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Dinuclear Aryloxide Chemistry. 2. Synthesis and Structure of 2,6-Dimethylphenoxide Complexes of Dimolybdenum (Mo≡Mo)[1]

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Treatment of the dimolybdenum compound $Mo_2(NMe_2)_6$ with 2,6-dimethylphenol (HOAr) leads initially to the partially substituted compound 1,2-$Mo_2(NMe_2)_2(OAr)_4$ (I) in nearly quantitative yield. Only on extended heating with excess phenol are all of the amido ligands displaced. Treatment of I with CO_2 leads to the compound $Mo_2(O_2CNMe_2)_2(OAr)_4$ (II). Structural analysis shows I to adopt an unbridged, anti conformation in the solid state while II is shown to contain two four-coordinate molybdenum atoms bridged by the two dimethylcarbamate groups. Crystal data for I at −168 °C were $a = 16.618$ (3) Å, $b = 10.208$ (1) Å, $c = 10.369$ (2) Å, $\beta = 95.25$ (1)°, $Z = 2$, and d(calcd) = 1.450 g cm^{-3} with space group $P2_1/n$ while II crystallized with space group $Pbna$, $a = 8.421$ (2) Å, $b = 20.648$ (8) Å, $c = 21.665$ (8) Å, $Z = 4$, and d(calcd) = 1.503 g cm^{-3}.

Introduction

Our recent discovery of the ability of some mononuclear early transition-metal systems to activate (cyclometalate) the *tert*-butyl groups of the sterically demanding ligand 2,6-di-*tert*-butylphenoxide[2-4] has prompted us to investigate other situations where metalation of the alkyl side chains of aryloxide ligands may take place. In particular, we have begun to investigate the possibility of cyclometalation of aryloxide ligands at dinuclear metal centers, bearing in mind that the ortho metalation of phenol itself on triosmium clusters was characterized some time ago[5] and extensively studied since.[6,7] The alkoxide ligand has played an important role in the development of early transition-metal dinuclear compounds containing multiple metal–metal bonds[8,9] as well as a leading one in the study of the reactivity of such species.[10,11] However, the chemistry of aryloxide ligands at dinuclear metal centers has been little explored.[12,13] This paper describes some initial studies on the chemistry of the ligand 2,6-dimethylphenoxide coordinated to the dimolybdenum core, Mo_2^{6+} (Mo≡Mo). This ligand was chosen as it offers the possibility of forming a stable bridging group across the dimetal center if activation of the CH bonds of one of the methyl groups is achieved: $\overline{MOC_6H_3(CH_3)CH_2M}$ to form a six-membered dimetallacycle.

Results and Discussion

Preparation of Compounds. The hexakis(dimethylamido)dimolybdenum compound $Mo_2(NMe_2)_6$[14] allows an easy access for the introduction of aryloxide ligands onto the Mo_2^{6+} core. Treatment of hexane solutions of $Mo_2(NMe_2)_6$ with 2,6-dimethylphenol (HOAr, greater than 4 equiv) leads to a rapid and almost quantitative precipitate of orange, crystalline $Mo_2(NMe_2)_2(OAr)_4$ (I). Although only sparingly soluble in hexane, I can be recrystallized from hot toluene as large orange cubes. The last two dimethylamido ligands can be replaced only on heating I with excess 2,6-dimethylphenol (melt, 100 °C) for 15–30 min to produce the hexakis(aryloxide), $Mo_2(OAr)_6$, previously described.[1] On exposure to 1 atm of CO_2, hydrocarbon solutions of I absorb 2 equiv per dimer, to give a dark brown solution from which dark red crystals of $Mo_2(O_2CNMe_2)_2(OAr)_4$ (II) can be obtained on cooling. This "insertion" of CO_2 into the M–NMe_2 bond is a typical reaction of early transition-metal dialkylamido groups, although studies have shown the reaction is not a true insertion, but an amine-catalyzed protonolysis reaction.[15]

