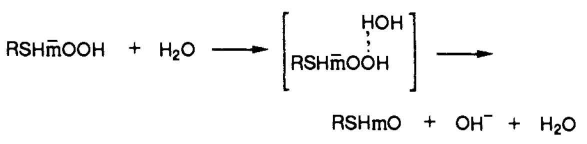
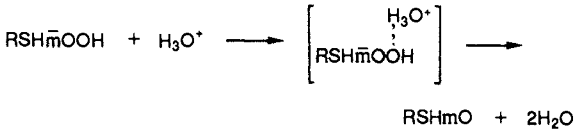
The present results put this idea on very solid ground, demonstrating that alcohols or water can serve as general acids/bases for catalysis of O–O bond cleavage. Therefore, we have provided viable mechanisms for cytochrome P-450 catalysis.

$$\mathrm{RS{-}H\bar{m}} + \mathrm{O_2} \rightleftharpoons \mathrm{RSH\bar{m}O_2} \xrightarrow[\text{[H}^+\text{]}]{e^-} \mathrm{RS{-}H\bar{m}OOH} \quad (38)$$



$$\mathrm{RSH\bar{m}OOH} + \mathrm{H_2O} \longrightarrow \left[\begin{matrix}\mathrm{HOH}\\ \vdots \\ \mathrm{RSH\bar{m}OOH}\end{matrix}\right] \longrightarrow \mathrm{RSHmO} + \mathrm{OH^-} + \mathrm{H_2O} \quad (39)$$



$$\mathrm{RSH\bar{m}OOH} + \mathrm{H_3O^+} \longrightarrow \left[\begin{matrix}\mathrm{H_3O^+}\\ \vdots \\ \mathrm{RSH\bar{m}OOH}\end{matrix}\right] \longrightarrow \mathrm{RSHmO} + 2\mathrm{H_2O} \quad (40)$$

An attractive alternative process would use the thiolate as a reductant.

$$\mathrm{RSH\bar{m}O_2} \rightleftharpoons \mathrm{RSH\bar{m}\overset{+}{O}OH} \xrightarrow{\mathrm{H_3O^+}} \mathrm{RS^{\bullet}Hm^+{=}O} + 2\mathrm{H_2O} \quad (41)$$

Conclusions. The effect of concentration and acidities of protic solvents on the rate of reactions of hydroperoxides with iron(III) porphyrins and the solvent isotope effects on these rates have been investigated and shown to be almost identical with those effects on the reaction of hydroperoxides with R_2S as well as with reactions of peracids with hemins. These and previously reported data allow two conclusions to be drawn. First, the reactions of hydrogen peroxide, hydroperoxides, and peracids with iron(III) porphyrins in protic solvents all proceed by heterolytic cleavage whether buffer catalyzed or solvent catalyzed. In the absence of efficient solvent buffer catalysis, the complex HmOOR is likely to cleave in a homolytic fashion.[14b,37] Second, alcohol and water catalyses of this reaction have been demonstrated, providing a rational mechanism for water-catalyzed breaking of the O–O bond in the cytochrome P-450 catalytic cycle.

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Molybdenum-Mediated Imido Group Transfer: Stoichiometric and Catalytic Reactions and Structures

