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Di-*tert*-butoxybis(arylimido)molybdenum(VI) Compounds, [Mo(O-*t*-Bu)$_2$(NAr)(μ-NAr)]$_2$, Where Ar = Phenyl and *p*-Tolyl

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Mo$_2$(O-*t*-Bu)$_6$ (M≡M) reacts in hydrocarbon solvents with aryl azides, ArN$_3$ ($\geq$4 equiv), where Ar = phenyl and *p*-tolyl, to give [Mo(O-*t*-Bu)$_2$(NAr)$_2$]$_2$ compounds along with N$_2$ and *tert*-butoxy radicals. No intermediates have been detected in this reaction which brings about oxidative cleavage of the molybdenum-to-molybdenum triple bond. A single-crystal structural determination of the *p*-tolylimido compound revealed unsymmetrically bridged imido ligands of the type recently noted by Nugent and Harlow. Each molybdenum atom is five-coordinate, and the central Mo$_2$O$_4$N$_2$N$'_2$ skeleton may be viewed as two trigonal-bipyramidal units fused along a common equatorial–axial edge through the agency of a pair of bridging imido ligands. The other pair of imido ligands occupies axial positions and has short Mo–N distances, 1.74 (1) Å (averaged), and near-linear Mo–N–C angles. The bridging imido ligands form alternately short (equatorial) 1.84 (1) Å and long (axial) 2.30 (2) Å (averaged) bonds to molybdenum, with the latter being trans to the terminal imido ligands. An interesting structural comparison is made with the Mo$_2$(O-*i*-Pr)$_8$ and [Mo(O-*i*-Pr)$_3$NO]$_2$ molecules. Crystal data for [Mo(O-*t*-Bu)$_2$(*N*-*p*-tolyl)$_2$]$_2$ at -170 °C were $a = 10.789$ (2) Å, $b = 25.904$ (6) Å, $c = 13.007$ (3) Å, $\alpha = 73.11$ (1)°, $\beta = 81.34$ (1)°, and $\gamma = 91.25$ (1)°, with space group $P\bar{1}$.

Introduction

The compounds Mo$_2$(OR)$_6$ (M≡M),[1] where R = *t*-Bu, *i*-Pr, CH$_2$CMe$_3$, and SiMe$_3$, have been shown to be coordinatively unsaturated and readily react with Lewis bases such as amines[2] and with unsaturated molecules such as CO,[3] NO,[4] and RC≡CR.[5] They also undergo oxidative-addition reactions with halogens and dialkyl peroxides to give products with metal single and double bonds.[6] As part of a continuing study of the reactivity of Mo$_2$(OR)$_6$ compounds, we have investigated their reactions with aryl azides, ArN$_3$.[7] The latter are known to react with low-valent coordinatively unsaturated mononuclear transition-metal complexes to give imido derivatives by elimination of N$_2$ according to the generalized equation[8]

$$L_nM^{x+} + ArN_3 \rightarrow L_mM^{(x+2)+}(NAr) + N_2 \tag{1}$$

Results and Discussion

Syntheses. Addition of phenyl and *p*-tolyl azides to hydrocarbon solutions (hexane or toluene) of Mo$_2$(O-*t*-Bu)$_6$ leads to the formation of Mo(O-*t*-Bu)$_2$(NAr)$_2$ compounds with the evolution of dinitrogen. On the basis of gas-buret experiments and NMR tube reactions, the stoichiometry of the reaction approximates that of eq 2.

$$\mathrm{Mo_2(O\text{-}\mathit{t}\text{-}Bu)_6 + 4ArN_3 \rightarrow [Mo(O\text{-}\mathit{t}\text{-}Bu)_2(NAr)_2]_2 + 4N_2 + 2\text{-}\mathit{t}\text{-}BuOH} \tag{2}$$

The formation of *t*-BuOH, the only detectable organic product, is believed to arise from hydrogen atom abstraction reactions involving *t*-BuO radicals. When the reaction was carried out in 1,4-hexadiene, benzene and *tert*-butyl alcohol were formed in the expected ratio for the reaction C$_6$H$_8$ + 2-*t*-BuO· → C$_6$H$_6$ + 2-*t*-BuOH. The reaction is, however, quite slow to go to completion, and the presence of excess aryl azide leads to problems in isolating pure Mo(O-*t*-Bu)$_2$(NAr)$_2$ since crystallization from hydrocarbon solvents yields crystals having aryl azides of inclusion. From ^{1}H NMR studies, these crystals have ca. four molecules of azide per three [Mo(O-*t*-Bu)$_2$(NAr)$_2$]$_2$ molecules. The infrared spectrum shows ν(NN) at 2100 cm^{-1}, comparable to that of the free azide, and thus, we are inclined to the view that this is an inclusion complex and not a coordination complex having aryl azide as a ligand. Because of these difficulties, the preferred method for the preparation of the new imido compounds used less than 4 equiv of aryl azides, followed by fractional crystallization to separate any unreacted Mo$_2$(O-*t*-Bu)$_6$ (see Experimental Section).

