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Registry No. Tc(DPPE)$_2$(SCN)$_2$, 85552-63-2; Tc(DPPE)$_2$Cl$_2$, 78656-00-5; Tc(DPPE)$_2$Br$_2$, 85552-64-3; Tc(DPPB)$_2$Cl$_2$, 85552-65-4; Tc(DPPV)$_2$Br$_2$, 85552-66-5; Tc(DPPV)$_2$Cl$_2$, 85552-67-6; Tc(DEPE)$_2$Cl$_2$, 85552-68-7; Tc(DMPE)$_2$Cl$_2$, 85552-69-8; Tc(DEPE)$_2$Br$_2$, 85552-70-1; Tc(DMPE)$_2$Br$_2$, 85552-71-2; [Tc(DPPV)$_2$Cl$_2$]BF$_4$, 85552-73-4; [Tc(DPPE)Cl$_2$]Cl, 85552-74-5; [Tc(DPPB)$_2$Cl$_2$]Cl, 85552-75-6; [Tc(DPPV)$_2$Cl$_2$]Cl, 85552-76-7; [Tc(DMPE)$_2$Cl$_2$]SO$_3$CF$_3$, 85552-78-9; [Tc(DMPE)$_2$Br$_2$]SO$_3$CF$_3$, 85552-80-3; [Tc(DPPE)$_2$Cl$_2$]SCN, 85552-81-4; [Tc(DPPE)$_2$Br$_2$]BF$_4$, 85552-82-5; [Tc(DEPE)$_2$Cl$_2$]SO$_3$CF$_3$, 85552-84-7; [Tc(DEPE)$_2$Br$_2$]Br, 85552-85-8; [Tc(DMPE)$_2$Br$_2$]ReO$_4$, 85552-86-9; [Tc(DPPE)$_2$Br$_2$]Br, 85552-87-0; Tc(DMPE)$_2$Cl$_2^-$, 85565-21-5; [Tc(DPPB)$_2$Cl$_2$]BF$_4$, 85552-89-2; [Tc(DPPB)$_2$Br$_2$]Br, 85552-90-5; [Tc(DEPE)$_2$Cl$_2$]Cl, 85552-91-6; Tc(DIARS)$_2$Cl$_2$, 14127-29-8; Tc(DIARS)$_2$Cl$_2^+$, 47512-11-8; Tc(DIARS)$_2$Br$_2^+$, 78610-19-2; Tc(DIARS)$_2$Br$_2$, 78610-21-6; Tc(DPPE)$_2$Br$_2$, 78656-01-6; Tc(DPPE)$_2$(SCN)$_2^+$, 85552-92-7; Tc(DPPE)$_2$(SCN)$_2^-$, 85552-93-8; Tc(DMPE)$_2$Br$_2^-$, 85552-94-9; [Tc(DPPE)$_2$Br$_2$]NO$_3$, 85552-95-0.

Supplementary Material Available: Tables A–D, showing F_c and F_o values, anisotropic thermal parameters, complete bond lengths and angles, and calculated hydrogen atom positions (25 pages). Ordering information is given on any current masthead page.

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Reactions of $Mo_2(OR)_6$ ($M\equiv M$) Compounds (R = *i*-Pr and *t*-Bu) with Benzoyl Peroxide