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Abstract: The isoelectronic relationship $O^{2-} = RN^{2-}$ implies imido group transfer chemistry related to oxygen atom transfer reactivity, which is extensive for certain elements. This matter has been subjected to its first systematic examination, using the *N*,*N*-diethyldithiocarbamate (Et_2dtc) complexes of molybdenum and the *N*-tosylimido (NTs) group. The imido group transfer reactions to Mo, $MoO(Et_2dtc)_2$ + XNR and $Mo(CO)_2(Et_2dtc)_2$ + XNR, afford $MoO(NTs)(Et_2dtc)_2$ and $Mo(NTs)_2(Et_2dtc)_2$, respectively, in high yield with the imido group transfer reagents XNR = C_5H_5NNTs, PhMeSNTs, Ph_3SbNTs, PhINTs, and TsN_3. $MoO(NTs)(Et_2dtc)_2\cdot{}^1/_2PhMe$ crystallizes in triclinic space group $P\bar{1}$ with a = 9.212 (2) Å, b = 12.080 (4) Å, c = 14.310 (4) Å, α = 115.02 (2)°, β = 95.51 (2)°, γ = 100.34 (2)°, and Z = 2; the structure was refined to R = 4.8%. $Mo(NTs)_2(Et_2dtc)_2$ was obtained in monoclinic space group $P2_1/n$ with a = 10.632 (2) Å, b = 16.307 (3) Å, c = 19.023 (5) Å, β = 101.29 (2)°, and Z = 4; the structure was refined to R = 4.0%. The two compounds have a distorted octahedral structure with the multiply bonded groups O and NTs in cis positions. Comparison of these structures with that of $MoO_2(Et_2dtc)_2$ reveals that the NTs group is a nearly isostructural replacement for oxo. The imido group transfer reactions from Mo, $MoO(NTs)(Et_2dtc)_2 + R_3P$, proceed but with the more basic phosphines favoring imido (R_3PNTs) rather than oxo (R_3PO) transfer. Imido transfers to and from Mo involve the purple intermediates $Mo_2O_2(NTs)(Et_2dtc)_4$ and $MoO(NTs)_2(Et_2dtc)_4$, respectively, which are in presumed equilibrium with Mo(IV,VI) complexes. The complex $Mo(NTs)(Et_2dtc)_2$, resulting from imido group transfer, was too unstable to be isolated. Group transfers to and from Mo were coupled to form the catalytic reactions $XNTs + R_3P \rightarrow X + R_3PNTs$, which did not proceed at a measurable rate in the absence of $Mo(NTs)_2(Et_2dtc)_2$. The system based on PhMeSNTs + Ph_2MeP showed 28 turnovers in 7.5 h in chloroform at 35 °C. The reaction PhMeSNTs + 2PhSH → PhSMe + PhSSPh + $TsNH_2$, in which benzenethiol acts as an electron donor, was also catalyzed by $Mo(NTs)_2(Et_2dtc)_2$. All known imidometal groups are tabulated, and oxo and imido group transfer reactions of Mo are schematically summarized.

A rapidly expanding research area is that including the preparations, structures, and reactions of compounds containing the metal–ligand multiple bond groups **1–8**. This set encompasses

$M{=}CR_2$ **1** $M{\equiv}CR$ **2** $M{\equiv}N$ **3**

$M{=}NR$ **4** $M{=}PR$ **5** $M{=}O$ **6**

$M{=}S$ **7** $M{=}Se$ **8**

oxo, alkylidene, alkylidyne, nitrido, imido, phosphido, sulfido, and selenido ligands that interact as four- or six-electron donors with metals in their high oxidation states to afford groups whose bond lengths are indicative of multiple bonding. Properties of compounds containing groups **1** and **2**,[1,2] **3**,[3] **4**,[1,4,5] **6**,[1,6,7] and **7**[8] have been summarized. The newest group is **5**, of which there are only several examples.[9] Of these groups, by far the greatest amount

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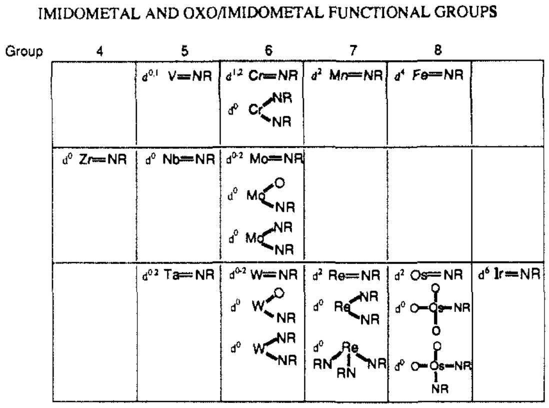

Figure 1. Imido and oxoimido functional groups established in isolated compounds or inferred in transient species (Mn, Fe) from reactivity properties. Two of the Os entries are molecules rather than groups but are included to show the existence of stable species with Os=O and Os=NR groups in the same molecule.

of structural and reactivity information is available for compounds containing one or more of the M=O bonds, **6**. A reaction type of oxometal compounds that is of particular current interest is oxygen atom transfer. The most numerous and best understood examples of this reaction type occur with molybdenum complexes,[6,10] the two most pervasive processes being the primary oxo transfer reaction 1[6], and the μ-oxo dimerization reaction 2. In the first, compounds XO/X function as oxo donors/acceptors.