Table I. Summary of the Crystallographic Data for the Compounds I and II

	I	II
formula	$Mo_2C_{36}H_{48}O_4N_2$	$Mo_2C_{38}H_{48}O_8N_2$
fw	764.67	852.69
space group	$P2_1/n$	$Pbna$
a, Å	16.618 (3)	8.421 (2)
b, Å	10.208 (1)	20.648 (8)
c, Å	10.369 (2)	21.665 (8)
β, deg	95.25 (1)	
Z	2	4
V, Å^3	1751.57	3767.19
d(calcd), g/cm^3	1.450	1.503
cryst size, mm	0.20 × 0.20 × 0.20	0.20 × 0.19 × 0.19
cryst color	orange	dark red
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.7106 Å)
linear abs coeff, cm^{-1}	7.36	7.00
temp, °C	−168	−168
detector aperture	3.0 mm wide × 4.0 mm high; 22.5 cm from crystal	
sample to source dist, cm	23.5	
takeoff angle, deg	2.0	
scan speed, deg/min	4.0	
scan width, deg	2.0 +0.692 tan θ	
bkgd counts, s	3 at each end of scan	
2θ-range, deg	6–45	
data collcd	3333	2667
no. of unique data	2287	2463
no. of unique data with $F_o > 2.33\sigma(F)$	1865	1775
$R(F)$	0.0304	0.0477
$R_w(F)$	0.0303	0.0442
goodness of fit	0.927	1.042
largest Δ/σ	0.05	0.05

Solid-State Structure of $Mo_2(NMe_2)_2(OAr)_4$ (I). An ORTEP view of I along with the numbering scheme is shown in Figure 1. Table I contains the crystallographic data while Tables II–IV contain fractional coordinates with isotropic thermal

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Table II. Fractional Coordinates and Isotropic Thermal Parameters for $Mo_2(NMe_2)_2(OAr)_4$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, $Å^2$
Mo(1)	9686.4 (2)	956.9 (4)	79.8 (4)	9
N(2)	10486 (2)	2128 (4)	−457 (3)	12
C(3)	11237 (3)	1976 (5)	−1082 (5)	20
C(4)	10274 (3)	3507 (5)	−376 (5)	18
O(5)	8734 (2)	980 (3)	−1127 (3)	13
C(6)	8359 (3)	622 (4)	−2320 (5)	14
C(7)	7634 (3)	−98 (5)	−2352 (5)	17
C(8)	7263 (3)	−437 (5)	−3574 (5)	21
C(9)	7569 (3)	−54 (5)	−4696 (6)	26
C(10)	8269 (3)	672 (5)	−4629 (5)	23
C(11)	8679 (3)	1022 (5)	−3447 (4)	16
C(12)	7291 (3)	−551 (5)	−1158 (5)	22
C(13)	9457 (3)	1791 (5)	−3403 (5)	20
O(14)	9574 (2)	1017 (3)	1945 (3)	13
C(15)	9414 (3)	2237 (4)	2431 (4)	12
C(16)	8608 (3)	2662 (5)	2405 (4)	14
C(17)	8462 (3)	3875 (5)	2944 (4)	14
C(18)	9086 (3)	4663 (5)	3463 (5)	17
C(19)	9879 (3)	4241 (5)	3463 (4)	14
C(20)	10062 (3)	3017 (5)	2969 (4)	14
C(21)	7932 (3)	1818 (5)	1822 (5)	20
C(22)	10909 (3)	2525 (5)	2999 (5)	19

Table III. Bond Distances (Å) for $Mo_2(NMe_2)_2(OAr)_4$

Mo(1)–Mo(1)′	2.227 (1)	C(8)–C(9)	1.370 (8)
Mo(1)–O(5)	1.926 (3)	C(9)–C(10)	1.375 (8)
Mo(1)–O(14)	1.961 (3)	C(10)–C(11)	1.393 (7)
Mo(1)–N(2)	1.908 (4)	C(11)–C(13)	1.510 (7)
O(5)–C(6)	1.382 (6)	C(15)–C(16)	1.407 (7)
O(14)–C(15)	1.379 (6)	C(15)–C(20)	1.412 (7)
N(2)–C(3)	1.466 (6)	C(16)–C(17)	1.389 (7)
N(2)–C(4)	1.455 (6)	C(16)–C(21)	1.498 (7)
C(6)–C(7)	1.410 (7)	C(17)–C(18)	1.382 (7)
C(6)–C(11)	1.388 (7)	C(18)–C(19)	1.386 (7)
C(7)–C(8)	1.401 (7)	C(19)–C(20)	1.394 (7)
C(7)–C(12)	1.483 (8)	C(20)–C(22)	1.492 (7)