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Hydrocarbon solutions of $Mo_2(OR)_6$ ($M\equiv M$) compounds, where R = *i*-Pr and *t*-Bu, react with benzoyl peroxide to give intensely blue solutions. Where R = *i*-Pr, a blue crystalline product has been isolated and is formulated as $Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2$ ($M=M$) on the basis of analytical and spectroscopic data. A structure involving two edge-sharing octahedral units is proposed for the central Mo_2O_{10} moiety: a pair of O-*i*-Pr ligands provide the bridging groups. Where R = *t*-Bu, the initially formed blue solution gives rise to a pale yellow-green crystalline product $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ ($M\equiv M$) and an uncharacterized purple paramagnetic molybdenum-containing compound. These products are proposed to arise from decomposition (disproportionation) of $Mo_2(O\text{-}t\text{-}Bu)_6(O_2CPh)_2$ ($M=M$). The $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ compound has been characterized by a single-crystal study and is shown to be closely related to the previously characterized compound $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$. The $Mo\equiv Mo$ bond, of distance 2.236 (2) Å, is spanned by a pair of cis-bridging O_2CPh groups, Mo–O = 2.14 (2) Å (averaged). The two *t*-BuO ligands attached to each molybdenum atom, Mo–O = 1.88 (2) Å (averaged), complete the roughly square-planar coordination geometry for each MoO_4 unit. The overall Mo_2O_8 geometry is slightly skewed to avoid an eclipsing of the bulky *t*-BuO ligands. Crystal data for $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$: space group $C2/c$, $a = 21.43$ (1) Å, $b = 14.006$ (6) Å, $c = 12.299$ (5) Å, $\beta = 113.75$ (1)°, $Z = 4$, and $d_{calcd} = 1.428$ g cm^{-3}.

Introduction

The M–M triple bond of configuration $\sigma^2\pi^4$ in compounds of formula $M_2(OR)_6$, where M = Mo or W and R = a bulky alkyl group such as *t*-Bu, *i*-Pr, or CH$_2$-*t*-Bu, is a reactive inorganic functionality. Stepwise transformations of bond order, $3 \rightarrow 4$, $3 \rightarrow 2 \rightarrow 1$, and even cleavage, $3 \rightarrow 0$, have been observed. Simple adducts involving $C\equiv O$,[2] $RC\equiv CR$,[3] $Me_2NC\equiv N$,[4] and R_2CN_2[5] have been isolated, and trinuclear[6] and tetranuclear clusters[7] have been obtained from condensation or oligomerization reactions. In the dinuclear chemistry of molybdenum and tungsten, the M–M double bond is relatively rare, at least when compared to quadruple, triple, and single bonds.[8] In part this may reflect a lability of the $\sigma^2\pi^2$ configuration toward oxidation, although one cannot be dogmatic on this point since detailed studies are lacking. However, in the simple oxidative-addition reaction sequence depicted by eq 1, only where X = O-*i*-Pr was it possible to isolate the

$$Mo_2(O\text{-}i\text{-}Pr)_6\ (M\equiv M) \xrightarrow{+X_2} Mo_2X_2(O\text{-}i\text{-}Pr)_6\ (M=M) \xrightarrow{+X_2} Mo_2X_4(O\text{-}i\text{-}Pr)_6 \quad (1)$$

$Mo=Mo$-containing compound of formula $Mo_2X_2(O\text{-}i\text{-}Pr)_6$. When X = Cl, Br, or I, reactions proceeded to give $Mo_2X_4(O\text{-}i\text{-}Pr)_6$ (M—M) compounds.[9]

Even the careful addition of 1 equiv of X_2 (X = Br or I), which gave initially blue or green solutions indicative of the $Mo=Mo)^{8+}$ unit, yielded ultimately orange solutions of a 1:1 mixture of $Mo_2(O\text{-}i\text{-}Pr)_6$ and $Mo_2X_4(O\text{-}i\text{-}Pr)_6$ compounds. This suggested that $Mo_2X_2(O\text{-}i\text{-}Pr)_6$ ($M=M$) compounds might be unstable with respect to disproportionation to $Mo_2(O\text{-}i\text{-}Pr)_6$ ($M\equiv M$) and $Mo_2X_4(O\text{-}i\text{-}Pr)_6$ (M—M) compounds. Reasoning that the Mo–Mo double bond might be

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(1) Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1 and references therein.

(2) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645. Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. *Ibid.* **1982**, *104*, 7030.

(3) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.

(4) Chisholm, M. H.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 2321.

(5) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1229.

(6) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 5967.

(7) Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025.

(8) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. Compounds containing W$\overset{4}{-}$W bonds are still quite rare.

(9) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871.

