of the two independent molecules and the framework of the $Mo_3O(OCH_2\text{-}t\text{-}Bu)_{10}$ molecule indicates the inner coordination geometry of the three are essentially identical. Anisotropic thermal parameters, complete listings of distances and angles, the molecular fit least squares, and observed and calculated structure amplitudes are available as supplementary material.

$Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$. A triclinic lattice was located in the diffraction maxima collected at −161 °C. The structure was readily solved by a combination of Patterson and Fourier techniques. Crystal and diffractometer data are given in Table XVII. Since there is only one molecule in the centrosymmetric space group, the molecule possesses crystallographic as well as molecular C_i symmetry. All hydrogen atoms were located in a difference Fourier phased on the non-hydrogen parameters and were allowed to vary isotropically for the final refinement. A final difference Fourier was featureless, with the largest peak being 0.5 e/Å^3. Anisotropic thermal parameters, hydrogen coordinates, complete distances and angles, and a listing of observed and calculated structure amplitudes are available as supplementary material.

Acknowledgment. We thank the Office of Naval Research for support of this work. M.H.C. is a recipient of a Henry and Camille Dreyfus Teacher-Scholar grant, 1979–1984, and C.C.K. is the Indiana University SOHIO Fellow, 1979–1982.

Registry No. I, 89015-24-7; II, 88947-09-5; III, 79256-75-0; IV, 83419-17-4; $MoO_2(O\text{-}t\text{-}Bu)_2$, 78134-32-4; $MoO_2(O\text{-}t\text{-}Bu)_2(bpy)$, 88916-52-3; $MoO_2(O\text{-}i\text{-}Pr)_2(bpy)$, 88979-78-6; $MoO_2(OCH_2\text{-}t\text{-}Bu)_2(bpy)$, 88916-55-6; $MoO(O\text{-}t\text{-}Bu)_4$, 88916-58-9; $MoO(O\text{-}i\text{-}Pr)_4$, 79210-24-5; $MoO(OCH_2\text{-}t\text{-}Bu)_4$, 79218-12-5; $Mo_3O(OCH_2\text{-}t\text{-}Bu)_{10}$, 88947-08-4; $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$, 88916-56-7; $MoO_2(O\text{-}t\text{-}Bu)_2(py)_2$, 88916-51-2; $MoO_2(O\text{-}i\text{-}Pr)_2(py)_2$, 88916-53-4; $MoO_2(OCH_2\text{-}t\text{-}Bu)_2(py)_2$, 88916-54-5; $MoO_2(O\text{-}i\text{-}Pr)_2$, 82123-87-3; $MoO_2(OCH_2\text{-}t\text{-}Bu)_2$, 88916-57-8; $Mo_2(O\text{-}t\text{-}Bu)_6$, 60764-63-8; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 62521-24-8; $Mo(O\text{-}t\text{-}Bu)_4$, 60624-53-5; $Mo_2(O\text{-}i\text{-}Pr)_8$, 66526-46-3; $[Mo(OCH_2\text{-}t\text{-}Bu)_4]_x$, 66917-89-3; O_2, 7782-44-7.

Supplementary Material Available: Listings of fractional coordinates, isotropic and anisotropic thermal parameters, and complete bond distances and angles, stereoviews, and listings of observed and calculated structure amplitudes for the single-crystal structural studies for all the compounds and a listing of hydrogen coordinates for $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ (215 pages). Ordering information is given on any current masthead page. Complete crystallographic data are also available, in microfiche form only, from the Indiana University Chemistry Library, Bloomington, IN 47405. Request MSC Report No. 81047 for $MoO_2(O\text{-}i\text{-}Pr)_2(bpy)$, No. 81006 for $Mo_3O(OCH_2\text{-}t\text{-}Bu)_{10}$, No. 81029 for $Mo_3O(O\text{-}i\text{-}Pr)_{10}$, and No. 81025 for $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ when ordering.

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Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Reactions of Metal–Metal Multiple Bonds. 11.[1] A Comparison of the Reactivity of $M_2(OR)_6$ ($M\equiv M$) and $M_2(OR)_4(R'COCHCOR')_2$ ($M\equiv M$) Compounds (M = Mo, W) with the π-Acid Ligands CO, $RC\equiv CR$, and RNC

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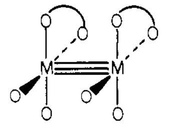
$M_2(OR)_6$ compounds (M = Mo, W; R = *t*-Bu, *i*-Pr, $CH_2\text{-}t\text{-}Bu$) react in hydrocarbon solvents with isocyanide ligands to give, upon workup with methanol and KPF_6, $M(CN\text{–}alkyl)_7^{2+}$ salts or $M(CNPh)_6$ compounds in a similar manner, noted by Walton and co-workers for reactions involving M–M quadruply bonded compounds. By contrast, $Mo_2(OR)_4(R'COCHCOR')_2$ compounds (R′ = Me, *t*-Bu) react in hydrocarbon solvents to give edge-shared (μ-OR) octahedral complexes and provide the first examples of the conversion of $L_4M\equiv ML_4$ compounds to $L_4M(\mu\text{-}L)_2ML_4$ compounds. These are also the first reactions wherein a multiple bond between molybdenum atoms is not cleaved by isocyanide ligands. The compound $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(t\text{-}BuNC)_2$ has been fully characterized by an X-ray study. Cell dimensions at −163 °C are a = 13.817 (5) Å, b = 12.518 (4) Å, c = 14.045 (5) Å, and β = 92.61 (2)° with Z = 2 in the space group $P2_1/n$. The conversion of an unbridged triple bond $\sigma^2\pi^4$ to an edge-bridged d^3–d^3 dimer of formal M–M configuration $\sigma^2\pi^2\delta^2$ is accompanied by an increase in Mo–Mo distance, 2.237 (1)–2.508 (2) Å. Related ditungsten alkoxide β-diketonates ($M\equiv M$) fail to react with *t*-BuNC under comparable conditions. Both molybdenum and tungsten alkoxide β-diketonates fail to react with CO and alkynes under conditions wherein $M_2(OR)_6$ and $M_2(OR)_6(L)_2$ compounds yield $M_2(\mu\text{-}X)$ derivatives (X = CO, alkynes) or products of cleavage of the M–M bond. $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ reacts with 2,2′-bipyridine to give $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$, which, on the basis of ^{1}H NMR spectroscopy, is proposed to be an edge-shared (μ-OR) bioctahedral compound. The marked differences in reactivity of $M_2(OR)_6$ and the mixed alkoxide β-diketonate complexes are discussed in terms of kinetic and/or thermodynamic factors.