$$Mo^{VI}O_2L_n + X \rightleftharpoons Mo^{IV}OL_n + XO \quad (1)$$

$$Mo^{VI}O_2L_n + Mo^{IV}OL_n \rightleftharpoons Mo^{V}{}_2O_3L_{2n} \quad (2)$$

After oxo, the imido ligand is probably the most common in the set **1**–**8**. There is an increasing number of essentially isostructural molecules that differ only in the substitution of group **6** by the M=NR group **2**. Molecules of this type that are pertinent to the present work include $MoO_2(Et_2dtc)_2/Mo(NPh)_2(Et_2dtc)_2$.[11-13] Similarly, the μ-O bridge may be replaced by μ-NR, as in the pair $[Fe(salen)]_2O/[Fe(salen)]_2(Ntol)$.[14,15] The known examples of metal–imido or mixed metal–oxo/imido functional groups[16] are shown in Figure 1. As would be expected, their occurrence usually follows those oxidation state and d-electron configuration parameters that stabilize the M=O group, **6**. These are an effective metal charge sufficient to reduce the basicity of the imido ligand such that it can survive electrophilic attack under the usual conditions of preparation and purification, and the configurations $d^{\leq 4}$, which in the expected orbital energy order for a M=NR unit, would maintain a bond order of at least 2.

A comparison of Figure 1 with an analogous presentation of oxometal functional groups[6] reveals that there are over a dozen more cases of the latter than the former. For example, there are no characterized imido complexes of Ti, Tc, and Ru, but there are three types of oxotechnetium groups and four types of oxoruthenium groups. Further, in comparison with the very large number of metal-mediated oxo transfer reactions, such as reaction 1, the number of imido group transfer reactions is minuscule. Such reactions have been limited to, primarily, the oxidation of metal complexes by organic azides and the oxidation of organic substrates by transient high-valent manganese and iron imidoporphyrin species. In addition, there is evidence for catalytic imido group transfer.[17-22] Overall, however, the relatively small number of M=NR groups and the narrow range of known imido group transfer reactivity have not made as apparent as might be desired the utility of imidometal species in stoichiometric and catalytic transformations.

We have begun an investigation of imido group transfer chemistry whose ultimate purpose is to develop and systematize group transfer reactivity. As molybdenum has the best understood oxo transfer chemistry, this metal was selected for the initial studies. Further, imidomolybdenum groups are well established for Mo(VI),[13,23-25] Mo(V),[26,27] and Mo(IV).[28] Reported herein are an examination of the reactivity of certain substrate molecules X=NR in group transfer, complete characterization of new Mo(VI) imido complexes, and certain reactivity aspects of these molecules.

Experimental Section

Preparation of Compounds.[11] The compounds *S*-methyl-*S*-phenyl-*N*-tosylsulfilimine,[29] *S*,*S*-dimethyl-*N*-tosylsulfilimine,[30] *S*,*S*-diphenyl-*N*-tosylsulfilimine,[29] *N*-1-pyridinium sulfonamidate,[31] triphenylphosphine *N*-tosylimine,[32] triphenylarsine *N*-tosylimine,[33] triphenylstibine *N*-tosylimine,[34] cyclohexano-*N*-tosylaziridine,[35] tosyl azide,[36] (*N*-tosylimino)phenyliodinane,[37] triethylphosphine *N*-tosylimine,[38] $Mo(CO)_3(MeCN)_3$,[39]

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(11) Abbreviations: Cp, cyclopentadienyl; Et_2dtc, *N*,*N*-diethyldithiocarbamate(1–); MeCp, methylcyclopentadienyl; py = pyridine; salen, *N*,*N*′-bis(salicylidenamino)ethane(2–); tol, *p*-tolyl, tosyl, *p*-toluenesulfonyl; TPP, tetraphenylporphyrinate(2–).

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and $MoO(Et_2dtc)_2$[40] were prepared by published methods. In the preparations below, all manipulations were performed under a purified dinitrogen atmosphere, and all solvents were rigorously dried and degassed prior to use.

$Mo(CO)_2(Et_2dtc)_2$. The following procedure is more convenient than that reported earlier[41] because it does not require the preparation of $Mo(CO)_4Cl_2$. To a solution of 2.00 g (6.60 mmol) of $Mo(CO)_3(MeCN)_3$ in 30 mL of methanol was added 2.00 g of tetraethylthiuram disulfide (Aldrich). Upon being stirred at room temperature, the mixture became yellow, and after about 15 min, an orange solid appeared. The product was collected by filtration, washed with methanol, and dried in vacuo to afford 2.43 g (82%) of a dark red-purple solid. The compound was identified by its IR spectrum.[41]