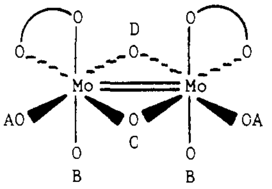
kinetically less labile to both oxidative-addition and disproportionation reactions if each metal atom were in an octahedral environment, we decided to examine the reactions between $Mo_2(OR)_6$ compounds[10] and benzoyl peroxide PhC(O)O–O(O)CPh.

Results and Discussion

$Mo_2(O\text{-}i\text{-}Pr)_6$ + $PhCO_2$–O_2CPh. Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ (M≡M) react with 1 equiv of benzoyl peroxide according to the stoichiometric reaction shown in eq 2.

$$Mo_2(O\text{-}i\text{-}Pr)_6 + PhCO_2\text{–}O_2CPh \rightarrow Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2 \quad (2)$$

The initially yellow solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ turn intensely green upon addition of benzoyl peroxide, and crystallization from pentane yields blue-green crystalline $Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2$, which is stable with respect to further oxidation with benzoyl peroxide under mild conditions. Crystals suitable for single-crystal X-ray studies were not obtained despite several attempts at their preparation. However, there is little doubt concerning the formulation of this compound: (1) Elemental analyses confirm the empirical formula $Mo(O\text{-}i\text{-}Pr)_3(O_2CPh)$. (2) The mass spectrum shows the ion of highest mass corresponds to $Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2^+$, m/e 792 based on ^{98}Mo. Though other Mo_2-containing ions are observed, several mononuclear ions such as $Mo(O\text{-}i\text{-}Pr)_3(O_2CPh)^+$ and $Mo(O\text{-}i\text{-}Pr)_4^+$ are also present. This parallels the mass spectrum observed for $Mo_2(O\text{-}i\text{-}Pr)_8$. (3) The compound is diamagnetic, being a d^2-d^2 dimer with μ-O-i-Pr bridges, which can most reasonably be accounted for by the presence of a Mo=Mo bond. Again, an analogy with $Mo_2(O\text{-}i\text{-}Pr)_8$ and the related tungsten dimer $W_2Cl_4(OEt)_4(HOEt)_2$[11] may be noted. (4) The IR spectrum in the benzoate ligand CO_2-stretching region shows bands at 1588 and 1595 cm^{-1}, indicative of bidentate ligands. (5) The ^1H NMR data are consistent with the adoption of the edge-shared octahedral Mo_2O_{10} unit shown in I. Specifically, the ^1H NMR spectrum, recorded at or below –45 °C, 220 MHz, shows (i) only one type of benzoate ligand, (ii) four septets in the integral ratio 2:2:1:1 assignable to the two types of terminal and bridging methyne protons (O-i-Pr), and (iii) six sets of doublets assignable to O-i-Pr methyl groups in the integral ratio 1:1:1:1:1:1. Note that in I the isopropoxy methyl groups associated with OA and OB are diastereotopic, whereas those associated with OC and OD are not. Only the structure depicted by I seems to fit all of the above spectroscopic data. At room temperature, however, rapid scrambling of all the O-i-Pr ligands gives rise to a time-averaged O-i-Pr signal. This is similar to the fluxional behavior observed for $Mo_2(O\text{-}i\text{-}Pr)_8$.[13]



I

The metal–metal double bond can easily be formulated for I. Let the xy plane contain the two molybdenum atoms and the oxygen atoms of the bridging O-i-Pr ligands, with the x axis coincident with the Mo–Mo axis. The orbital scheme is then as follows: (i) the octahedral metal–ligand σ-bonds are formed from molybdenum atomic orbitals s, p_x, p_y, p_z, d_{z^2}, and d_{xy}; (ii) the lobes of the $d_{x^2-y^2}$ orbitals are directed between the ligands in the xy plane and form the Mo–Mo σ-bond; (iii) the d_{xz} orbitals have the correct symmetry to form the Mo–Mo π-bond; and (iv) molybdenum d_{yz} orbitals are available for π-bonding to alkoxide B and/or the axial benzoate oxygen atom.