Introduction

In a previous paper, we described[3] the preparation and characterization of mixed alkoxide–β-diketonate complexes, $M_2(OR)_4(R'COCHCOR'')_2$, which contained two four-ligated metal atoms (M = Mo, W) united by an unbridged $M\equiv M$ bond. These are schematically represented by I. Both the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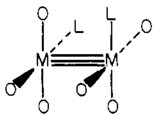
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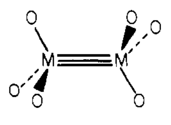
III

O = OR, $\overset{\frown}{O\,O}$ = β-diketonate

formal negative charge and the chelate effect serve to keep the metal atoms four-ligated in hydrocarbon solvents, and only at +110 °C for M = Mo is there any evidence for rapid reversible bidentate ⇌ monodentate behavior of the β-di-

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ketonate ligand. This contrasts with the Lewis base adducts of the parent hexaalkoxides, $M_2(OR)_6L_2$ (II), which are labile to reversible loss of L to give $M_2(OR)_6$ compounds, III.[4-7]

In this paper, we compare and contrast the reactivity of the $M_2(OR)_6$ and $M_2(OR)_4(\widehat{O\,O})_2$ compounds toward the π-acid ligands, carbon monoxide, isocyanides, alkynes, and other ligands. Previously it has been shown that compounds of types II and III react with CO[8,9] and alkynes[10,11] to give adducts of the formulas $M_2(OR)_6(\mu\text{-}X)$ and $M_2(OR)_6L_2(\mu\text{-}X)$, where X = CO or an alkyne. A further reaction in the case of CO leads to cleavage of the M–M triple bond.[8] This is also seen in the reactions between $W_2(O\text{-}t\text{-}Bu)_6$ and $RC{\equiv}CR$, which give $(t\text{-}BuO)_3W{\equiv}CR$, where R = Me, Et, and Pr.[12] Two other examples of cleavage have been noted. One involves the reactions between $Mo_2(OR)_6$ compounds (R = *i*-Pr, $CH_2\text{-}t\text{-}Bu$) and 2,2′-bipyridine,[13] and the other involves reactions between $W_2(O\text{-}t\text{-}Bu)_6$ and $RC{\equiv}N$ (R = Me, Ph, $PhCH_2$).[12] Reactions between $M_2(OR)_6$ compounds and isocyanide ligands have not been described previously and are presented here.

Results and Discussion

$M_2(OR)_6$ + RNC. Hydrocarbon solutions of $M_2(OR)_6$, with or without added pyridine, react rapidly with isocyanide ligands. No simple adducts or products have been isolated from these reactions, but it is reasonable to suppose that the $M{\equiv}M$ bond is cleaved in a disproportionation reaction on the basis of the following. (1) From a reaction between $Mo_2(O\text{-}t\text{-}Bu)_6$ and *t*-BuNC, the monomeric compound $Mo(O\text{-}t\text{-}Bu)_4$ was isolated. (2) When, subsequent to the reaction between $Mo_2(OR)_6$ compounds and RNC ($\geq$15 equiv), methanol was added in large excess along with $K^+PF_6^-$, the known compounds $Mo(CNR)_7^{2+}(PF_6^-)_2$ were isolated. Similar results were obtained for reactions involving $W_2(O\text{-}t\text{-}Bu)_6$, though the isolated yields of $W(CNR)_7^{2+}$ salts were lower. (3) Reactions employing PhNC yielded, after workup in methanol, the zerovalent metal isocyanides $M(CNPh)_6$. These results directly parallel the observations of Walton and co-workers in their studies of the reactions between Mo–Mo and W–W quadruply bonded compounds.[14]

Since we had been able to isolate $M_2(\mu\text{-}CO)$-containing compounds and show that these were intermediates in the reaction pathway leading to cleavage of the $M{\equiv}M$ bond, we searched for related μ-CNR compounds, but without any success. Upon addition of 1 equiv of isocyanide ligand to $M_2(OR)_6$ solutions at −78 °C, there is an immediate color change from yellow to red or purple. This parallels the color change observed in reactions employing CO (1 equiv). Using a low-temperature solution infrared cell,[15] we observed the fleeting appearance of a band at ca. 1710 cm^{-1}, while the purple color was still present in solution. Upon warmup, this band disappears, and $\nu(C{\equiv}N)$ bands were only seen in the region of terminal M–CNR groups, namely 2100–2200 cm^{-1}. It is thus possible that the reaction pathway parallels that for CO and that the $M_2(OR)_6(\mu\text{-}CNR')$ intermediates are less stable and/or more reactive.