Physicochemical Properties. The compounds [Mo(O-*t*-Bu)$_2$(NAr)$_2$]$_2$, where Ar = phenyl and *p*-tolyl, are air-sensitive yellow-orange crystalline solids. They are thermally unstable above 80 °C but may be stored indefinitely in sealed ampules in vacuo at room temperature. In the mass spectrometer, they show only mononuclear ions, with the ions of highest *m*/*e* corresponding to [Mo(O-*t*-Bu)$_2$(NAr)$_2$]$^+$ and [Mo(O-*t*-Bu)$_3$NAr]$^+$. A cryoscopic molecular weight determination indicated that the dimeric structure found in the solid state (vide infra) was not maintained in solution: the observed molecular weight corresponded to the monomeric species Mo(O-*t*-Bu)$_2$(NAr)$_2$. ^{1}H NMR studies at 220 MHz in toluene-*d*$_8$ solution over the temperature range -50 to $+16$ °C showed the presence of only one type of aryl group.

Solid-State Structure. In the space group $P\bar{1}$, there are three [Mo(O-*t*-Bu)$_2$(NAr)(μ-NAr)]$_2$ molecules in the unit cell, one of which, being located at the origin, has a crystallogrphically imposed center of inversion. The other molecules, which are related by the center of symmetry, do not, but they do have a virtual center of symmetry.

Fractional coordinates are given in Table I; bond distances and bond angles for the two crystallographically independent molecules are given in Tables II and III, respectively. Note that in molecule A, which has a virtual but not crystallographically imposed center of inversion, atoms indicated by a prime are related to unprimed atoms by the virtual center of symmetry in the molecule. In molecule B, which has a crystallographically imposed center of symmetry, atoms so related are indicated by double and triple primes, e.g., Mo(1)$''$ and Mo(1)$'''$. ORTEP views of molecules A and B are shown in Figures 1 and 2, respectively, from which it can be seen that they differ little in conformation, except for the specific orientations of the phenyl groups of the bridging imido ligands. Figure 3 shows molecule B viewed down the Mo–Mo axis and reveals the planar central Mo$_2$N$_2$N$'_2$ skeleton of the molecule.

Each molybdenum atom is in a five-coordinate environment which may be viewed as that of a distorted trigonal bipyramid.

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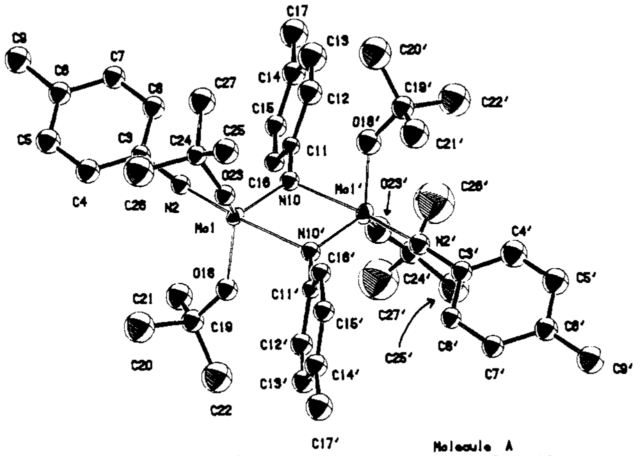


Figure 1. ORTEP view of the noncentrosymmetric [Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$ molecule (molecule A) showing the atom numbering scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

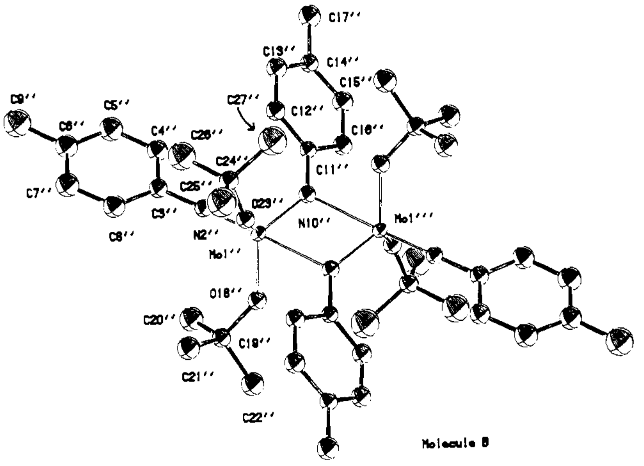
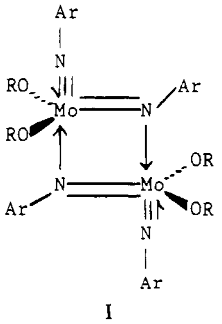


Figure 2. ORTEP view of the centrosymmetric [Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$ molecule (molecule B) showing the atom numbering scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

The terminal, essentially linear, imido group, M≡N→Ar, occupies an axial site trans to the long and apparently weak dative bond formed from an amido group that occupies an equatorial site on its neighboring molybdenum atom. The latter bond, based on its considerations of bond length and Mo–N–C angle, may be viewed as a Mo═N—R moiety. This leads to the schematic valence bond description of the molecule shown in I.



I

The presence of an unsymmetrical bridging group was first seen in the structural characterization of [MoMe$_2$(N-*t*-Bu)$_2$]$_2$[9] and then again in the tungsten analogue [W$_2$Me$_2$(N-*t*-Bu)$_2$]$_2$.[10] This contrasts with the symmetrical bridges seen in [(Me$_2$N)$_2$M(μ-N-*t*-Bu)]$_2$, where M = Ti[10] and Zr.[11] The observation of symmetrical vs. unsymmetrical imido bridges has been correlated with "aromatic" and "antiaromatic" electronic structures, respectively, on the basis of molecular orbital calculations. While we have no particular quarrel with this view, we would like to point out that an alternate explanation can be offered based on more classical (straightforward) concepts of chemical bonding. A comparison with the structures of Mo$_2$(O-*i*-Pr)$_8$[12] and Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$[4] is instructive.