$MoO(NTs)(Et_2dtc)_2 \cdot 0.5C_6H_5Me$. A. With *S*-Methyl-*S*-phenyl-*N*-tosylsulfilimine. A solution of 1.00 g (2.50 mmol) of $MoO(Et_2dtc)_2$ in 25 mL of dichloromethane was treated with a solution of 0.80 g (2.7 mmol) of the sulfilimine in 10 mL of dichloromethane. The solution rapidly became dark purple and over the course of 2 h changed to dark red-brown. The solution was layered with 25 mL of toluene and was maintained overnight at −20 °C. The solid that separated was collected by filtration, washed with hexane, and dried in vacuo to give 1.20 g (85%) of red-orange crystalline product. IR (Nujol): ν_{MoO} 876 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (t, 12), 2.33 (s, 1.5), 2.38 (s, 3), 3.73 (q, 8), 7.1–7.2 (m, 2.5), 7.25 (d, 2), 7.88 (d, 2). UV λ_{max} (ϵ_M) (CH_2Cl_2): 375 (5200), 500 (sh) nm. Anal. Calcd for $C_{20.5}H_{31}N_3O_3S_5Mo$: C, 39.47; H, 5.01; N, 6.74; S, 25.70; Mo, 15.38. Found: C, 39.25; H, 4.95; N, 6.74; S, 26.95; Mo, 15.59.

B. With Tosyl Azide. The previous procedure on the same scale but with 1.1 equiv of tosyl azide in place of the sulfilimine afforded 1.32 g (94%) of product.

C. With *N*-1-Pyridinium Sulfonamidate. A mixture of 0.400 g (0.0098 mmol) of $MoO(Et_2dtc)_2$ and 0.260 g (0.011 mmol) of the amidate was suspended in 20 mL of toluene. The stirred mixture rapidly turned deep purple and then more slowly assumed a yellow-orange color. The yellow-orange solid was collected and recrystallized from dichloromethane/toluene to yield 0.450 g (74%) of product.

D. With Triphenylstibine *N*-Tosylimine. The reaction and recrystallization were performed as in preparation C but with 1.1 equiv of the stibinimine in place of the pyridinium sulfonamidate and gave 0.380 g (62%) of product.

$Mo(NTs)_2(Et_2dtc)_2$. To a solution of 2.00 g (4.50 mmol) of $Mo(CO)_2(Et_2dtc)_2$ in 30 mL of dichloromethane was added 2.90 g (9.90 mmol) of *S*-methyl-*S*-phenyl-*N*-tosylsulfilimine. Gas evolution was accompanied by a gradual color change from red-purple to red-brown. The solution was stirred for 10 h, and then 30 mL of hexane was added. After storage overnight at −20 °C, the solid was collected by filtration, washed with hexane, and dried in vacuo to afford 2.40 g (73%) of red microcrystalline product. ^1H NMR ($CDCl_3$): δ 1.24 (t, 12), 2.39 (s, 6), 3.69 (q, 8), 7.20 (d, 4), 7.75 (d, 4). UV λ_{max} (ϵ_M) (CH_2Cl_2): 332 (12800), 400 (sh). Anal. Calcd for $C_{24}H_{34}N_4O_4S_6Mo$: C, 39.44; H, 4.69; N, 7.67; S, 26.32; Mo, 13.13. Found: C, 39.20; H, 4.59; N, 7.60; S, 26.32; Mo, 13.90.

Similar reactions with other tosylimido donors gave the following isolated yields: *N*-1-pyridinium sulfonamidate, 60%; triphenylstibine *N*-tosylimine, 77%; tosyl azide, 75%.

Methyldiphenylphosphine *N*-Tosylimine. A toluene solution of 0.50 g (2.5 mmol) of Ph_2MeP was warmed to 50 °C and treated dropwise with 0.50 g (2.5 mmol) of tosyl azide. After N_2 evolution ceased, the solution volume was reduced to one-half in vacuo, and the solution was maintained at −20 °C for 4 h. The product was collected by filtration and dried in vacuo to give 0.84 g (91%) of white crystalline solid: mp 83–85 °C. ^1H NMR ($CDCl_3$): δ 2.29 (d, 3), 2.30 (s, 3), 7.03 (d, 2), 7.38–7.48 (m, 4), 7.50–7.70 (m, 8).

Collection and Reduction of X-ray Data. Diffraction-quality crystals of $MoO(NTs)(Et_2dtc)_2 \cdot {}^1/_2PhMe$ (A, dark orange) and $Mo(NTs)_2(Et_2dtc)_2$ (B, red) were obtained by slow evaporation of concentrated dichloromethane/toluene solutions (4:1 v/v). The crystals were sealed in glass capillaries under a dinitrogen atmosphere. Data were collected on a Nicolet P3F diffractometer. Unit cells were determined by using 25 machine-centered reflections over 20° ≤ 2θ ≤ 25°. Three check reflections registered every 123 reflections showed no significant decay over the course of the data collections. Data were processed with XTAPE of the SHELXTL program package (Nicolet XRD Corporation, Madison, WI 53711), and empirical absorption corrections were applied with the program PSICOR. Space groups were uniquely determined by axial symmetries from axial photographs and, for B, by systematic absences. They were confirmed by successful solutions and refinements of the structures. Crystallographic data are presented in Table I.