Reactions of $M_2(OR)_4(\widehat{O\,O})_2$ Compounds. (a) With Carbon Monoxide and Alkynes. Hydrocarbon solutions of the mixed alkoxy β-diketonate compounds do not react with CO or alkynes ($HC{\equiv}CH$ and $MeC{\equiv}CMe$) under comparable conditions to those wherein $M_2(OR)_6$ or $M_2(OR)_6L_2$ compounds yield $M_2(\mu\text{-}X)$-containing compounds. Furthermore, even under more forcing conditions (60–70 °C, 24 h, 1 atm), we have observed no reaction of the dinuclear compounds. They were recovered completely unreacted. Alkyne polymerization was noted, but as before it is not believed to involve the dinuclear alkoxides.[9]

(b) With *t*-BuNC. The molybdenum compounds react with *t*-BuNC to give $Mo_2(OR)_4(\widehat{O\,O})_2(CN\text{-}t\text{-}Bu)_2$, but no reaction is observed for the tungsten compounds. The influence of steric factors is seen in the qualitative rates of reaction as a function of the alkoxy ligand OR and the substituents R′ on the β-diketonate ligand. When R = $CH_2\text{-}t\text{-}Bu$ and R′ = Me, the purple color of the isocyanide complex appears immediately upon addition of the isocyanide to a hydrocarbon solution of the $Mo_2(OR)_4(\widehat{O\,O})_2$ compound at 0 °C, but when R = R′ = *t*-Bu, this color appears only slowly at 25 °C.

(c) With $MeC{\equiv}N$. Though $Mo_2(OR)_6$ compounds show little or no affinity for adduct formation or reaction with $MeC{\equiv}N$,[7] $W_2(OR)_6$ compounds react rapidly to cleave the $W{\equiv}W$ and $-C{\equiv}N$ bond in a metathesis-like reaction.[12] Addition of $MeC{\equiv}N$ (1 equiv) to $W_2(O\text{-}t\text{-}Bu)_6$ in hexane yields a white precipitate of the linear polymer $[(t\text{-}BuO)_3W{\equiv}N]_x$ and a yellow solution of $[(t\text{-}BuO)_3W{\equiv}CMe]_2$.[16] By contrast, we find that $W_2(OR)_4(\widehat{O\,O})_2$ compounds show no sign of reaction with $MeC{\equiv}N$, even when the latter is present in large excess.

(d) With 2,2′-Bipyridine. $Mo_2(OR)_6$ compounds, where R = *i*-Pr and $CH_2\text{-}t\text{-}Bu$, react with bpy in hydrocarbon solutions to give, by cleavage of the $Mo{\equiv}Mo$ bond and disproportionation, $Mo(OR)_2(bpy)_2$ and $Mo_2(OR)_8$ compounds.[13] $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and bpy also react in hydrocarbon solutions in a rather different manner, yielding the d^3–d^3 dimer $(bpy)(i\text{-}PrO)W(\mu\text{-}O)(\mu\text{-}O\text{-}i\text{-}Pr)_2W(O\text{-}i\text{-}Pr)(bpy)$.[13] We find that the $W_2(OR)_4(\widehat{O\,O})_2$ compounds do not show any reactivity toward bpy but that $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ reacts slowly to give $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$, which, on the basis of spectroscopic data, we formulate as an edge-shared bioctahedral complex (see later text).

$M_2(OR)_4(\widehat{O\,O})_2(CN\text{-}t\text{-}Bu)_2$ compounds are purple, hydrocarbon-soluble, diamagnetic, air-sensitive crystalline materials. Only the neopentoxy-2,4-pentanedionate compound has been fully characterized. In the infrared spectrum, a strong band at 2015 cm^{-1} is assignable to $\nu(N{\equiv}C)$; cf. $\nu(N{\equiv}C)$ = 2115 cm^{-1} in free *t*-BuNC. Two bands, 1578 and 1521 cm^{-1}, are characteristic of the acac ligand. The ^{1}H NMR spectrum shows only one resonance for the *t*-BuNC ligand. Addition of *t*-BuNC to a toluene-d_8 solution of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ leads to the appearance of two sharp resonances in the ^{1}H NMR spectrum assignable to free and coordinated *t*-BuNC. Evidently the coordinated isocyanide ligand is quite tightly bound and is not labile to exchange. When mixtures of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ and $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ were dissolved in toluene-d_8 and examined

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Table I. Crystallographic Data for the Molecule $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$

formula	$C_{40}H_{74}Mo_2N_2O_8$
fw	904.93
space group	$P2_1/n$
a, Å	13.817 (5)
b, Å	12.518 (4)
c, Å	14.045 (5)
β, deg	92.61 (2)
Z	2
V, Å^3	2426.67
d_{calcd}, g/cm^3	1.238
cryst size, mm	0.15 × 0.15 × 0.15
cryst color	reddish brown
radiation	Mo Kα (λ = 0.71069 Å) graphite monochromator
linear abs coeff, cm^{-1}	5.46
temp, °C	−163
instrument	Picker 4-circle diffractometer locally modified and interfaced
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	1.8 + 0.692 tan θ
bkgd counts, s	5 at each end of scan
2θ range, deg	6–45
data collcd	3632 total
no. of unique data	3181
no. of unique data with $F_o > 3\sigma(F_o)$	2273
$R(F)$	0.066
$R_w(F)$	0.060
goodness of fit	1.230
largest Δ/σ	0.05