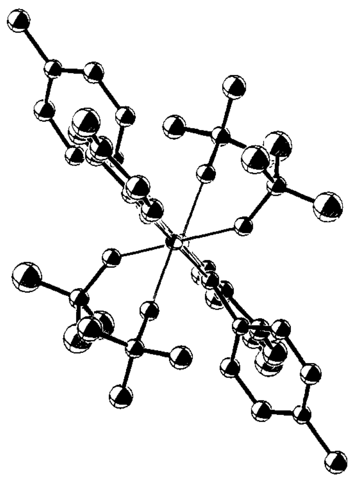


Figure 3. ORTEP view of the centrosymmetric [Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$ molecule (molecule B) viewed down the Mo–Mo axis.

Comparison with Mo$_2$(O-*i*-Pr)$_8$ and Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$. Figure 4 shows the central skeletons of the Mo$_2$(O-*i*-Pr)$_8$, Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$, and Mo$_2$(O-*t*-Bu)$_4$(NAr)$_4$ molecules. In each molecule, the molybdenum atoms are in distorted trigonal-bipyramidal environments with respect to the ligands to which they are directly bonded. In this geometry, the d_{xz} and d_{yz} orbitals are not involved in metal–liand σ bonding and thus lie lowest in energy in a simple crystal field energy diagram. In Mo$_2$(O-*i*-Pr)$_8$, each molybdenum is a d^2 ion and the resulting Mo-to-Mo double bond, $\sigma^2\pi^2$ may be seen to arise from d_{xz}–d_{xz} and d_{yz}–d_{yz} interactions. In Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$, which may for the sake of counting electrons be viewed as a Mo^{2+}-containing species (a linear M–N–O moiety being viewed as M$^-$←(NO$^+$)), there are four electrons that occupy the (d_{xz},d_{yz}) orbitals. There should, therefore, be no net Mo-to-Mo bonding and this readily accounts for the 0.8-Å increase in Mo-to-Mo distance in going from Mo$_2$(O-*i*-Pr)$_8$ to Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$. The (d_{xz},d_{yz})^4 electrons have appropriate symmetry to back-bond to the nitrosyl π^* orbitals. The short Mo–N bond distance, the long N–O bond distance, and the low value of ν(NO) (1620 cm^{-1}) all point to significant Mo-to-NO π^* back-bonding. In [Mo(O-*t*-Bu)$_2$(N-*t*-Bu)$_2$]$_2$, which contains Mo^{6+} ions, the (d_{xz},d_{yz}) orbitals, which are not used in σ bonding, may receive π electrons from the terminally bonded near-linear imido ligand to comply with the resonance form M≡N—R. There are also metal orbitals in the *xy* plane, either (p_x,p_y) or (d_{xy},$d_{x^2-y^2}$), whichever set is not used to form σ bonds, that may be used in π bonding with the ligands (ligand-to-metal). In [Mo(O-*t*-Bu)$_2$(NAr)$_2$]$_2$, one of these orbitals is used exclusively to form a π bond with the bent imido ligand in the equatorial plane, while the other is available for equal competition from the two alkoxy ligands. In this way,