Table I. Crystallographic Data[a]

	$MoO(NTs)(Et_2dtc)_2 \cdot 0.5C_6H_5Me$	$Mo(NTs)_2(Et_2dtc)_2$
formula	$C_{20.5}H_{31}MoN_3O_3S_5$	$C_{24}H_{34}MoN_4O_4S_6$
formula wt	623.71	730.84
a, Å	9.212 (2)	10.632 (2)
b, Å	12.080 (4)	16.307 (3)
c, Å	14.310 (4)	19.023 (5)
α, deg	115.02 (2)	
β, deg	95.51 (2)	101.29 (2)
γ, deg	100.34 (2)	
V, Å^3	1393.0 (7)	3234.2 (1.1)
Z	2	4
space group	$P\bar{1}$	$P2_1/n$
ρ_{calcd} (ρ_{obsd})	1.49 (1.51)	1.50 (1.49)
μ, cm^{-1}	8.4	8.0
R (F_o), %	4.79	3.98
R_w (F_o^2), %	4.71	4.81

[a] T = 298 K, λ = 0.71069 Å (Mo Kα).

Table II. Atom Positional Parameters (×10^4) for $MoO(NTs)(Et_2dtc)_2 \cdot 0.5C_7H_8$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo(1)	3326.5 (8)	1961.6 (5)	1468.3 (4)
S(41)	2342 (3)	1428 (2)	2431 (1)
C(41)	971 (9)	2001 (7)	2110 (5)
S(42)	1140 (3)	2634 (2)	1425 (1)
N(41)	−64 (8)	1928 (7)	2368 (5)
C(42)	−271 (14)	1223 (9)	2890 (7)
C(44)	−1409 (19)	2304 (13)	1980 (11)
C(45)	−1199 (16)	2920 (11)	2315 (9)
C(43)	−12 (18)	1557 (12)	3568 (10)
N(21)	4078 (8)	2930 (5)	1711 (4)
S(21)	4510 (3)	3877 (2)	1742 (2)
O(21)	5756 (8)	3918 (6)	1612 (6)
O(22)	4263 (10)	4187 (5)	2405 (4)
C(21)	3498 (10)	4398 (6)	1040 (5)
C(26)	2464 (11)	4827 (7)	1171 (5)
C(22)	3789 (11)	4397 (7)	369 (6)
C(24)	2019 (11)	5292 (6)	−50 (6)
C(23)	3039 (13)	4851 (8)	−173 (5)
C(25)	1718 (11)	5277 (7)	620 (6)
C(27)	1246 (16)	5792 (8)	−653 (7)
S(32)	3143 (3)	2315 (2)	201 (1)
C(31)	2132 (9)	1495 (6)	−39 (5)
S(31)	1968 (3)	898 (2)	680 (1)
N(31)	1543 (8)	1345 (5)	−694 (4)
C(32)	618 (10)	658 (7)	−866 (5)
C(34)	1788 (13)	1845 (9)	−1293 (5)
C(35)	919 (18)	2537 (11)	−1437 (8)
C(33)	1247 (12)	−123 (8)	−1020 (7)
N(11)	4583 (7)	1228 (5)	1752 (4)
S(11)	5236 (3)	397 (2)	2118 (2)
O(11)	6542 (7)	404 (5)	2049 (5)
O(12)	4934 (9)	333 (5)	2819 (4)
C(11)	4479 (10)	−381 (6)	1583 (6)
C(12)	3476 (12)	−801 (7)	1786 (6)
C(16)	4797 (14)	−588 (8)	933 (7)
C(14)	3121 (18)	−1586 (9)	763 (10)
C(15)	4092 (20)	−1206 (11)	501 (8)
C(13)	2846 (15)	−1402 (9)	1372 (10)
C(17)	2449 (29)	−2278 (13)	282 (15)

Structure Solutions and Refinements. Atom scattering factors were taken from the tabulation of Cromer and Waber.[42] For A, the Mo atom was located by Patterson methods. The position of the Mo atom in B was determined by direct methods (MULTAN). All other non-hydrogen atoms were found by successive Fourier and difference Fourier maps and were refined with the program CRYSTALS. The asymmetric unit of A consists of one molecule of $MoO(NTs)(Et_2dtc)_2$ and one-half of a toluene molecule of solvation. The latter resides on an inversion center and is

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(42) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