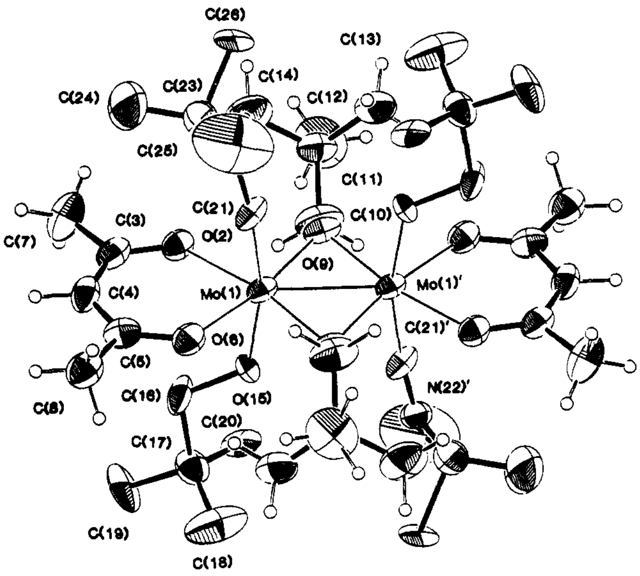

Figure 1. ORTEP view of the centrosymmetric $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ molecule showing the atom-number scheme used in the tables.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	9945 (1)	971 (1)	9785 (1)	25
O(2)	10889 (4)	2288 (5)	9742 (4)	30
C(3)	10680 (8)	3246 (9)	9504 (7)	34
C(4)	9741 (8)	3625 (8)	9232 (7)	35
C(5)	8895 (7)	3032 (9)	9171 (7)	33
O(6)	8839 (5)	2023 (5)	9322 (4)	33
C(7)	11522 (8)	3991 (9)	9501 (8)	48
C(8)	7970 (8)	3579 (9)	8926 (8)	42
O(9)	11131 (4)	147 (5)	10329 (4)	30
C(10)	12077 (8)	88 (11)	9994 (8)	48
C(11)	12849 (8)	324 (10)	10742 (8)	40
C(12)	13844 (8)	143 (13)	10359 (10)	68
C(13)	12724 (8)	−383 (10)	11611 (8)	48
C(14)	12746 (9)	1499 (11)	11066 (10)	60
O(15)	10244 (5)	818 (6)	8397 (5)	26
C(16)	10343 (20)	1704 (19)	7719 (16)	42
C(17)	10352 (8)	1218 (8)	6656 (7)	38
C(18)	9364 (10)	760 (14)	6331 (10)	79
C(19)	10588 (21)	2125 (22)	6000 (17)	51
C(20)	11335 (15)	440 (18)	6714 (16)	36
C(21)	9622 (6)	1502 (6)	11074 (6)	33
N(22)	9513 (13)	1962 (15)	11876 (13)	37
C(23)	9332 (9)	2689 (10)	12494 (8)	42
C(24)	9381 (16)	3837 (12)	12424 (15)	123
C(25)	8325 (13)	2254 (21)	12707 (14)	134
C(26)	9979 (23)	2433 (20)	13484 (16)	54
N(16)*	10384 (12)	928 (19)	7587 (13)	38
C(19)*	11108 (18)	611 (25)	6037 (17)	60
C(20)*	10448 (18)	2456 (21)	6593 (21)	46
C(22)*	9448 (16)	2623 (19)	11308 (15)	37
C(26)*	10250 (19)	2227 (21)	12906 (18)	46

Table III. Selected Bond Distances (Å) for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ Molecule

Mo(1)–Mo(1)'	2.508 (2)	O(2)–C(3)	1.273 (12)
Mo(1)–O(2)	2.105 (6)	O(6)–C(5)	1.283 (12)
Mo(1)–O(6)	2.098 (7)	O(9)–C(10)	1.412 (11)
Mo(1)–O(9)'	2.042 (6)	O(15)–C(16)	1.474 (24)
Mo(1)–O(9)	2.054 (6)	N(22)–C(21)	1.281 (19)
Mo(1)–O(15)/C(21)	2.020 (8)	N(22)–C(23)	1.289 (21)
Mo(1)–C(21)/O(15)	1.998 (8)		

Table IV. Selected Bond Angles (deg) for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ Molecule

Mo(1)'–Mo(1)–O(2)	137.3 (2)	O(9)'–Mo(1)–O(9)	104.5 (2)
Mo(1)'–Mo(1)–O(6)	135.9 (2)	O(9)'–Mo(1)–O(15)	92.2 (3)
Mo(1)'–Mo(1)–O(9)	52.0 (2)	O(9)–Mo(1)–C(21)	92.1 (3)
Mo(1)'–Mo(1)–O(15)	97.3 (2)	O(15)–Mo(1)–C(21)	165.9 (3)
Mo(1)'–Mo(1)–C(21)	96.8 (2)	Mo(1)–O(2)–C(3)	127.7 (6)
O(2)–Mo(1)–O(6)	86.7 (3)	Mo(1)–O(6)–C(5)	128.3 (6)
O(2)–Mo(1)–O(9)'	169.8 (3)	Mo(1)'–O(9)–Mo(1)	75.5 (2)
O(2)–Mo(1)–O(15)	83.8 (3)	Mo(1)–O(9)–C(10)	129.6 (7)
O(2)–Mo(1)–C(21)	86.0 (3)	Mo(1)–O(15)–C(16)	125.6 (11)
O(6)–Mo(1)–O(9)'	83.6 (3)	Mo(1)–C(21)–N(22)	170.8 (10)
O(6)–Mo(1)–O(15)	86.5 (3)	C(21)–N(22)–C(23)	160.7 (18)
O(6)–Mo(1)–C(21)	83.2 (3)		

by ^1H NMR spectroscopy, the only signals observed corresponded to those of the known compounds. There was no evidence for the formation of a compound of formula $Mo_2(OR)_4(O\frown O)_2(CN\text{-}t\text{-}Bu)$.

In the ^{13}C NMR spectrum, a signal at δ 173.5 is assigned to the α-carbon of the coordinated t-BuNC ligand. This is somewhat downfield of the range commonly observed for diamagnetic metal isocyanide complexes; cf. δ 133.7 in $Rh(CN\text{-}t\text{-}Bu)_4{}^+PF_6{}^-$[17] and δ 162.1 in $Mo(CN\text{-}t\text{-}Bu)_5(O_2CMe)_2$.[18] However, it is not clear what significance can be attributed to this low chemical shift value. In $Mo_2(OR)_6L_2(\mu\text{-}CO)$ compounds, the δ values for the carbonyl ligands were shifted 60–80 ppm downfield from the range commonly observed for bridging carbonyl ligands in organometallic compounds.

Solid-State and Molecular Structures. In the space group $P2_1/n$, there are two symmetry-related $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ molecules in the unit cell with crystallographically imposed C_i symmetry, see Table I. Fractional coordinates are given in Table II, and selected bond distances and bond angles are given in Tables III and IV, respectively. An ORTEP view of the molecule giving the atom-number scheme used in the tables is shown in Figure 1.

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(18) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2040.