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Table I. Fractional Coordinates for the $[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$ Molecule[a,b]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	5595 (1)	2922	4208 (1)	16
Mo(1)′	7967 (1)	3582	2433 (1)	20
Mo(1)″	1114 (1)	284	−1026 (1)	14
N(2)	4239 (7)	3014 (3)	5034 (6)	20 (1)
C(3)	3219 (8)	3143 (4)	5685 (7)	20 (2)
C(4)	2291 (10)	2745 (4)	6291 (8)	31 (2)
C(5)	1275 (10)	2877 (4)	6940 (9)	32 (2)
C(6)	1145 (9)	3399 (4)	7001 (8)	27 (2)
C(7)	2092 (9)	3798 (4)	6370 (8)	26 (2)
C(8)	3116 (9)	3671 (4)	5723 (8)	26 (2)
C(9)	60 (10)	3551 (5)	7694 (9)	36 (2)
N(10)	6081 (7)	3634 (3)	3462 (6)	20 (1)
C(11)	5493 (8)	4124 (3)	3387 (7)	16 (2)
C(12)	6046 (10)	4520 (4)	3741 (8)	32 (2)
C(13)	5474 (11)	5010 (5)	3647 (10)	43 (3)
C(14)	4333 (9)	5090 (4)	3266 (8)	28 (2)
C(15)	3830 (9)	4693 (4)	2916 (8)	24 (2)
C(16)	4391 (8)	4210 (4)	2971 (7)	20 (2)
C(17)	3693 (11)	5613 (5)	3224 (10)	41 (2)
O(18)	4966 (6)	2523 (3)	3357 (5)	25 (1)
C(19)	3810 (9)	2319 (4)	3208 (8)	26 (2)
C(20)	3411 (12)	1801 (5)	4245 (11)	49 (3)
C(21)	2815 (10)	2703 (5)	3155 (9)	37 (2)
C(22)	4033 (12)	2114 (5)	2203 (11)	49 (3)
O(23)	6593 (6)	2596 (2)	5274 (5)	22 (1)
C(24)	6636 (9)	2547 (4)	6386 (7)	21 (2)
C(25)	8000 (10)	2418 (4)	6531 (9)	34 (2)
C(26)	5683 (12)	2101 (5)	7102 (11)	49 (3)
C(27)	6358 (10)	3097 (5)	6566 (9)	37 (2)
N(2)′	9351 (7)	3492 (3)	1626 (6)	22 (1)
C(3)′	10407 (9)	3397 (4)	959 (8)	24 (2)
C(4)′	11269 (11)	3821 (5)	339 (9)	38 (2)
C(5)′	12329 (10)	3722 (5)	−319 (9)	36 (2)
C(6)′	12521 (9)	3199 (4)	−403 (8)	28 (2)
C(7)′	11632 (9)	2778 (4)	237 (8)	26 (2)
C(8)′	10586 (9)	2877 (4)	910 (8)	23 (2)
C(9)′	13643 (11)	3090 (5)	−1121 (9)	40 (2)
N(10)′	7450 (7)	2866 (3)	3127 (6)	19 (1)
C(11)′	8022 (8)	2386 (3)	3132 (7)	16 (2)
C(12)′	7587 (9)	2041 (4)	2584 (8)	26 (2)
C(13)′	8203 (9)	1574 (4)	2565 (8)	28 (2)
C(14)′	9250 (9)	1454 (4)	3049 (8)	27 (2)
C(15)′	9657 (9)	1787 (4)	3613 (8)	23 (2)
C(16)′	9059 (8)	2247 (4)	3666 (7)	20 (2)
C(17)′	9936 (11)	942 (5)	3006 (9)	38 (2)
O(18)′	8571 (6)	3932 (3)	3365 (6)	33 (1)
C(19)′	9712 (9)	4158 (4)	3527 (8)	27 (2)
C(20)′	9478 (13)	4311 (5)	4577 (11)	53 (3)
C(21)′	10725 (11)	3743 (5)	3618 (10)	43 (3)
C(22)′	10116 (13)	4664 (6)	2543 (11)	54 (3)
O(23)′	7035 (7)	3955 (3)	1369 (6)	38 (2)
C(24)′	6955 (9)	4202 (4)	283 (8)	27 (2)
C(25)′	7996 (12)	4064 (5)	−481 (10)	49 (3)
C(26)′	7027 (18)	4804 (8)	201 (15)	89 (5)
C(27)′	5702 (17)	4084 (7)	76 (15)	86 (5)
N(2)″	2428 (7)	205 (3)	−1927 (6)	18 (1)
C(3)″	3520 (8)	177 (4)	−2627 (7)	22 (2)
C(4)″	3963 (9)	−317 (4)	−2633 (8)	26 (2)
C(5)″	5106 (10)	−339 (4)	−3323 (9)	34 (2)
C(6)″	5784 (10)	132 (4)	−3986 (8)	31 (2)
C(7)″	5327 (10)	636 (4)	−3973 (9)	34 (2)
C(8)″	4179 (9)	652 (4)	−3291 (8)	29 (2)
C(9)″	7016 (12)	113 (5)	5300 (10)	47 (3)
N(10)″	9345 (7)	415 (3)	157 (6)	18 (1)
C(11)″	−1204 (8)	923 (3)	13 (7)	17 (2)
C(12)″	−2485 (9)	957 (4)	23 (8)	23 (2)
C(13)″	−2992 (9)	1461 (4)	−90 (8)	25 (2)
C(14)″	−2250 (8)	1925 (4)	−229 (7)	19 (2)
C(15)″	−958 (9)	1890 (4)	−283 (8)	26 (2)
C(16)″	−422 (9)	1392 (4)	−158 (8)	22 (2)
C(17)″	−2815 (10)	2471 (4)	−344 (8)	30 (2)
O(18)″	−42 (6)	565 (2)	−1982 (5)	21 (1)
C(19)″	9971 (8)	886 (4)	6918 (7)	21 (2)
C(20)″	622 (10)	603 (4)	−3861 (9)	35 (2)
C(21)″	662 (10)	1429 (4)	−3225 (8)	31 (2)
C(22)″	−1411 (10)	951 (4)	−3201 (9)	32 (2)
O(23)″	1918 (5)	719 (2)	−343 (5)	20 (1)
C(24)″	3000 (9)	761 (4)	133 (8)	22 (2)
C(25)″	3049 (12)	1294 (5)	349 (11)	51 (3)
C(26)″	4183 (12)	681 (5)	−598 (10)	46 (3)
C(27)″	2804 (12)	290 (5)	1245 (10)	50 (3)

[a] The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent. [b] Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