Table I. Fractional Coordinates for the $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	523.4 (4)	207.9 (5)	185.9 (6)	15
O(2)	5947 (3)	2898 (4)	2239 (5)	21
C(3)	6386 (5)	3633 (7)	2947 (8)	24
C(4)	5946 (5)	4403 (7)	3195 (9)	28
C(5)	6887 (5)	3177 (7)	4092 (9)	31
C(6)	6765 (5)	4039 (8)	2215 (10)	36
O(7)	4539 (3)	2628 (4)	522 (5)	22
C(8)	4542 (6)	2722 (8)	9340 (8)	37
C(9)	5108 (7)	2092 (13)	–749 (10)	76
C(10)	3871 (8)	2326 (21)	–1535 (12)	124
C(11)	4637 (22)	3687 (11)	–846 (20)	212
O(12)	4667 (3)	739 (4)	1064 (5)	18
C(13)	4167 (4)	546 (6)	1303 (7)	17
O(14)	4084 (3)	927 (4)	2176 (5)	19
C(15)	3642 (4)	–144 (6)	543 (7)	21
C(16)	3677 (5)	9541 (6)	9493 (8)	23
C(17)	3180 (5)	–1090 (7)	–1244 (8)	24
C(18)	2663 (5)	–1415 (6)	–924 (8)	24
C(19)	2633 (5)	–1097 (7)	158 (9)	28
C(20)	3116 (5)	–453 (6)	881 (8)	23

$Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2$ is extremely soluble in all aromatic and hydrocarbon solvents. It is stable in solution and as a solid when stored under nitrogen or in vacuo but rapidly decomposes upon exposure to oxygen or water. Attempts to sublime $Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2$ in vacuo resulted in decomposition at temperatures above 60 °C.

$Mo_2(O\text{-}t\text{-}Bu)_6$ + $PhCO_2$–O_2CPh. Upon addition of benzoyl peroxide to hydrocarbon solutions of $Mo_2(O\text{-}t\text{-}Bu)_6$, there is a color change from orange to blue, which implies oxidative addition to give $Mo_2(O\text{-}t\text{-}Bu)_6(O_2CPh)_2$. However, with continued stirring, pale yellow-green crystals are formed and the solution turns purple.

The crystalline precipitate has been identified as $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ (see below) and we believe that this is formed from $Mo_2(O\text{-}t\text{-}Bu)_6(O_2CPh)_2$ by a disproportionation reaction. After $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ is removed by filtration, the resultant purple solution yields a purple solid upon removal of solvent. We have not characterized this product fully. It appears paramagnetic and does not yield ^1H NMR spectra. It does not sublime in vacuo, and it did not give a mass spectrum with any molybdenum-containing ions. The infrared spectrum shows bands at 1588 and 1596 cm^{-1}, indicative of bidentate benzoate groups. When the reaction between $Mo_2(O\text{-}t\text{-}Bu)_6$ and benzoyl peroxide was carried out in an NMR tube, no organic products, e.g. t-BuOH, t-BuOO-t-Bu, or $PhCO_2$-t-Bu, were detected, which is consistent with a disproportionation reaction rather than reductive elimination. The simplest disproportionation reaction would be of the form $2Mo_2(O\text{-}t\text{-}Bu)_6(O_2CPh)_2 \rightarrow Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2 + 2Mo(O\text{-}t\text{-}Bu)_4(O_2CPh)$. We propose that the instability of $Mo_2(O\text{-}t\text{-}Bu)_6(O_2CPh)_2$ relative to $Mo_2(O\text{-}i\text{-}Pr)_6(O_2CPh)_2$ arises from the greater steric crowding in a dimer of type I for t-BuO relative to i-PrO.

Solid-State Structure of $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$. Positional and thermal parameters are given in Table I. Bond distances and bond angles are given in Tables II and III, respectively.

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[10] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

[11] Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Isley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

[12] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

[13] Chisholm, M. H.; Reichert, W. W.; Thornton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744.