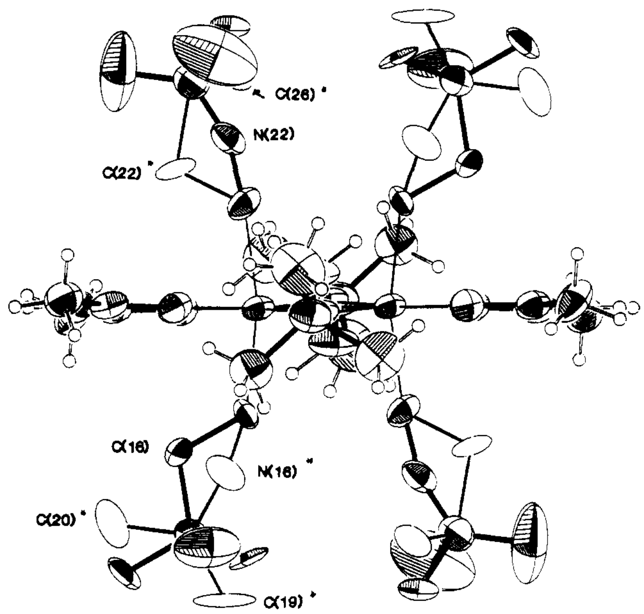
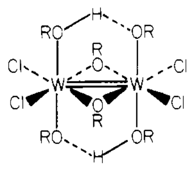


Figure 2. View of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ molecule emphasizing the edge-shared bioctahedral geometry and showing the disorder of the trans $OCH_2\text{-}t\text{-}Bu$ and CN-*t*-Bu ligands. The atoms that are disordered and do not overlap are numbered and given an asterisk.

The $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ molecule contains two octahedrally coordinated molybdenum atoms joined along a common edge through the agency of a pair of bridging neopentoxy ligands. The 2,4-pentanedionate ligands are contained in the $Mo_2(\mu\text{-}O)_2$ plane, while the terminal neopentoxy ligands and *tert*-butyl isocyanide ligands are mutually trans and are disordered such that the α-carbon and oxygen atoms are virtually coincident, as are the γ-carbon atoms, while the β-carbon and -nitrogen atoms are separated by approximately 1 Å. The disorder is also apparent in the *tert*-butyl methyl carbons. A view of the molecule emphasizing the edge-shared bioctahedral geometry and showing the disorder of the mutually trans $OCH_2\text{-}t\text{-}Bu$ and CN-*t*-Bu ligands is shown in Figure 2.

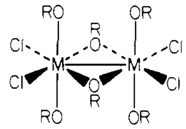
Although the disorder obviates accurate distances and angles associated with the mutually trans $OCH_2\text{-}t\text{-}Bu$ and CN-*t*-Bu ligands, the other atoms within the molecules are well located and lead to distances typically seen for Mo-μ-OR[7] and molybdenum 2,4-pentanedionate ligands.[3]

The most important aspect of this structural study is that it provides the first unequivocal demonstration of the conversion of an $L_4M{\equiv}ML_4$ unbridged d^3–d^3 dimer to an edge-shared octahedral $L_4M(\mu\text{-}L)_2ML_4$ d^3–d^3 dimer. The Mo-Mo distance, 2.508 (2) Å, is nearly 0.3 Å longer than in the parent compound. In a formal sense, the M–M triple bond is maintained but is transformed from one of configuration $\sigma^2\pi^4$ in the unbridged starting material to $\sigma^2\pi^2\delta^2$ in the edge-shared octahedral product. The formation of alkoxy bridges naturally tends to move the metal atoms apart[19] and at a distance of 2.5 Å, the δ contribution to the bonding must be very weak indeed. The M–M distance is, in fact, typical of M–M double bonds between molybdenum and tungsten atoms, and a comparison with the distances 2.48–2.49 Å, found in d^2–d^2 mixed chloride alkoxide dimers of formula $W_2Cl_4(OR)_4(HOR)_2$,[20] which have the μ-OR edge-shared octahedral geometry shown in IV, is worthy of mention.



IV

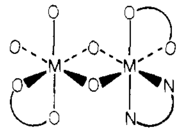
In the present case, the M–M orbital configuration $\sigma^2\pi^2\delta^2$ is a very simplistic bonding scheme since the presence of π-donor ligands (RO) and π-acceptor ligands (CNR) will interact with the t_{2g} metal orbitals, which in turn will lead to a mixing of M–M bonding and M–L π bonding. It is not obvious what will result from these combined interactions, but the observed M–M distance is 0.2 Å shorter than in simple alkoxide d^1–d^1 dimers of type V, which implies that there is supplemental Mo–Mo π bonding in the present case.



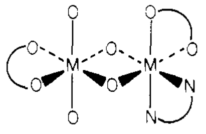
V, M = Mo[22] or W[23]

It is also worthy to note that calculations, employing both Fenske–Hall[20] and extended Hückel[21] methods, suggest a $\sigma^2\pi^2\delta^{*2}$ ground-state configuration for an edge-shared, bioctahedral d^3–d^3 dimer, rather than the simplistic $\sigma^2\pi^2\delta^2$ pictures that arise when a mixing of M–M and M–L bonding is ignored. Occupation of a δ^* orbital could also contribute to a lengthening of the M–M bond in d^3–d^3, edge-shared, bioctahedral dimers relative to related d^2–d^2 dimers.

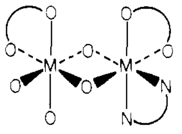
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$ is a purple, hydrocarbon-soluble, diamagnetic, air-sensitive crystalline compound. It is extremely soluble in common organic solvents and has only been isolated as a fine microcrystalline powder which has precluded a full structural characterization. However, ^1H NMR studies serve to characterize the compound fairly well. There are four acac–methyl resonances in the integral ratio 1:1:1:1 and four neopentoxy–methyl signals in the integral ratio 1:1:1:1. The neopentoxy methylene protons appear as four AB quartets of equal integral intensity. If we assume that the addition of bpy converts an $L_4M{\equiv}ML_4$ compound to a $L_4M(\mu\text{-}L)_2ML_4$ compound in an analogous manner to that found for the addition of *t*-BuNC (2 equiv), then only one of three structures satisfies the ^1H NMR data, namely VIA–C.