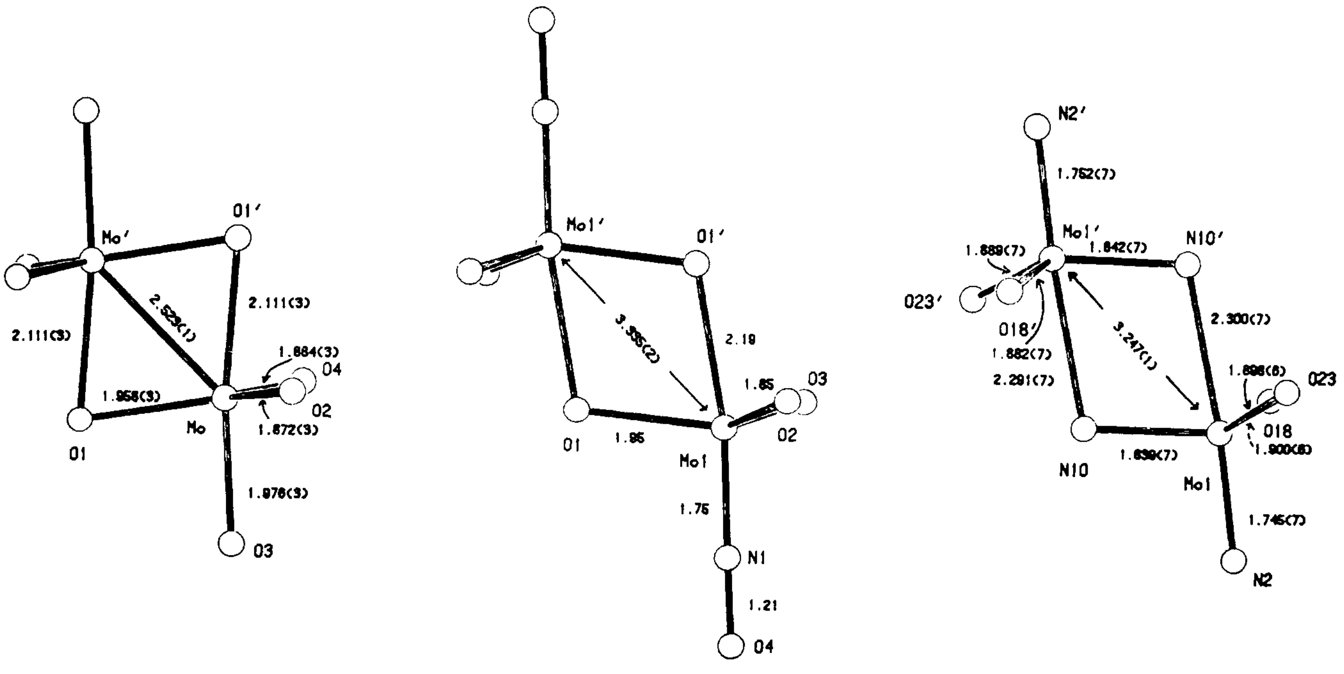

Figure 4. Comparison of the central skeletons of the $Mo_2(O\text{-}i\text{-}Pr)_8$ (left), $[Mo(NO)(O\text{-}t\text{-}Pr)_3]_2$ (center), and $[Mo(NC_7H_8)_2(O\text{-}t\text{-}Bu)_2]_2$ (right) molecules. The terminal imido ligands in $[Mo(NC_7H_8)_2(O\text{-}t\text{-}Bu)_2]_2$ have Mo–N–C angles = 175° (average); the Mo–N–O angle in $[Mo(NO)(O\text{-}i\text{-}Pr)_3]_2$ is 178°.

Table II. Bond Distances (Å) for the $[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$ Molecule