Table II. Bond Distances (Å) for the $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(1)'	2.236 (2)	C(3)	C(6)	1.544 (12)
Mo(1)	O(2)	1.868 (6)	C(8)	C(9)	1.539 (17)
Mo(1)	O(7)	1.903 (6)	C(8)	C(10)	1.512 (20)
Mo(1)	O(12)	2.158 (6)	C(8)	C(11)	1.399 (20)
Mo(1)	O(14)'	2.125 (6)	C(13)	C(15)	1.492 (11)
O(2)	C(3)	1.430 (10)	C(15)	C(16)	1.395 (12)
O(7)	C(8)	1.464 (10)	C(15)	C(20)	1.417 (12)
O(12)	C(13)	1.250 (9)	C(16)	C(17)	1.400 (12)
O(14)	C(13)	1.274 (9)	C(17)	C(18)	1.393 (12)
C(3)	C(4)	1.542 (12)	C(18)	C(19)	1.429 (13)
C(3)	C(5)	1.525 (13)	C(19)	C(20)	1.391 (12)

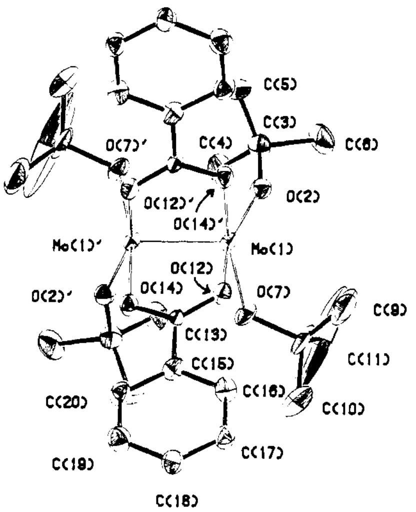

Figure 1. ORTEP view of the $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ molecule showing the atom-numbering scheme used in the tables. Atoms are represented by ellipsoids drawn to include 40% probability of thermal displacement. The large thermal motion seen in this view for C(11) and C(11)' is also present for C(9), C(9)' and C(10), C(10)' but is not so apparent from this viewing angle. Examination of the anisotropic thermal parameters shows all three atoms are vibrating excessively.

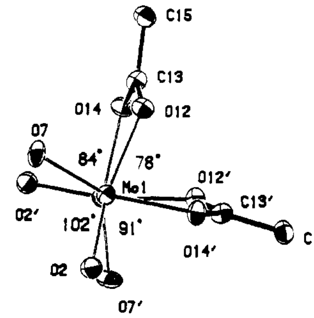

Figure 2. ORTEP diagram of the central $Mo_2O_4(O_2C)_2$ skeleton of the $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ molecule viewed down the Mo–Mo bond and showing the O–Mo–O angles.

Table III. Bond Angles (deg) and Torsion Angles (deg) for the $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ Molecule

A	B	C	angle
Mo(1)'	Mo(1)	O(2)	111.5 (2)
Mo(1)'	Mo(1)	O(7)	101.0 (2)
Mo(1)'	Mo(1)	O(12)	89.0 (1)
Mo(1)	Mo(1)'	O(14)	89.4 (1)
O(2)	Mo(1)	O(7)	101.9 (3)
O(2)	Mo(1)	O(12)	156.9 (2)
O(2)	Mo(1)	O(14)'	91.3 (2)
O(7)	Mo(1)	O(12)	83.6 (2)
O(7)	Mo(1)	O(14)'	158.6 (2)
O(12)	Mo(1)	O(14)'	77.9 (2)
Mo(1)	O(2)	C(3)	154.7 (5)
Mo(1)	O(7)	C(8)	124.6 (6)
Mo(1)	O(12)	C(13)	117.4 (5)
Mo(1)	O(14)'	C(13)'	119.1 (5)
O(2)	C(3)	C(4)	108.6 (7)
O(2)	C(3)	C(5)	107.9 (7)
O(2)	C(3)	C(6)	106.3 (7)
C(4)	C(3)	C(5)	111.7 (8)
C(4)	C(3)	C(6)	111.5 (8)
C(5)	C(3)	C(6)	110.6 (8)
O(7)	C(8)	C(9)	109.8 (8)
O(7)	C(8)	C(10)	106.8 (10)
O(7)	C(8)	C(11)	108.0 (10)
C(9)	C(8)	C(10)	106.9 (13)
C(9)	C(8)	C(11)	111.8 (18)
C(10)	C(8)	C(11)	113.4 (20)
O(12)	C(13)	O(14)	122.1 (8)
O(12)	C(13)	C(15)	119.7 (7)
O(14)	C(13)	C(15)	118.2 (7)
C(13)	C(15)	C(16)	118.4 (8)
C(13)	C(15)	C(20)	120.1 (8)
C(16)	C(15)	C(20)	121.4 (8)
C(15)	C(16)	C(17)	119.2 (8)
C(16)	C(17)	C(18)	120.5 (8)
C(17)	C(18)	C(19)	120.1 (8)
C(18)	C(19)	C(20)	119.8 (8)
C(15)	C(20)	C(19)	119.0 (8)