Table III. Atom Positional Parameters ($\times 10^4$) for $Mo(NTs)_2(Et_2dtc)_2$

atom	x/a	y/b	z/c
Mo(1)	2263.2 (9)	3995.1 (8)	2422.7 (7)
S(41)	4489 (3)	5442 (2)	3756 (2)
C(41)	5582 (9)	4368 (9)	3247 (7)
S(42)	4632 (3)	3025 (2)	2160 (2)
N(41)	6991 (8)	4596 (7)	3690 (5)
C(42)	7864 (10)	3630 (10)	3326 (7)
C(44)	7795 (11)	5803 (10)	4575 (7)
C(45)	8607 (13)	6698 (11)	4181 (8)
C(43)	7720 (12)	2856 (12)	3938 (10)
N(11)	1402 (7)	2726 (7)	2691 (5)
S(11)	759 (3)	1250 (2)	2389 (2)
O(12)	−504 (7)	765 (6)	1541 (5)
O(11)	521 (8)	1174 (6)	3334 (5)
C(11)	2202 (10)	488 (8)	1948 (7)
C(13)	4422 (12)	−180 (9)	2319 (8)
C(12)	3260 (11)	451 (10)	2683 (8)
C(14)	4442 (11)	−740 (9)	1258 (8)
C(16)	2232 (10)	−59 (9)	865 (7)
C(15)	3369 (11)	−658 (10)	541 (8)
C(17)	5679 (13)	−1419 (13)	880 (11)
O(1)	1314 (7)	5129 (6)	2963 (5)
S(32)	1023 (3)	2645 (2)	602 (2)
C(31)	2007 (10)	3690 (9)	217 (8)
S(31)	3244 (3)	4952 (3)	1253 (2)
N(31)	1841 (9)	3501 (8)	−778 (6)
C(34)	2751 (12)	4463 (12)	−1043 (9)
C(35)	2016 (15)	5493 (13)	−959 (11)
C(32)	801 (13)	2343 (12)	−1648 (9)
C(33)	−576 (17)	2545 (14)	−1970 (13)

disordered. The toluene methyl group was fixed with half-occupancy. Isotropic refinements converged at R values of 7.1% (A) and 7.8% (B). Because of the large thermal parameters, certain ethyl carbon atoms of B were refined isotropically; all other atoms in both crystals were refined anisotropically. In the final stages of refinement, hydrogen atoms were placed at 0.95 Å from, and assigned thermal parameters 1.2 times those of, the bonded carbon atoms. Final R factors are included in Table I, and positional parameters are collected in Tables II and III.[43]

Other Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were determined on a Perkin-Elmer Lambda 4C spectrophotometer, and infrared spectra were measured on a Perkin-Elmer 599B spectrophotometer. ^1H NMR spectra were obtained on a Brüker AM 250 or 300 spectrometer and were referenced to Me_4Si. ^{31}P NMR spectra were measured at 121.4 MHz on a Brüker WM 300 spectrometer and are referenced to external 85% H_3PO_4.

Results and Discussion

Classes of Imido Group Transfer Reactions and Imido Group Donors. Two classes of these reactions can be recognized. The first class of imido group transfer processes, described generally by reaction 3, is an oxo/imido substitution process without change

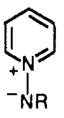
$$M^zO_aL_n + XNR \rightarrow M^zO_{a-1}(NR)L_n + XO \qquad (3)$$

$$XNR = ArNCO,^{46}\ ArNSO,^{47}\ Ph_3PNR,^{23,48}\ (Me_3Si)_2NR^{49}$$

$$M^z(NR)_aL_n + XNR \rightleftharpoons M^{z+2}(NR)_{a+1}L_n + X \qquad (4)$$

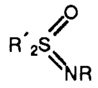
$$M^zO_aL_n + XO \rightleftharpoons M^{z+2}O_{a+1}L_n + X \qquad (5)$$

in the oxidation state of the metal.[44] Principal imido group donors in this reaction include aryl isocyanates, sulfinylamines, and phosphinimines, and bis(silyl)amines. Selected works using these reagents are cited; other synthetic routes by substitution reactions are summarized elsewhere.[4,5] The second class of imido group transfer processes is represented by reaction 4, which involves oxidation or reduction of the metal. It is strictly analogous to the primary oxo transfer reaction 5,[6] of which there are many examples, and with M = Mo, it is the subject of this investigation. Compounds **9–17** have been identified as potential or known donors of the imido group in reaction 4. These include the pyridinium 1-amidates (**9**), sulfilimines (**10**), sulfoximes (**11**), sulfonediimines (**12**),[45] phosphinimines (**13**), arsinimines (**14**), and stibinimines (**15**), all of which to our knowledge have never been used for this purpose. (N-Tosylimino)phenyliodinane (**16**) has been employed in the generation of transient manganese and iron imido species whose existence has been inferred from their reactivities,[17–22] which find analogy with the behavior of the corresponding oxo complexes. Aryl azides (**17**) have been the most frequently utilized reagent in reaction 4.[15,23,25f,50]