Mo(1)–Mo(1)'	3.247 (1)	C(19)–C(22)	1.536 (15)
Mo(1)–O(18)	1.900 (6)	C(24)–C(25)	1.543 (14)
Mo(1)–O(23)	1.898 (6)	C(24)–C(26)	1.514 (16)
Mo(1)–N(2)	1.745 (7)	C(24)–C(27)	1.539 (14)
Mo(1)–N(10)	1.839 (7)	C(3)'–C(4)'	1.392 (14)
Mo(1)–N(10)'	2.300 (7)	C(3)'–C(8)'	1.383 (13)
Mo(1)'–O(18)'	1.889 (7)	C(4)'–C(5)'	1.396 (15)
Mo(1)'–O(23)'	1.882 (7)	C(5)'–C(6)'	1.409 (14)
Mo(1)'–N(10)	2.291 (7)	C(6)'–C(7)'	1.409 (14)
Mo(1)'–N(2)'	1.752 (7)	C(6)'–C(9)'	1.499 (15)
Mo(1)'–N(10)'	1.842 (7)	C(7)'–C(8)'	1.396 (13)
Mo(1)''–Mo(1)'''	3.270 (2)	C(11)'–C(12)'	1.406 (12)
Mo(1)''–O(18)''	1.901 (6)	C(11)'–C(16)'	1.403 (12)
Mo(1)''–O(23)''	1.893 (6)	C(12)'–C(13)'	1.398 (13)
Mo(1)''–N(2)''	1.754 (7)	C(13)'–C(14)'	1.372 (13)
Mo(1)''–N(10)''	1.844 (7)	C(14)'–C(15)'	1.386 (13)
Mo(1)''–N(10)'''	2.360 (7)	C(14)'–C(17)'	1.544 (14)
O(18)–C(19)	1.406 (11)	C(15)'–C(16)'	1.382 (13)
O(23)–C(24)	1.422 (11)	C(19)'–C(20)'	1.517 (16)
O(18)'–C(19)'	1.422 (11)	C(19)'–C(21)'	1.544 (15)
O(23)'–C(24)'	1.388 (12)	C(19)'–C(22)'	1.542 (16)
O(18)''–C(19)''	1.428 (11)	C(24)'–C(25)'	1.505 (15)
O(23)''–C(24)''	1.418 (11)	C(24)'–C(26)'	1.531 (21)
N(2)–C(3)	1.392 (11)	C(24)'–C(27)'	1.460 (19)
N(10)–C(11)	1.416 (11)	C(3)''–C(4)''	1.377 (13)
N(2)'–C(3)'	1.397 (12)	C(3)''–C(8)''	1.388 (13)
N(10)'–C(11)'	1.400 (11)	C(4)''–C(5)''	1.424 (14)
N(2)''–C(3)''	1.394 (11)	C(5)''–C(6)''	1.387 (14)
N(10)''–C(11)''	1.430 (11)	C(6)''–C(7)''	1.410 (14)
C(3)–C(4)	1.389 (13)	C(6)''–C(9)''	1.513 (16)
C(3)–C(8)	1.389 (13)	C(7)''–C(8)''	1.420 (14)
C(4)–C(5)	1.390 (14)	C(11)''–C(12)''	1.385 (12)
C(5)–C(6)	1.388 (14)	C(11)''–C(16)''	1.408 (12)
C(6)–C(7)	1.412 (14)	C(12)''–C(13)''	1.403 (13)
C(6)–C(9)	1.498 (14)	C(13)''–C(14)''	1.379 (13)
C(7)–C(8)	1.392 (13)	C(14)''–C(15)''	1.391 (13)
C(11)–C(12)	1.397 (13)	C(14)''–C(17)''	1.530 (13)
C(11)–C(16)	1.374 (12)	C(15)''–C(16)''	1.402 (13)
C(12)–C(13)	1.405 (15)	C(19)''–C(20)''	1.516 (14)
C(13)–C(14)	1.392 (15)	C(19)''–C(21)''	1.527 (13)
C(14)–C(15)	1.371 (13)	C(19)''–C(22)''	1.529 (13)
C(14)–C(17)	1.526 (15)	C(24)''–C(25)''	1.488 (15)
C(15)–C(16)	1.390 (13)	C(24)''–C(26)''	1.527 (15)
C(19)–C(20)	1.597 (16)	C(24)''–C(27)	1.580 (15)
C(19)–C(21)	1.475 (14)		

Table III. Pertinent Angles (Deg) for the $[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$ Molecule

O(18)–Mo(1)–O(23)	120.8 (3)
O(18)–Mo(1)–N(2)	102.9 (3)
O(18)–Mo(1)–N(10)	114.3 (3)
O(18)–Mo(1)–N(10)'	81.2 (3)
O(23)–Mo(1)–N(2)	100.7 (3)
O(23)–Mo(1)–N(10)	114.3 (3)
O(23)–Mo(1)–N(10)'	78.8 (3)
N(2)–Mo(1)–N(10)	99.1 (3)
N(2)–Mo(1)–N(10)'	175.3 (3)
N(10)–Mo(1)–N(10)'	77.0 (3)
O(18)'–Mo(1)'–O(23)'	120.3 (3)
O(18)'–Mo(1)'–N(10)	81.8 (3)
O(18)'–Mo(1)'–N(2)'	102.7 (3)
O(18)'–Mo(1)'–N(10)'	112.7 (3)
O(23)'–Mo(1)'–N(10)	77.8 (3)
O(23)'–Mo(1)'–N(2)'	101.6 (3)
O(23)'–Mo(1)'–N(10)'	116.2 (3)
N(10)–Mo(1)'–N(2)'	175.0 (3)
N(10)–Mo(1)'–N(10)'	77.1 (3)
N(2)'–Mo(1)'–N(10)'	98.8 (3)
O(18)''–Mo(1)''–O(23)''	121.8 (3)
O(18)''–Mo(1)''–N(2)''	102.2 (3)
O(18)''–Mo(1)''–N(10)''	113.1 (3)
O(18)''–Mo(1)''–N(10)'''	76.8 (2)
O(23)''–Mo(1)''–N(2)''	98.2 (3)
O(23)''–Mo(1)''–N(10)'''	81.4 (2)
O(23)''–Mo(1)''–N(10)''	114.3 (3)
N(2)''–Mo(1)''–N(10)''	103.0 (3)
N(2)''–Mo(1)''–N(10)'''	178.4 (3)
N(10)''–Mo(1)''–N(10)'''	78.6 (3)
Mo(1)–O(18)–C(19)	139.3 (6)
Mo(1)–O(23)–C(24)	138.0 (5)
Mo(1)'–O(18)'–C(19)'	140.2 (6)
Mo(1)'–O(23)'–C(24)'	149.6 (7)
Mo(1)''–O(18)''–C(19)''	139.2 (5)
Mo(1)''–O(23)''–C(24)''	142.2 (5)
Mo(1)–N(2)–C(3)	173.7 (7)
Mo(1)–N(10)–Mo(1)'	103.1 (3)
Mo(1)–N(10)–C(11)	133.4 (6)
Mo(1)'–N(10)–C(11)	123.3 (6)
Mo(1)'–N(2)'–C(3)'	176.2 (7)
Mo(1)–N(10)'–Mo(1)'	102.7 (3)
Mo(1)–N(10)'–C(11)'	124.9 (6)
Mo(1)'–N(10)'–C(11)'	132.2 (6)
Mo(1)''–N(2)''–C(3)''	175.5 (6)
Mo(1)''–N(10)''–Mo(1)'''	101.4 (3)
Mo(1)'''–N(10)''–C(11)''	135.0 (6)
Mo(1)''–N(10)''–C(11)''	123.0 (5)

each molybdenum atom in $[Mo(O\text{-}t\text{-}Bu)_2(NAr)_2]_2$ achieves an 18-electron valence shell.