A	B	C	D	angle
O(2)'	Mo(1)'	Mo(1)	O(2)	89.6 (4)
O(2)'	Mo(1)'	Mo(1)	O(7)	−18.0 (3)
O(2)'	Mo(1)'	Mo(1)	O(12)	−101.3 (2)
O(2)'	Mo(1)'	Mo(1)	O(14)'	−179.2 (2)
O(7)'	Mo(1)'	Mo(1)	O(7)	−125.6 (4)
O(7)'	Mo(1)'	Mo(1)	O(12)	151.1 (2)
O(7)'	Mo(1)'	Mo(1)	O(14)'	73.2 (2)
O(12)'	Mo(1)'	Mo(1)	O(12)	67.8 (3)
O(12)'	Mo(1)'	Mo(1)	O(14)'	−10.1 (2)

An ORTEP view of the molecule showing the atom-numbering scheme used in the tables is given in Figure 1, and a view down the metal–metal bond of the central skeleton is shown in Figure 2.

The $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CPh)_2$ molecule has crystallographically imposed C_2 symmetry. The central $Mo_2O_4(O_2C)_2$ skeleton has C_{2v} symmetry and is isostructural with the previously characterized molecule $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$.[14] The rotational axis is perpendicular to the metal–metal axis, passing through its midpoint, and relates atoms by number and prime, e.g. O(12) and O(12)'. One mirror plane contains the C_2 axis and the benzoate carboxylic carbon atoms. The other mirror plane contains the C_2 axis and the metal–metal bond. The Mo–Mo distance, 2.236 (2) Å, is comparable to that in $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$, 2.241 (1) Å, and other compounds containing Mo≡Mo bonds where each molybdenum atom is coordinated to four ligands, e.g. $Mo_2(OSiMe_3)_6(HNMe_2)_2$.[15]

The Mo–O distances to the carboxylate ligands, 2.158 (6) and 2.125 (6) Å, are considerably longer than those distances involving the *t*-BuO ligands, 1.868 (6) and 1.903 (6) Å. This is as expected and results from two factors: (i) The formal charge on the oxygen atoms is 1− for the O-*t*-Bu ligands and 0.5− on each of the benzoate oxygen atoms. (ii) *t*-BuO is a better π-donor ligand than $PhCO_2$. The angles subtended at molybdenum to the oxygen atoms (see Figure 2), specifically the large angle between the cis O-*t*-Bu ligands, 102°, compared with the small angle between the carboxylate groups, 78°, also are understood in terms of steric and electronic factors. We expect that the partial double-bond character associated with the Mo–O-*t*-Bu bonds would result in a large *t*-BuO–Mo–O-

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(14) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

(15) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153.

t-Bu angle relative to that between the carboxylate oxygen atoms.

