4 H), 1.22 (br, 72 H), 0.67 (t, 12 H).

2 ($M = \text{Mo}$): a green solution of **1** ($M = \text{Mo}$) (260 mg, 0.17 mmol) in 8 ml of pyridine was refluxed for 0.5 h, the resulting amber solution was cooled and allowed to stand at room temp. overnight to yield amber crystals of 2-4py ($M = \text{Mo}$) (203 mg, yield: 65%), which were suitable for X-ray analysis. Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.24 (s, 16 H), 5.29 (d, 8 H), 3.34 (d, 8 H), 1.58 (s, 12 H), 1.23 (s, 72 H). Yellow solid **2** ($M = \text{Mo}$) can be also prepared by addition of an excess of NHMe_2 to **3** ($M = \text{Mo}$).

3 ($M = \text{Mo}$): a reaction mixture of $\text{Mo}_2(\text{OBu}^t)_6$ (202 mg, 0.32 mmol) and H_4L (326 mg, 0.50 mmol) in 10 ml of toluene was stirred at room temp. for 2 days. The volatile components were removed *in vacuo* and the residue was suspended in hexanes to give a pale brown precipitate **3** ($M = \text{Mo}$), which was collected and dried *in vacuo* (336 mg, yield: 91%). Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.09 (s, 16 H), 5.17 (d, 8 H), 3.39 (d, 8 H), 1.12 (s, 72 H).

3 ($M = W$): the same procedure as **3** ($M = \text{Mo}$), (yield: 86%). Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.10 (s, 16 H), 5.14 (d, 8 H), 3.39 (d, 8 H), 1.12 (s, 72 H).

2 ($M = W$): NHMe_2 (2.4 mmol) was added to the frozen reddish brown solution of **3** ($M = W$) (480 mg, 0.29 mmol) at -196°C employing a calibrated gas manifold. After the solution was warmed to room temp., the green precipitate **2** ($M = W$) was collected and dried *in vacuo* (482 mg, yield: 95%).

4 ($M = W$): a reaction mixture of **2** ($M = W$) (105 mg, 0.060 mmol) and **3** ($M = W$) (100 mg, 0.060 mmol) in 10 ml of benzene was stirred at room temp. The green solid was gradually dissolved in solution, and the brown solution turned green. After 3 h, the volatile components were removed *in vacuo* and the residue was suspended in hexanes to give a pale green precipitate **4** ($M = W$), which was collected and dried *in vacuo* (186 mg, yield: 89%). Recrystallization in benzene afforded green crystals of 4-7C₆H₆ ($M = W$) suitable for X-ray analysis. Selected ^1H NMR data (300 MHz, C_6D_6): δ 7.20 (s, 16 H), 5.18 (d, 8 H), 3.42 (d, 8 H), 1.45 (br, 6 H), 1.20 (s, 72 H).

§ *Crystal data*: for 1-4thf ($M = \text{Mo}$): $T = -170^\circ\text{C}$ monoclinic, space group $P2_1$, $a = 13.105(4)$, $b = 18.631(6)$, $c = 20.543(6)$ \AA , $\beta = 94.04(2)^\circ$, $Z = 2$. Final residuals are $R(F) = 0.067$ and $R_w(F) = 0.066$ using 7500 observed data.

For 1-4thf ($M = W$): $T = -170^\circ\text{C}$: $a = 13.08(2)$, $b = 18.61(3)$, $c = 20.60(3)$ \AA , $\beta = 94.03(3)^\circ$. Collection of diffraction data was not processed because of the poor quality of the crystal.

For 2-4py ($M = \text{Mo}$): $T = -170^\circ\text{C}$, monoclinic, space group $P2_1/n$, $a = 12.384(2)$, $b = 22.130(3)$, $c = 18.621(3)$ \AA , $\beta = 100.26(1)^\circ$, $Z = 2$. Final residuals are $R(F) = 0.059$ and $R_w(F) = 0.058$ using 4799 observed data.

For 4-7C₆H₆ ($M = W$): $T = -168^\circ\text{C}$, orthorhombic, space group $Pnma$, $a = 25.421(3)$, $b = 34.611(3)$, $c = 13.113(1)$ \AA , $Z = 4$. Final residuals are $R(F) = 0.058$ and $R_w(F) = 0.052$ using 6231 observed data. CCDC 182/704.

Full crystallographic data are also available from the Reciprocal Data Base via Internet at URL <http://www.iomsc.indiana.edu>. Request data and files for 97055 for 1-4thf ($M = \text{Mo}$), 97056 for 2-4py ($M = \text{Mo}$) and 97064 for 4-7C₆H₆ ($M = W$).

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