9

$R'_2S{=}NR$

10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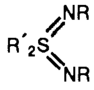
12

$R'_3E{=}NR$

E = P, **13**
As, **14**
Sb, **15**

$PhI{=}NR$

16

$RN{=}N^+{=}N^-$

17

In this work, we have investigated the stoichiometric and catalytic imido group transfer reactions of molybdenum, utilizing dithiocarbamate complexes as convenient vehicles in reactions with a variety of imido compounds. Of the members of the preceding set, the reactivities of all but **12**, with the invariant substituent N-tosyl,[11] have been examined. The related oxo chemistry of these complexes, in the form of reactions 1 and 2, has been worked out in considerable detail.[6] These reactions proceed readily with a variety of oxo donors and acceptors, and Mo(VI,V,IV) complexes have been isolated. Somewhat similar behavior might be expected in imido systems. At the outset, we note the earlier contributions of Wentworth, Maatta, and their co-workers to the chemistry of imidomolybdenum compounds.[13,23,25f,26,27a–d,28b,50–52]

Imido Transfer to Mo(II,IV). N-Tosyl derivatives of all imido reagents except **12** have been reported. We have employed most of these compounds in this work. Reactions 6–10 with 1 equiv

$$MoO(Et_2dtc)_2 + \begin{bmatrix} pyNTs \\ PhMeS{=}NTs \\ Ph_3Sb{=}NTs \\ PhI{=}NTs \\ TsN_3 \end{bmatrix} \rightarrow MoO(NTs)(Et_2dtc)_2 \begin{array}{lr} + \ py & (6) \\ + \ PhSMe & (7) \\ + \ Ph_3Sb & (8) \\ + \ PhI & (9) \\ + \ N_2 & (10) \end{array}$$

of imido donor proceed smoothly at room temperature, resulting in facile imido group transfer via a deep purple intermediate (vide infra). On a preparative scale in dichloromethane, each of these reactions proceeds in high yield. When examined in situ by ^1H

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[43] See the paragraph at the end of this article concerning supplementary material available.

[44] We adopt here a nomenclature analogous to that used for oxo complexes and their atom transfer reactions.[6] When used to designate a ligand, the term "imido" refers to the formal anion RN^{2-}, inasmuch as we know of no persuasive reason why in the molecules of interest here the ligands should be regarded otherwise. Reactions of type 3 in which the metal changes oxidation state by two units result, in effect, in the transfer of a nitrene (RN) group. Some may prefer the description "nitrene" instead of "imido" transfer reactions. For simplicity of nomenclature, we retain the latter usage.

[45] For a summary of the chemistry of compounds **10–12**, cf.: Oae, S.; Furukawa, N. *Sulfilimines and Related Derivatives*; ACS Monograph 179; American Chemical Society: Washington, DC, 1983.

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[49] Slawisch, T. *Z. Anorg. Allg. Chem.* **1970**, *374*, 291; *Naturwissenschaften* **1969**, *56*, 369. Related reactions employ Me_3SiNHR.[5]

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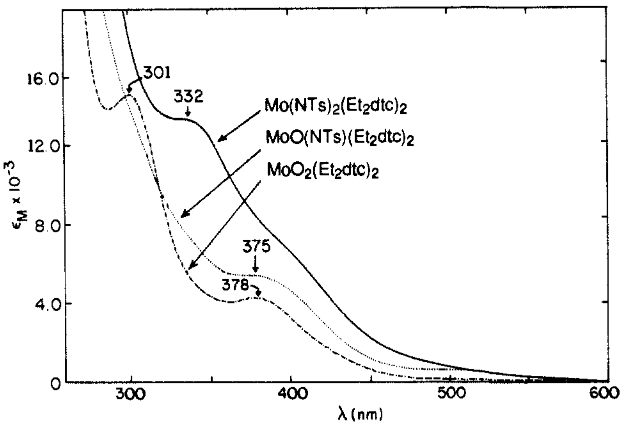

Figure 2. Absorption spectra of $MoO_2(Et_2dtc)_2$, $MoO(NTs)(Et_2dtc)_2$, and $Mo(NTs)_2(Et_2dtc)_2$ in dichloromethane solutions; absorption maxima are indicated.