VIA



VIB



VIC

O = $OCH_2\text{-}t\text{-}Bu$, $\overset{\frown}{O\,O}$ = MeCOCHCOMe, $\overset{\frown}{N\,N}$ = bpy

Though it is not obvious which of VIA-C should be favored to the exclusion of the others, it is reasonable to envisage the formation of a pair of μ-OR bridges and furthermore that the chelate ligands (acac and bpy) would not span the Mo–Mo

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(19) The shortest Mo–Mo distance thus far seen in the presence of μ-OR ligands is 2.37 Å in the square $Mo_4(\mu\text{-}O\text{-}i\text{-}Pr)_8Cl_4$ molecule: Chisholm, M. H.; Errington, R. J.; Folting, F.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025.

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bond. It may be noted that in the d^1–d^1 dimer $Mo_2(\mu\text{-}O)_2(O)_2PH_2)_2(bpy)_2$, where O_2PH_2 is the hypophosphite ligand, the bidentate bpy ligands do not span the Mo–Mo bond of distance 2.553 (4) Å.[24]

Concluding Remarks. The mixed alkoxide–β-diketonate compounds $M_2(OR)_4(\widehat{OO})_2$ are remarkably less reactive toward the π-acid ligands, CO, alkynes, and isocyanides than are $M_2(OR)_6$ and $M_2(OR)_6L_2$ compounds. Though this could be due to thermodynamic factors, the alternate explanation, that the inertness is a kinetic phenomenon, is worthy of consideration. The presence of the bidentate β-diketonate ligand blocks access to an in-plane (xy) metal site. The observed reaction with t-BuNC to give $Mo_2(OR)_4(\widehat{OO})_2(t\text{-}BuNC)_2$ compounds provides the first examples wherein a multiple bond between molybdenum atoms is not cleaved by the addition of isocyanide ligands.[25] Again, the chelate effect could be critical in preventing further associative reactions that otherwise would lead to cleavage of the dinuclear unit. It is also interesting to speculate why the tungsten compounds $W_2(OR)_4(\widehat{OO})_2$ fail to react with t-BuNC and bpy when the molybdenum compounds do react. Could this be because tungsten binds the chelate more tightly and the equilibrium for the reaction bidentate ⇌ monodentate is virtually in complete favor of the bidentate ligand? The preference for the bidentate ligand, W > Mo, was noted from high-temperature ^1H NMR studies and parallels the known binding of Lewis bases to the $M_2(OR)_6$ compounds.[6,7]

In the more general context of reactions leading to the rupture of multiple bonds between Mo, W, and Re atoms, we note that although a pathway involving initial axial ligation of the π-acid ligand has been suggested, the alternate pathway involving an initial dissociation of one of the four in-plane (xy) ligands has not been ruled out.[14,25] The demonstration that PEt_3 ligands in $Mo_2Me_4(PEt_3)_4$ ($M\overset{4}{-}M$) compounds undergo substitution by either PMe_3 or PMe_2Ph in a stepwise manner via an initial dissociation of PEt_3[26] further emphasizes the possibility that reactions involving π-acid ligands may also proceed by an initial dissociative pathway. The detailed mechanisms of the reactions of π-acid ligands with these interesting dinuclear compounds is clearly an area worthy of further investigations.

Experimental Section

General Procedures. All reactions and manipulations of samples were carried out by using dry and oxygen-free atomospheres and solvents employing either standard Schlenk techniques or a Vacuum Atmospheres Co. Dri-Box assembly.

Materials. The compounds $M_2(OR)_6$,[4,6] $M_2(OR)_4(\widehat{OO})_2$[3] (where $\widehat{OO}$ is a β-diketonate), MeNC,[27] and PhNC[27] were prepared by previously described procedures. $PhCH_2NC$ and t-BuNC were purchased from Strem Chemicals, distilled at reduced pressure, and stored under N_2. Tetra-n-butylammonium hexafluorophosphate (TBAH) was prepared from the reaction of tetra-n-butylammonium iodide with KPF_6 in hot water. It was recrystallized from an ethanol/H_2O mixture, washed with Et_2O, and dried in vacuo prior to use.

Physical and Analytical Measurements. Elemental analyses were performed by Canadian Microanalytical Services Ltd. and by Alfred Bernhardt, Elbach, West Germany.

Infrared spectra were obtained from Nujol mulls between CsI plates with use of a Perkin-Elmer 283 spectrophotometer.

Electrochemical measurements were made by using a Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer. Cyclic voltammograms were recorded on an Ommigraphic 2000 X-Y recorder (Houston Instruments). Potentials were measured at a Pt-bead working electrode using a homemade Ag/AgCl reference electrode. A Pt coil was used as the counterelectrode.

^1H and ^{13}C NMR spectra were obtained on Varian HR 220 and Nicolet 360 spectrometers using toluene-d_8 as solvent. Chemical shift values, δ, are quoted relative to Me_4Si.

$M_2(OR)_6$ or $M_2(OR)_6L_2$ + R′NC. The following procedures are representative of our studies for M = Mo, R = t-Bu, i-Pr, and CH_2-t-Bu, R′ = Me, t-Bu, CH_2Ph, and Ph; for M = W, R = i-Pr and t-Bu, R′ = Ph and t-Bu; and for the adducts $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ with R′ = CH_2Ph and t-Bu.

(I) $Mo_2(O\text{-}t\text{-}Bu)_6$ (0.572 g, 0.91 mmol) was dissolved in hexane (20 mL), and the solution was cooled to −78 °C (CO_2/acetone slush bath). t-BuNC was added via syringe. The color of the solution changed immediately from orange to deep purple. After 30 min at −78 °C (or upon warming to −60 °C), the color of the solution became brown. At this point, one of two procedures was followed: (a) investigation of solution and (b) derivatization of the mixture.