Conclusions. The metal–metal bond order is reduced from 3 to 2 when Mo$_2$(O-*i*-Pr)$_6$ is treated with 1 equiv of PhCO$_2$–O$_2$CPh. Though crystals suitable for a detailed X-ray study were not obtained, the spectroscopic data are entirely consistent with the adoption of the structure depicted by I. The analogous reaction involving Mo$_2$(O-*t*-Bu)$_6$ leads ultimately to disproportionation products Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$ and an as yet uncharacterized purple product. It may be noted that, whereas Mo$_2$(O-*i*-Pr)$_6$ and *i*-PrOO-*i*-Pr reacted to give Mo$_2$(O-*i*-Pr)$_8$, Mo$_2$(O-*t*-Bu)$_6$ and *t*-BuO–O-*t*-Bu failed to react.[9] Both in the previous finding and in the present one, the differences in the reactivities of the Mo$_2$(OR)$_6$ compounds, where R = *t*-Bu and *i*-Pr, may be traced to steric factors.

Experimental Section

Materials. Mo$_2$(OR)$_6$ compounds (R = *t*-Bu and *i*-Pr) were prepared as described previously.[10] Benzoyl peroxide was obtained from Matheson Coleman and Bell and used without further purification.

General Procedures. Dry and oxygen-free solvents and atmospheres were used throughout.

Physical and Analytical Methods. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Infrared spectra were obtained with a Perkin-Elmer IR 283 spectrometer.

^{1}H NMR spectra were obtained on a Varian Associates HR220 spectrometer equipped with a variable-temperature probe. Toluene-*d*$_8$ was used as solvent, and chemical shifts are reported in δ relative to Me$_4$Si.

Mass spectra were obtained courtesy of Peter Cook, Queen Mary College, London, using an AEI MS902 spectrometer by the method of direct insertion.

Preparation of Mo$_2$(O-*i*-Pr)$_6$(O$_2$CPh)$_2$. Mo$_2$(O-*i*-Pr)$_6$ (1.50 g, 2.75 mmol) was dissolved in hexane (20 mL) in a 100-mL round-bottomed flask containing a magnetic spin-bar. Benzoyl peroxide (0.66 g, 2.75 mmol) was added to the solution with stirring. The color changed immediately from yellow to green. After 1 h, the solvent was stripped in vacuo. The resulting green-blue solid was redissolved in pentane (ca. 10 mL), and the solution was cooled to −10 °C in the freezer section of a refrigerator. After 3 days, blue-green crystals of Mo$_2$(O-*i*-Pr)$_6$(O$_2$CPh)$_2$ had formed and were collected by filtration and dried in vacuo. Anal. Calcd for Mo$_2$(O-*i*-Pr)$_6$(O$_2$CPh)$_2$: C, 48.74; H, 6.64. Found: C, 48.51; H, 6.50. Numerous crystals were examined for X-ray classification studies, but all were found to be split, yielding broad anisotropic ω scans.

The mass spectrum of Mo$_2$(O-*i*-Pr)$_6$(O$_2$CPh)$_2$ (151 °C) showed a weak molecular ion peak at *m*/*e* 792, based on ^{98}Mo. Other ions were observed at *m*/*e* 396 [Mo(O-*i*-Pr)$_3$(O$_2$CPh)$^+$], 334 [Mo(O-*i*-Pr)$_4$$^+$], 291 [MoO(O-*i*-Pr)$_3$$^+$], 249 [MoO(OH)(O-*i*-Pr)$_2$$^+$], 207 [MoO(OH)$_2$(O-*i*-Pr)$^+$], and 165 [MoO(OH)$_3$$^+$].

IR data (Nujol mull between KBr plates): 482 w, 583 m, 612 m, 645 m, 688 s, 715 s, 800 w, 845 s, 868 s, 950 s, 992 w, 1021 w, 1069 w, 1102 s, 1110 m, 1260 w, 1312 m, 1520 s, 1588 m, 1595 s cm^{-1}.