Table IV. Bond Angles (deg) for $Mo_2(NMe_2)_2(OAr)_4$

Mo(1)–Mo(1)–O(5)	109.0 (1)	C(8)–C(9)–C(10)	119.3 (5)
Mo(1)–Mo(1)–O(14)	100.8 (1)	C(9)–C(10)–C(11)	121.7 (5)
Mo(1)–Mo(1)–N(2)	100.6 (1)	C(6)–C(11)–C(10)	118.1 (5)
O(5)–Mo(1)–O(14)	119.6 (1)	C(6)–C(11)–C(13)	121.3 (4)
O(5)–Mo(1)–N(2)	110.8 (1)	C(10)–C(11)–C(13)	120.5 (5)
O(14)–Mo(1)–N(2)	113.6 (1)	O(14)–C(15)–C(16)	119.1 (4)
Mo(1)–O(5)–C(6)	148.7 (3)	O(14)–C(15)–C(20)	119.3 (4)
Mo(1)–O(14)–C(15)	115.3 (3)	C(16)–C(15)–C(20)	121.6 (4)
Mo(1)–N(2)–C(3)	134.9 (3)	C(15)–C(16)–C(17)	117.9 (4)
Mo(1)–N(2)–C(4)	114.2 (3)	C(15)–C(16)–C(21)	120.6 (4)
C(3)–N(2)–C(4)	110.4 (4)	C(17)–C(16)–C(21)	121.6 (4)
O(5)–C(6)–C(7)	118.3 (4)	C(16)–C(17)–C(18)	121.6 (5)
O(5)–C(6)–C(11)	120.0 (4)	C(17)–C(18)–C(19)	119.9 (5)
C(7)–C(6)–C(11)	121.7 (4)	C(18)–C(19)–C(20)	121.2 (5)
C(6)–C(7)–C(8)	117.1 (5)	C(15)–C(20)–C(19)	117.8 (4)
C(6)–C(7)–C(12)	122.4 (4)	C(15)–C(20)–C(22)	120.1 (4)
C(8)–C(7)–C(12)	120.5 (5)	C(19)–C(20)–C(22)	122.1 (4)
C(7)–C(8)–C(9)	122.1 (5)		

parameters, bond distances, and bond angles, respectively, for the molecule.

It can be seen that in the solid state 1,2-$Mo_2(NMe_2)_2(OAr)_4$ contains an unbridged $Mo_2O_4N_2$ skeleton, which is best described as "ethane-like", with the substituents adopting the anti rotamer. Solution studies indicate (vide infra) that this is also the preferred conformation in solution. A crystallographically imposed center of inversion is present, giving the molecule C_i symmetry. The Mo–Mo distance of 2.227 (1) Å is only slightly longer than that found in $Mo_2(OCH_2CMe_3)_6$ (2.222 (2) Å)[16] and $Mo_2(NMe_2)_6$ (2.211 (2) and 2.217 (2) Å)[14] and is hence typical for an Mo_2^{6+} core.

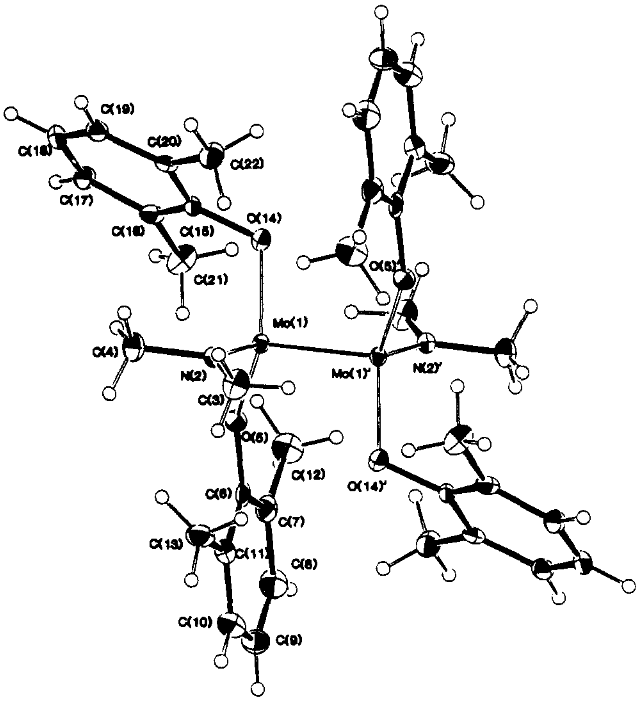

Figure 1. ORTEP view of the $Mo_2(NMe_2)_2(OAr)_4$ (I) molecule showing the numbering scheme used.