(a) The reaction mixture was allowed to warm to room temperature, and the solvent was stripped, leaving a brown oil and some dark solids. The residue was extracted with hexane and the filtrate again stripped to dryness, yielding a brown oil. When the mixture was warmed to +65–70 °C (10^{-4} torr), a small quantity of green crystalline solid, $Mo(O\text{-}t\text{-}Bu)_4$, sublimed, which was identified by infrared spectroscopy. The nonvolatile gummy product showed $\nu(N{\equiv}C)$ at 2125, 2095, and 2040 cm^{-1} but was not further characterized.

(b) Anhydrous methanol (10 mL) was added to the reaction mixture at −60 °C along with KPF_6 (0.2 g). A crude yellow crystalline substance separated from the solution upon stirring. The solids were collected by filtration and recrystallized from acetone/isopropyl alcohol; $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}[PF_6^-]_2$, 0.43 g (0.445 mol). The infrared spectrum showed $\nu(N{\equiv}C)$ at 2145 cm^{-1} (vs) with shoulders at 2220, 2195, and 2050 cm^{-1} and also bands attributable to PF_6^-. Cyclic voltammetry in 0.2 M TBAH in CH_2Cl_2 solvent showed a one-electron oxidation at +1.0 V with peak separation ca. 90–100 mV and i_{pa}/i_{pc} = 1. These properties were in good agreement with data obtained on a sample of $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}[PF_6^-]_2$ prepared from $K_4Mo_2Cl_8$, t-BuNC, and $NaPF_6$.[28,29]

(II) $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (0.6 g, 0.68 mmol) was dissolved in pentane (15 mL), and t-BuNC (0.7 mL) was added. A reaction occurred immediately, and the color of the solution changed from orange to brown. Stripping the solvent gave a yellow-brown powder. A solution of $NaPF_6$ (2 g) in methanol (25 mL) was added. A further addition of t-BuNC (1 mL) was made, and the volume of the solution was reduced to ca. 15 mL, yielding a yellow precipitate. The latter was collected by filtration and characterized as in section I above: $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}[PF_6^-]_2$, 0.45 g (0.42 mmol).

(III) $Mo_2(O\text{-}t\text{-}Bu)_6$ (0.132 g, 0.21 mmol) was dissolved in hexane (15 mL), and the resultant mixture was cooled to 0 °C. An excess of PhNC (2 mL) was added via syringe followed by methanol (5 mL). The reaction was left to stir for 1 h, after which time additional methanol (10 mL) was added. A small quantity of a bright red precipitate was collected by filtration and recrystallized from benzene/methanol. Anal. Calcd for $Mo(CNPh)_6$: C, 70.59; H, 4.20; N, 11.76. Found: C, 70.81; H, 4.16; N, 11.68.

The infrared spectrum showed a very broad intense absorption at ca. 1950 cm^{-1}, with a shoulder just above 2000 cm^{-1}. Cyclic voltammetry in 0.2 M TBAH in THF gave $E_{1/2} = -0.226$ V, E_p = 60 mV, and i_{pa}/i_{pc} = 0.99. These properties compared very favorably to literature data for $Mo(CNPh)_6$ and were checked against an authentic sample of $Mo(CNPh)_6$ prepared from the reaction between $Mo_2(OAc)_4$ and excess PhNC.[30]

Preparation of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$. $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ (0.251 g, 3.4 mmol) was dissolved in pentane (5 mL). The solution was frozen at −196 °C (liquid N_2), and by use of a calibrated vacuum manifold, t-BuNC (6.77 mmol) was added to the reaction vessel. Upon warming, the solution changed from red to purple before reaching room temperature.

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A purple precipitate formed, toluene (2 mL) was added, and the solution was stirred until the precipitate had redissolved. Slow cooling of the solution to −15 °C yielded purple crystals: $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$. Anal. Calcd: C, 53.08; H, 8.48; N, 3.10. Found: 52.95; H, 8.07; N, 2.93.

The reaction between $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ and t-BuNC was also monitored by ^1H NMR spectroscopy by reactions in NMR tubes. Formation of the isocyanide complex is quantitative, and the presence of excess t-BuNC does not cause any further reaction at room temperature.

IR data: 2900 (s), 2064 (w), 2015 (m), 1578 (s), 1521 (s), 1462 (s), 1375 (s), 1281 (w), 1260 (m), 1205 (m), 1075 (m), 1047 (s), 1018 (s), 930 (w), 900 (w), 800 (w), 761 (m), 718 (w), 652 (s), 648 (s), 455 (m), 423 (w), 410 (m) cm^{-1}.

^1H NMR data: δ 0.91 (s, 18 H), 0.95 (s, 18 H), 1.59 (s, 18 H), 2.08 (s, 12 H), 3.62 (s, 4 H), 4.89 (s, 4 H), 5.75 (s, 2 H).

^{13}C NMR data: δ 27.39 ($\mathit{C}H_3(O)CHC(O)\mathit{C}H_3$), 27.63 and 28.84 ($OCH_2C(\mathit{C}H_3)_3$), 31.20 ($CNC(\mathit{C}H_3)_3$), 34.18 and 35.46 ($OCH_2\mathit{C}(CH_3)_3$), 56.42 ($CN\mathit{C}(CH_3)_3$), 82.97 and 93.39 ($O\mathit{C}H_2C(CH_3)_3$), 101.00 ($CH_3C(O)\mathit{C}HC(O)CH_3$), 173.52 ($\mathit{C}NC(CH_3)_3$), 186.68 ($CH_3\mathit{C}(O)CH\mathit{C}(O)CH_3$).

Under analogous conditions, the tungsten alkoxide β-diketonates showed no evidence of reaction with t-BuNC. Similarly, both molybdenum and tungsten compounds failed to react with CO (1 atm) and $HC{\equiv}CH$ and $MeC{\equiv}CMe$.