Thus, although it is not obvious why $Mo_2(O\text{-}i\text{-}Pr)_8$, $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$, and $Mo_2(O\text{-}t\text{-}Bu)_4(NAr)_4$ should adopt structures based on fused trigonal bipyramids sharing common equatorial–axial edges to the exclusion of all other possible structures, it is clear that simple bonding descriptions can rationalize changes in M–M and M–L bonding within the group. Moreover, since in a trigonal-bipyramidal environment there are two sets of bonds not related by symmetry, namely, axial and equatorial bonds, we would expect unsymmetrical bridges to be the norm and not the exception for molecules having structures based on fused trigonal bipyramids sharing common equatorial–axial edges. On the other hand, two fused tetrahedra or octahedra should have symmetrical bridges unless the symmetry of the molecule is lowered by the presence of more than one type of ligand. Thus, in $Mo_2(O\text{-}i\text{-}Pr)_8$, the unsymmetrical bridge provides a measure of the "natural" difference in axial–equatorial bonding, whereas in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$, this difference is further exaggerated. The situation in $[Mo(O\text{-}t\text{-}Bu)_2(NAr)_2]_2$ is rather similar to that in $W(O\text{-}t\text{-}Bu)_3(NO)(py)$, which has axial NO and py ligands with W–N distances of 1.732 (8) and 2.323 (7) Å, respectively.

Experimental Section

General Procedures. All preparations and operations were carried out under a dry and oxygen-free nitrogen atmosphere with standard Schlenk techniques or a Vacuum Atmospheres Co. Dri-Lab assembly. ^1H NMR spectra were recorded on a Varian HR 220 spectrometer. Infrared spectra were obtained from Nujol mulls between CsI plates with a Perkin-Elmer 273 spectrophotometer. Mass spectra were obtained by the method of direct insertion with use of an AEI MS902 spectrometer, courtesy of Peter Cook, Queen Mary College, London.

Materials. $Mo_2(O\text{-}t\text{-}Bu)_6$ was prepared in the previously described manner.[1] Aryl azides were prepared by reacting the diazonium salts $ArN_2^+PF_6^-$ with sodium azide at 0 °C, followed by extraction with ether. The ethereal solution was dried over $MgSO_4$ and then stripped to yield an oil, which was distilled at 55–60 °C (10 mmHg).[14] The viscous liquid was dissolved in pentane to give a ca. 2 M solution, which was stored at 0 °C prior to use. $Ph^{15}N^{14}N_2$ was prepared similarly from $Ph^{15}N^{14}N^+PF_6^-$ but was used without vacuum distillation.

Preparation of $[Mo(O\text{-}t\text{-}Bu)_2(NPh)_2]_2$. $Mo_2(O\text{-}t\text{-}Bu)_6$ (0.72 g, 1.14 mmol) was dissolved in hexane (30 mL) and was cooled to −78 °C. A pentane solution of phenyl azide (1.1 mL, 2.3 M) was added by syringe. The solution was allowed to warm to room temperature over a period of 0.5 h, and stirring was continued for 24 h. The solvent was reduced in volume to ca. 10 mL, and the solution was cooled to −15 °C for 24 h. Yellow crystals of $[Mo(O\text{-}t\text{-}Bu)_2(NPh)_2]_2$, ca. 300 mg, 20% yield based on Mo, were collected by filtration and dried in vacuo.

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^{1}H NMR (obtained from benzene-d_6 solution at +16 °C relative to Me_4Si) δ 1.43 (s, 18 H), 7.20 (m, 10 H).

IR 2917 s, 1575 m, 1465 s, 1368 s, 1310 s, 1260 m, 1232 w, 1170 s, 1027 m, 945 s, 785 m, 760 s, 688 s, 670 w, 570 m, 520 w, 465 m cm^{-1}.

In the mass spectrum, the ion of highest mass corresponded to $Mo(O\text{-}t\text{-}Bu)_2(NC_6H_5)_2^+$ at m/e 426 based on ^{98}Mo.

A reaction involving $C_6H_5{}^{15}N^{14}N_2$ gave $Mo(O\text{-}t\text{-}Bu)_2({}^{15}NC_6H_5)_2^+$ at m/e 428 based on ^{98}Mo. The IR spectrum showed a shift of the band at 1310 cm^{-1} to 1280 cm^{-1}, assignable to ν(Mo–^{14}N) and ν(Mo–^{15}N), respectively.

[Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$, where C_7H_7 = *p*-tolyl, was prepared similarly as a yellow crystalline solid, appreciably soluble in hexane, benzene, and toluene. In the mass spectrometer, the ion of highest mass corresponded to $Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2^+$ at m/e 454. ^{1}H NMR (obtained from toluene-d_8 at +16 °C relative to Me_4Si) δ 1.47 (s, 18 H), 2.06 (s, 6 H), 6.80 (d, 4 H); 7.31 (d, 4 H); IR 2900 s, 1490 m, 1460 s, 1370 s, 1292 w, 1258 s, 1230 w, 1155 s, 1111 w, 1098 w, 1004 w, 950 s, 915 w, 895 s, 808 s, 780 m, 712 w, 524 w cm^{-1}.

X-ray Structural Determination of [Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$. General operating procedures and computational techniques have been described previously.[15]

A crystal of dimensions 0.24 × 0.26 × 0.28 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid nitrogen boil-off cold stream of the diffractometer. The cell dimensions, determined from 44 reflections by using Mo Kα radiation, λ = 0.71069 Å, at –170 °C were a = 10.789 (2) Å, b = 25.904 (6) Å, c = 13.007 (3) Å, α = 73.11 (1)°, β = 81.34 (1)°, γ = 91.25 (1)°; V = 3430.3 (1) Å^3, Z = 3, d_{calcd} = 1.314 g cm^{-3}, and space group $P\bar{1}$.

A total of 9734 reflections were collected, including redundancies, and were reduced to 8946 unique reflections by using standard moving-crystal, moving-detector techniques, with the following values: scan speed = 6.0°/min, scan width = 1.7 + dispersion, single background at extreme of scan = 3 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were 6° $< 2\theta <$ 45°. The number of reflections with $F > 2.33\sigma(R)$ was 7701. Since the crystal was nearly equidimensional, no absorption correction was attempted (μ(Mo Kα) = 5.76 cm^{-1}).

The structure was solved by a combination of direct methods and Fourier techniques. All nonhydrogen atoms were located and refined with anisotropic thermal parameters. The refinement was carried out in a cyclic manner due to the large number of parameters. Becuase of the size of the problem, no attempt was made to locate hydrogen atoms. The final residuals are R_F = 0.076 and R_{wF} = 0.086. The goodness of fit for the last cycle was 2.127 and the maximum σ/Δ was 0.05.

The rather large residuals and goodness of fit are partically due to the large thermal motion observed in several of the *tert*-butoxy ligands. A careful examination of a final difference Fourier synthesis did not reveal any apparent disorder and was essentially featureless.

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Registry No. [Mo(O-*t*-Bu)$_2$(NPh)$_2$]$_2$, 78134-34-6; [Mo(O-*t*-Bu)$_2$(NC$_7$H$_7$)$_2$]$_2$, 78134-33-5; Mo$_2$(O-*t*-Bu)$_6$, 60764-63-8; phenyl azide, 622-37-7; *p*-tolyl azide, 2101-86-2.

Supplementary Material Available: Listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal, Molecular, and Electronic Structure of 1,1,5,5-Tetramethylbicyclo[3.3.0]-1,5-diphospha-3,7-dithia-2,4,6,8-tetrazene: A Bicyclic PSN System with a Sulfur–Sulfur Bond

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1,1-Dimethyl-1-phospha-3,5-dithia-2,4,6-triazene, $Me_2PS_2N_3$, prepared by the reaction of Me_2PPMe_2 with S_4N_4, undergoes a ring expansion at ambient temperature to give 1,1,5,5-tetramethylbicyclo[3.3.0]-1,5-diphospha-3,7-dithia-2,4,6,8-tetrazene, $Me_2P(NSN)_2PMe_2$, whose crystal and molecular structure has been determined by single-crystal X-ray diffraction. The crystals of $Me_2P(NSN)_2PMe_2$ are orthorhombic, space group $Pnma$, with a = 11.081 (5) Å, b = 8.216 (5) Å, c = 11.837 (6) Å, V = 1077.7 Å^3, Z = 4, and D_c = 1.49 g cm^{-3}. The structure was solved by direct methods and refined anisotropically to a final conventional R factor of 0.033 for 692 reflections with $I > 3\sigma(I)$. The structure consists of a folded eight-membered ring (butterfly) with a cross-ring S–S contact of 2.551 (2) Å. The angle between the two intersecting planes of the eight-membered ring is 114.9 (2)°. The mean endocyclic P–N and S–N bond lengths are 1.636 (3) and 1.595 (3) Å, respectively. The ^{1}H and ^{13}C NMR spectra of $Me_2P(NSN)_2PMe_2$ are consistent with nonequivalent pairs of methyl groups, suggesting that the folded structure is maintained in solution. Simple Hückel calculations have been carried out for eight-membered ring systems of the type E(NSN)$_2$E that lead to the prediction that a planar structure will be favored over a structure folded about a transannular S–S bond for the more electronegative substituents, E.

Introduction

We have recently extended our studies of the reactions of phosphines with S_4N_4[1] to the diphosphines R_2PPR_2 (R = Ph,[2] Me[3]). The products of these reactions, $R_2PS_2N_3$, are six-membered 8-π-electron ring systems whose intense color (R = Ph, λ_{max} = 550 nm; R = Me, λ_{max} = 543 nm) is attributed to a low-energy $\pi^* \rightarrow \pi^*$ electronic transition.[2,3] The dimethyl derivative, a purple oil, decomposes at room temperature to give a yellow crystalline solid, identified in this study as an eight-membered bicyclic ring. We discuss here the formation and spectroscopic and X-ray structural characterization of this

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