The distances and angles to the substitutents are of some interest. The Mo–NMe_2 distance of 1.908 (4) Å is very short; compare distances of 1.98 (1) Å in $Mo_2(NMe_2)_6$[14] and 1.92–1.93 (1) Å in 1,2-$Mo_2Cl_2(NMe_2)_4$.[17] This indicates that considerable nitrogen-p to molybdenum-d π bonding is occurring between this group and the metal (see ^1H NMR discussion). The two aryloxide ligands at each end of the molecule are significantly different. However, they have in common the fact that they are both oriented so that the aryl groups of the ligand lie almost perpendicular to the Mo–Mo axis. This effect was also observed in the compound 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(OAr)_4$.[1] This contrasts with the dimethylamido ligand where the NMe_2 group orientates itself so that the methyl substituents are along the metal–metal axis. In this conformation the π donation to the empty molybdenum d_{xy} and $d_{x^2-y^2}$ (placing the z axis along the Mo–Mo bond) orbitals is maximized. The packing of the aryl groups we believe to be for a mixture of steric and electronic effects. We have noticed in other studies of early-transition-metal aryloxide compounds that the aryloxide ligand has the ability to relieve steric strain at the metal by opening up the M–O–Ar angles, in some cases to 180°.[1,18] This is because both an electron-deficient metal center and the aryl substituent can π bond to the oxygen atom to give a situation that can be represented M═O═Ar. Oxygen bridges between early transition metals or silicon tend to linearity for the same reason.[19,20] In the case of metal aryloxides, however, the situation imposes a preferred conformation on the aryl substituents. To maximize interaction with both the groups, the aryl ring should be coplanar with the metal d orbital to which the oxygen is interacting. Hence, for a dimolybdenum center, the preferred

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Table V. Fractional Coordinates and Isotropic Thermal Parameters for $Mo_2(O_2CNMe_2)_2(OAr)_4$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	867 (1)	2298.9 (3)	5475.1 (3)	10
O(2)	−1083 (6)	2899 (2)	5685 (2)	14
C(3)	−1486 (9)	3336 (4)	5294 (3)	13
O(4)	−907 (6)	1663 (2)	5258 (2)	14
N(5)	−2501 (7)	3792 (3)	5462 (3)	17
C(6)	−3125 (9)	4266 (4)	5026 (4)	19
C(7)	−3098 (11)	3816 (4)	6101 (4)	23
O(8)	2540 (6)	1654 (2)	5434 (2)	14
C(9)	3225 (9)	1352 (3)	5936 (3)	14
C(10)	2485 (9)	816 (4)	6220 (3)	16
C(11)	3252 (10)	531 (4)	6723 (4)	19
C(12)	4691 (10)	749 (4)	6920 (4)	22
C(13)	5406 (9)	1268 (4)	6627 (4)	22
C(14)	4694 (9)	1577 (3)	6142 (3)	13
C(15)	907 (11)	558 (4)	5992 (3)	19
C(16)	5451 (9)	2138 (4)	5812 (4)	18
O(17)	1956 (6)	2945 (2)	5979 (2)	15
C(18)	1456 (9)	3291 (3)	6481 (3)	13
C(19)	673 (10)	2980 (3)	6969 (3)	17
C(20)	131 (10)	3368 (4)	7447 (4)	20
C(21)	360 (9)	4029 (4)	7455 (4)	22
C(22)	1166 (10)	4316 (4)	6976 (4)	20
C(23)	1726 (9)	3959 (4)	6471 (3)	14
C(24)	416 (9)	2259 (4)	6962 (3)	20
C(25)	2520 (10)	4278 (4)	5926 (4)	22