Preparation of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$. $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ (900 mg, 1.10 mmol) was dissolved in toluene (10 mL), and 2,2′-bipyridine (176 mg, 1.12 mmol) was added as a solid. The solution was stirred at room temperature for 36 h, during which time the color of the solution slowly changed from red to purple. The solution was reduced in volume to ca. 0.5 mL, and hexane (3 mL) was added. The solution was cooled to −15 °C, and a small quantity of a purple powder precipitated. The powder was collected by filtration and the filtrate stripped and redissolved in CH_2Cl_2 (3 mL) and CH_3CN (2 mL). The volume of solution was again reduced to ca. 1 mL and cooled to -15°C, yielding additional microcrystalline powder: $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$. Anal. Calcd: C, 53.68; H 7.45; N, 3.13. Found: C, 53,49; H, 7.28, N, 2.78.

$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$ is extremely soluble in common organic solvents (alkanes, toluene, ether, and isopropyl alcohol) and only slightly less soluble in dichloromethane and acetonitrile, which impedes its crystallization. However, its formation in the above reaction appears quantitative from ^1H NMR studies.

IR data: 2900 (s), 1570 (s), 1515 (s), 1455 (s), 1371 (s), 1298 (w), 1265 (m), 1207 (w), 1150 (m), 1062 (w), 1035 (w), 1012 (m), 1002 (m), 925 (w), 798 (w), 749 (s), 728 (m), 715 (w), 665 (m), 610 (w), 455 (m), 430 (m) cm^{-1}.

^1H NMR data: $OCH_2\text{-}t\text{-}Bu$, δ 0.944 (9 H), 1.04 (9 H), 1.09 (9 H), 1.18 (9 H); $C\mathit{H}_3C(O)CHC(O)C\mathit{H}_3$, δ 1.62 (3 H), 1.91 (3 H), 2.00 (3 H), 2.14 (3 H); $OC\mathit{H}_2\text{-}t\text{-}Bu$, δ 3.59–3.61 (2 H), 3.79–3.91 (2 H), 3.95–4.05 (2 H), 4.59–4.65 (2 H, AB quartets, J_{AB} = 10 Hz); $CH_3C(O)C\mathit{H}C(O)CH_3$, δ 4.96 (1 H), 5.327 (1 H); $C_{10}H_8N_2$, δ 6.71, 7.29, 7.31, 7.82, 8.01, 8.55, 8.75.

The compound showed a molecular ion, M^+, at 898 (based on ^{98}Mo) with the characteristic isotope distribution for dimolybdenum, in the mass spectrum. The parent compound, $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$, shows a molecular ion M^+ at 742 (^{98}Mo).

X-ray Structural Determination. General operating facilities and procedures have been described previously.[1,31] Crystal dta for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ molecule are summarized in Table I.

The structure was solved by a combination of Patterson and direct methods. After an initial refinement of the Mo atom, the remaining non-hydrogen atoms were located. A disorder problem was observed in the case of $OCH_2(CH_3)_3$ and the $CNC(CH_3)_3$ group that are trans to one another. The disorder causes the α-C and O atoms, as well as the γ-C atoms, to be virtually overlapped, while the β-C and N atoms are separated by approximately 1 Å. The disorder is also apparent in the tertiary butyl groups. In the least-squares refinements, the disorder was handled in the following manner. The α-C and O atoms (O(15) and C(21)) were assigned a scattering factor of 50% C and 50% O, while the separated β and δ atoms were assigned an occupancy of 0.50. This value was arrived at by an initial refinement in which the occupancy factors were allowed to vary. The hydrogen atoms on the nondisordered parts of the molecule were located in a difference Fourier and included in the least-squares refinements as fixed atoms. No hydrogen atoms were located on the disordered groups. In the final least-squares refinement, all non-hydrogen atoms were refined with use of anisotropic thermal parameters; the total number of variables was 281, and 2273 reflections having $F_o > 3\sigma(F_o)$ were used. The final difference map was essentially featureless; the largest peak was 0.58 e/Å^3.

The molecule contains a crystallographic center of inversion.[32] Atoms labeled with primes are symmetry related, while the atoms labeled with asterisks are the disordered atoms that did not overlap.

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Registry No. $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$, 88867-19-0; $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(bpy)$, 88867-20-3; $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$, 88393-48-0; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$, 81987-92-0; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; $Mo_2(O\text{-}t\text{-}Bu)_6$, 60764-63-8; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 62521-24-8; $W_2(O\text{-}t\text{-}Bu)_6$, 71391-16-7; $W_2(O\text{-}i\text{-}Pr)_6$, 57125-20-9; $[Mo(CNMe)_7]^{2+}[PF_6^-]_2$, 66632-84-6; $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}[PF_6^-]_2$, 41982-05-2; $[Mo(CNCH_2Ph)_7]^{2+}[PF_6^-]_2$, 88867-18-9; $[W(CN\text{-}t\text{-}Bu)_7]^{2+}[PF_6^-]_2$, 66687-57-8; $Mo(CNPh)_6$, 14154-60-0; $W(CNPh)_6$, 14128-11-1; W, 7440-33-7; Mo, 7439-98-7.

Supplementary Material Available: Complete listings of atomic positional parameters, isotropic and anisotropic thermal parameters, and bond distances and angles, stereoviews, and listings of structure factor amplitudes for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2(CN\text{-}t\text{-}Bu)_2$ (25 pages). Ordering information is given on any current masthead page. The complete structure report, MSC No. 83027, is available from the Indiana University Library in microfiche form only.

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

(32) A reviewer pointed out that the crystallographic data do not rule out a disordered structure in which the RO/NCR groups are both syn to each other; i.e., the molecule does not contain a center of inversion, but the disordered model involving two molecules in the unit cell does. It may also be noted that the two isomers are not distinguishable by ^1H NMR spectroscopy, though only one is present in solution. We are inclined to the view tht molecular packing of a syn-syn structure would lead to a different space group, one lacking apparent molecular symmetry.