^{1}H NMR data at −40 °C, δ (multiplicity, integration): 8.14 (m, 4 H), 6.89 (m, 2 H), 6.75 (m, 4 H), 6.08 (sept, 1 H), 5.66 (sept, 2 H), 5.59 (sept, 2 H), 5.41 (sept, 1 H), 1.66 (m, 12 H), 1.63 (d, 6 H), 1.56 (d, 6 H), 1.46 (d, 6 H), 1.31 (d, 6 H). As the temperature is raised, the peaks begin to coalesce, until decomposition begins to occur at 75 °C.

Preparation of Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$. Mo$_2$(O-*t*-Bu)$_6$ (1.35 g, 2.16 mmol) was dissolved in pentane (20 mL) in a 100-mL beaker containing a Teflon-covered spin-bar in a Vacuum Atmosphere Co. Dri-Lab assembly. Benzoyl peroxide (0.523 g, 2.16 mmol) was added to the solution with stirring. The color slowly changed from yellow to green to black. After the solution was stirred for 2 h, a precipitate began to form. The solids were collected by filtration and dried in vacuo. Recrystallization using a hexane–toluene (50:50) solent mixture yielded pale yellow-green X-ray quality crystals of Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$. Anal. Calcd for Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$: C, 49.59; H, 6.38. Found: C, 49.65; H, 7.20.

The mass spectrum showed a strong molecular ion at *m*/*e* 730 (^{98}Mo).

IR data (Nujol mull between KBr plates): 475 m, 499 w, 549 m, 689 s, 719 s, 770 s, 791 s, 845 s, 892 s, 918 s, 985 vs, 1025 m, 1072 m, 1170 vs, 1190 w, 1234 s, 1310 w, 1490 m, 1521 s, 1589 s, 1598 s cm^{-1}.

^{1}H NMR data, 16 °C, δ (multiplicity, integration): 8.31 (m, 2 H), 7.00 (m, 3 H), 1.62 (s, 18 H). The spectrum does not change upon cooling to −40 °C.

A purple solid was isolated from the pentane filtrate after Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$ had been isolated. The waxy solid did not yield any molybdenum-containing ions in the mass spectrum, and the ^{1}H NMR spectrum contained very broad peaks that were unresolved at high and low temperatures. The sample was presumed to be paramagnetic, but this point was not pursued.

X-ray Structural Determination of Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$. General operating procedures and computational techniques have been described previously.[16]

A crystal of dimensions 0.12 × 0.13 × 0.20 mm was mounted in the nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cold stream of the diffractometer. The cell dimensions, determined from 50 reflections at −164 °C by using Mo Kα radiation (λ = 0.710 69 Å), were a = 21.428 (10) Å, b = 14.006 (6) Å, c = 12.299 (5) Å, β = 113.75 (1)°, V = 3378 (1) Å^3, Z = 4, d_{calcd} = 1.428 g cm^{-3}, and space group $C2/c$.

A total number of 3353 reflections were collected including redundancies and reduced to 2992 reflections by using standard moving-crystal, moving-detector techniques with the following values: scan speed = 4.0°/min, scan width = (2.0 + dispersion)°, single background at extreme of scan = 5 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $6° < 2\theta < 50°$. The number of reflections with $F > 2.33\sigma(F)$ = 2280.

The structure was solved by a combination of direct methods and Fourier techniques. All non-hydrogen atoms were located and refined anisotropically. Hydrogen attoms were not located. Some of the carbon atoms in the *t*-BuO ligands have large thermal parameters indicating possible rotational disorder. The final residuals are $R(F)$ = 0.064 and $R_w(F)$ = 0.062. The goodness of fit for the last cycle was 1.376, and the maximum Δ/σ was 0.10.

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Registry No. I, 85405-70-5; Mo$_2$(O-*t*-Bu)$_4$(O$_2$CPh)$_2$, 85390-45-0; Mo$_2$(O-*i*-Pr)$_6$, 62521-20-4; Mo$_2$(O-*t*-Bu)$_6$, 60764-63-8.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(16) Caulton, K. G.; Huffman, J. C.; Lewis, L. N. *Inorg. Chem.* **1980**, *19*, 2755.