Table VI. Bond Distances (Å) for $Mo_2(O_2CNMe_2)_2(OAr)_4$

Mo(1)–Mo(1)	2.220 (1)	C(10)–C(11)	1.398 (11)
Mo(1)–O(2)	2.106 (5)	C(10)–C(15)	1.514 (12)
Mo(1)–O(4)	2.043 (5)	C(11)–C(12)	1.362 (12)
Mo(1)–O(8)	1.941 (5)	C(12)–C(13)	1.384 (13)
Mo(1)–O(17)	1.953 (5)	C(13)–C(14)	1.368 (12)
O(2)–C(3)	1.283 (8)	C(14)–C(16)	1.503 (11)
O(4)–C(3)	1.292 (8)	C(18)–C(19)	1.402 (11)
O(8)–C(9)	1.381 (9)	C(18)–C(23)	1.398 (11)
O(17)–C(18)	1.367 (9)	C(19)–C(20)	1.387 (12)
N(5)–C(3)	1.323 (9)	C(19)–C(24)	1.504 (11)
N(5)–C(6)	1.457 (11)	C(20)–C(21)	1.377 (12)
N(5)–C(7)	1.475 (11)	C(21)–C(22)	1.375 (13)
C(9)–C(10)	1.410 (11)	C(22)–C(23)	1.400 (11)
C(9)–C(14)	1.395 (11)	C(23)–C(25)	1.509 (12)

conformation will be with the aryl group perpendicular to the Mo–Mo axis and, hence, coplanar with the d_{xy} and $d_{x^2-y^2}$ orbitals to which the oxygen can π bond. In the solid-state structure of I, one of the aryl groups lies over the metal–metal bond, while the other lies away from it. The former has a short Mo–O distance (Mo–O(5) = 1.926 (3) Å) with a large Mo–O–Ar angle (148.7°) while the other has a longer distance to the metal (Mo–O(14) = 1.961 (3) Å) and a small angle at oxygen (115.3°). This implies that O(5) is undergoing significantly more interaction with the metal than O(14). The bending away of the aryl group on O(14) also probably reflects an attempt to alleviate some of the steric crowding at the metal.

Solid-State Structure of $Mo_2(O_2CNMe_2)_2(OAr)_4$ (II). Table I contains the crystallographic data for the structural analysis of this compound. An ORTEP view of the molecule is shown in Figure 2 while Tables V–VII contain the fractional coordinates and isotropic thermal parameters, bond distances, and bond angles, respectively. In the solid state, a crystallographically imposed C_2 axis is present, giving the molecule C_2 symmetry.

The molecule can be seen to possess two four-coordinate molybdenum atoms bridged by the two $Me_2NCO_2^-$ groups arranged cis to each, giving rise to an almost eclipsed Mo_2O_8 skeleton. The distances to the substituent oxygen atoms are different however. The Mo–OAr distances of 1.945 Å (average) are much shorter than those to the carbamate oxygens (2.07 Å average), indicating the stronger π-bonding capabilities of the former oxygen atoms. However, the somewhat weaker π-donor powers of aryloxide over alkoxide is shown by a comparison with the somewhat related molecule $Mo_2(O_2CO\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)_4$, which adopts an almost identical skeletal arrangement.[21] In this case the Mo–O distances to the alkoxides are 1.89 Å (average) while those to the carbonate ligands are 2.13 Å (average). Despite the four-coordinate and bridged nature of the metal centers, molecule II still contains an Mo_2^{6+} core, and the Mo–Mo distance of 2.220 (1) Å is consistent with this.

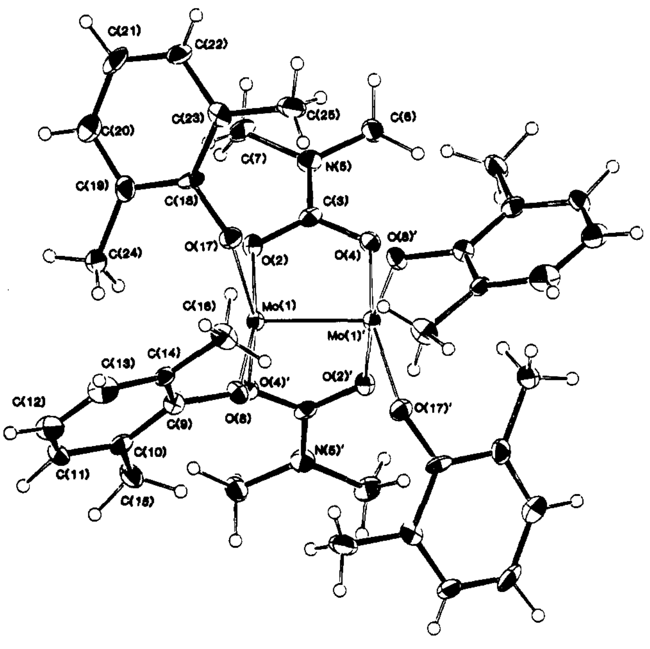

Figure 2. ORTEP view of the $Mo_2(O_2CNMe_2)_2(OAr)_4$ (II) molecule with the numbering scheme used.

Table VII. Bond Angles (deg) for $Mo_2(O_2CNMe_2)_2(OAr)_4$

Mo(1)–Mo(1)–O(2)	88.9 (1)	C(10)–C(9)–C(14)	121.0 (7)
Mo(1)–Mo(1)–O(4)	91.5 (1)	C(9)–C(10)–C(11)	117.8 (8)
Mo(1)–Mo(1)–O(8)	102.3 (2)	C(9)–C(10)–C(15)	121.5 (7)
Mo(1)–Mo(1)–O(17)	105.2 (2)	C(11)–C(10)–C(15)	120.7 (7)
O(2)–Mo(1)–O(4)	81.8 (2)	C(10)–C(11)–C(12)	121.1 (8)
O(2)–Mo(1)–O(8)	168.4 (2)	C(11)–C(12)–C(13)	120.0 (9)
O(2)–Mo(1)–O(17)	81.0 (2)	C(12)–C(13)–C(14)	121.6 (9)
O(4)–Mo(1)–O(8)	94.5 (2)	C(9)–C(14)–C(13)	118.6 (8)
O(4)–Mo(1)–O(17)	155.7 (2)	C(9)–C(14)–C(16)	118.8 (7)
O(8)–Mo(1)–O(17)	98.8 (2)	C(13)–C(14)–C(16)	122.6 (8)
Mo(1)–O(2)–C(3)	118.5 (4)	O(17)–C(18)–C(19)	120.4 (6)
Mo(1)–O(4)–C(3)	119.2 (5)	O(17)–C(18)–C(23)	116.9 (7)
Mo(1)–O(8)–C(9)	125.2 (4)	C(19)–C(18)–C(23)	122.6 (7)
Mo(1)–O(17)–C(18)	131.0 (5)	C(18)–C(19)–C(20)	116.9 (7)
C(3)–N(5)–C(6)	122.2 (7)	C(18)–C(19)–C(24)	120.9 (7)
C(3)–N(5)–C(7)	120.2 (7)	C(20)–C(19)–C(24)	122.2 (8)
C(6)–N(5)–C(7)	117.6 (7)	C(19)–C(20)–C(21)	122.4 (9)
O(2)–C(3)–O(4)	120.8 (7)	C(20)–C(21)–C(22)	119.1 (9)
O(2)–C(3)–N(5)	119.4 (7)	C(21)–C(22)–C(23)	121.9 (8)
O(4)–C(3)–N(5)	119.8 (7)	C(18)–C(23)–C(22)	117.0 (8)
O(8)–C(9)–C(10)	120.8 (7)	C(18)–C(23)–C(25)	121.0 (8)
O(8)–C(9)–C(14)	118.1 (7)	C(22)–C(23)–C(25)	122.0 (8)

^{1}H NMR Spectral Studies. The room-temperature (25° C/200 MHz) ^{1}H NMR spectrum of I is consistent with the overall structure adopted in the solid state. Only one set of aryloxide resonances is observed, indicating that, although different in the crystal, these ligands either rapidly exchange in solution or else are identically bound. This is consistent with the adoption of an anti rotamer, as a gauche form would lead to two types of aryloxide ligand. Furthermore, the observation of only one resonance for the aryloxide methyl groups implies,

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[21] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

as might be expected, that relatively free rotation about the M–O–Ar bonds can take place. Another possibility that has to be considered is that rotation about the Mo–Mo triple bond is facile. If this was the case, then the solution could contain only the gauche rotamer, but the bond rotation would lead to only one set of OAr peaks. However, studies of the barrier to rotation about the triple bond in such systems show that when two dimethylamido groups are present, a steric barier to rotation of around 14 kcal mol^{-1} or greater is to be expected.[22] This is high enough that it should be discernible in the variable-temperature ^1H NMR spectrum.

At room temperature only one type of NMe_2 group is present in the NMR spectrum. However, the N–CH_3 resonances are nonequilvalent due to restricted rotation about the Mo–NMe_2 bond, one of the methyl groups lying over (or proximal to) while the other lies away from (or distal to) the metal–metal triple bond (Figure 1). Due to the diamagnetic anisotropy of the Mo≡Mo group, a chemical shift separation of 2.72 ppm is observed. When the temperature of the solution is raised, these signals broaden and finally coalesce at a temperature of 155 °C in a sealed ^1H NMR tube (toluene-d_8). This allows us to estimate the value of the rotational barrier to be 20.1 ± 0.5 kcal mol^{-1} for rotation about this bond.[23] This figure represents the highest rotational barrier thus far reported for an Mo–NMe_2 group in such a system[22] and is consistent with the fact that the Mo–NMe_2 distance in I is the shortest so far seen for an Mo_2^{6+} core. Clearly there is a very strong π bond between the nitrogen atom and molybdenum. It is interesting to compare the data for I with the previously reported 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$.[22] The latter compound exists only in the gauche isomer in solution and has a Mo–NMe_2 rotational barrier of 15.0 ± 0.5 kcal mol^{-1}. The higher barrier in I may reflect steric pressure from OAr compared to CH_2SiMe_3 as coligand. Unfortunately, due to its liquid nature, structural studies of 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ for comparison with I cannot be obtained.

In contrast to I, the ^1H NMR spectrum of II is relatively straightforward, showing one set of OAr ligands and one type of O_2CNMe_2 group consistent with the solid-state structure (see Experimental Section).

Conclusions. The bonding of 2,6-dimethylphenoxide to an Mo_2^{6+} center results in a coordination geometry in which the plane of the aryl group lies perpendicular to the Mo–Mo axis, instead of the expected geometry with the methyl groups lying over and away from the metal–metal bond. Recent work by Nugent and co-workers has shown that it is possible for amido and alkoxide ligands to act as leaving groups during early transition-metal cyclometalation reactions.[24] The lack of metalation of the methyl groups on thermolysis of I up to 160 °C either may be due to the lack of activity of this Mo_2^{6+} system to metalate or else may be due to the preferred conformation of the aryloxide ligands not allowing the methyl group to come into close proximity with the second metal atom of the dimer.

Experimental Section

Synthesis of 1,2-$Mo_2(NMe_2)_2(OAr)_4$ (I). To a hexane suspension of $Mo_2(NMe_2)_6$ (1 g in 25 cm^3) was added 2,6-dimethylphenol (HOAr, 2.2 g dried over molecular sieves). The resulting orange solution rapidly deposited orange crystals of product after a few minutes at room temperature. After 1 h the orange solid was filtered off, washed with hexane, and dried in vacuo; yield 1.6 g (95%). Anal. Calcd for $Mo_2C_{36}H_{48}N_2O_4$: C, 56.53; H, 6.33; N, 3.66. Found: C, 56.44; H, 6.49; N, 3.64. ^1H NMR (toluene-d_8 25 °C): δ 4.45, 1.73 (s, proximal and distal NMe_2); δ 2.22 (s, $OC_1H_3\mathit{Me}_2$); δ 6.6–7.1 (m, OC_6H_3). Recrystallization from hot toluene gave large crystals suitablr for X-ray analysis.

Synthesis of $Mo_2(O_2CNMe_2)_2(OAr)_4$ (II). A solution of $Mo_2(NMe_2)_2(OAr)_4$ (I) in toluene was exposed to 1 atm of CO_2 for 72 h at 25 °C. The initially orange solution turned dark brown and deposited crystals of product (II). Filtration and drying under vacuum gave the pure product. Evaporation of the mother liquor gave more of the product (identified by ^1H NMR) as a fine powder. Anal. Calcd for $Mo_2C_{38}H_{48}N_2O_8$: C, 53.50; H, 5.68; N, 3.29. Found: C, 53.71; H, 5.75; N, 3.27. ^1H NMR (toluene-d_8, 25 °C): δ 1.93 (s, O_2CNMe_2); δ 2.07 (s, $OC_6H_3\mathit{Me}_2$); δ 6.5–6.8 (m, $OC_6\mathit{H}_3Me_2$).

X-ray Structural Determinations. General operating procedures and computational techniques have been described.[26] Crystal and experimental data are given in Table I. The structures of I and II were solved by using standard heavy-atom and Fourier techniques. All atoms including hydrogens were located, and final refinement was carried out by using full-matrix least squares, utilizing isotropic thermal parameters for hydrogen atoms and anistropic thermal parameters for all non-hydrogen atoms.

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Registry No. I, 89322-08-7; II, 89322-09-8; $Mo_2(NMe_2)_6$, 51956-20-8; CO_2, 124-38-9; Mo, 7439-98-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, fractional coordinates of hydrogen atoms, and observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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[24] Nugent, W. A.; Overall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.