NMR, the reactions were found to be quantitative. No other Mo-containing product was detected. Use of toluene as a cosolvent in these reactions resulted in the isolation of the oxoimido-Mo(VI) complex as the toluene hemisolvate. In refluxing 1,2-dichloroethane, 2–3 equiv of Ph_3PNTs, Ph_3AsNTs, Me_2SNTs, Ph_2SNTs, and $PhMeS(O)NTs$ did not react with $MoO(Et_2dtc)_2$. Parallel behavior is found with Ph_3PO and several sulfones, which have not been shown to be oxo donors to any Mo(IV) complex. It is also reported that the foregoing two sulfilimines do not react with *tert*-phosphines in DMF at 120 °C.[53]

The behavior of the imido reactants in reactions 6–8 parallels the behavior of their oxo analogues, which afford high-yield conversions to $MoO_2(R_2dtc)_2$.[6,54,55] However, Ph_3AsO, unlike Ph_3AsNTs, does oxidize $MoO(Et_2dtc)_2$.[55] Also, while cyclohexano-*N*-tosylaziridine reacts with the Mo(IV) complex, no cyclohexene was observed, in contrast to the reaction with the epoxide,[56] and the ^1H NMR spectrum revealed multiple Mo-containing products. Two previously established mechanistic features of oxo and imido group transfer are expected to apply to the reaction systems examined here: reactions that are first-order in Mo(IV) and XNR,[54] and retention of the α-N atom of TsN_3 in the NTs group.[50a]

The bis(imido)molybdenum(VI) complex was accessible in good yield by four-electron oxidation of $Mo(CO)_2(Et_2dtc)_2$ with 2 equiv of the same imido donors as in reactions 6–10. The compound is analogous to $Mo(Ntol)_2(Et_2dtc)_2$, which has been obtained by a similar reaction using *p*-tolyl azide.[13] Use of 1 equiv of imido donor led to formation of $Mo(NTs)_2(Et_2dtc)_2$ in reduced yield, indicating that reaction 12 is competitive in rate or much faster than reaction 11. Spectra of $MoO_2(Et_2dtc)_2$ (yellow), $MoO(NTs)(Et_2dtc)_2$ (orange), and $Mo(NTs)_2(Et_2dtc)_2$ (red-orange) are compared in Figure 2 for the purpose of identification. Introduction of the tosylimido group causes a red shift of the absorption profile. Imido group transfer reactions to Mo are summarized in Figure 3.

$$Mo(CO)_2(Et_2dtc)_2 + XNTS \rightarrow Mo(NTs)(Et_2dtc)_2 + X + 2CO \quad (11)$$

$$Mo(NTs)(Et_2dtc)_2 + XNTs \rightarrow Mo(NTs)_2(Et_2dtc)_2 + X \quad (12)$$

Structures of Molybdenum(VI) Tosylimido Complexes. The structures of $MoO(NTs)(Et_2dtc)_2\cdot{}^1/_2PhMe$ and $Mo(NTs)_2(Et_2dtc)_2$ are shown in Figures 4 and 5, respectively, and selected interatomic distances and angles are contained in Table IV. Both molecules display severely distorted octahedral coordination. The multiply bonded ligands are mutually cis, as expected for a d^0 complex.[57] The distortions arise from the large N–Mo–O/N and small (mean) dithiocarbamate bite angles, which are 104.8 (3)° and 69° in $MoO(NTs)(Et_2dtc)_2$ and 103.9 (4)° and 72° in

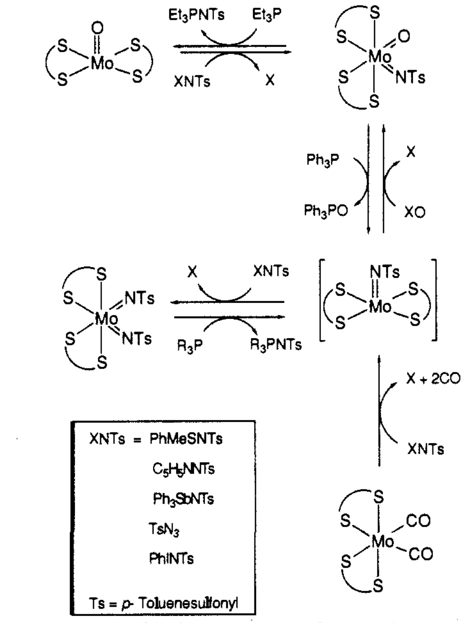

Figure 3. Summary of imido group transfer reactions to and from Mo in Et_2dtc complexes.

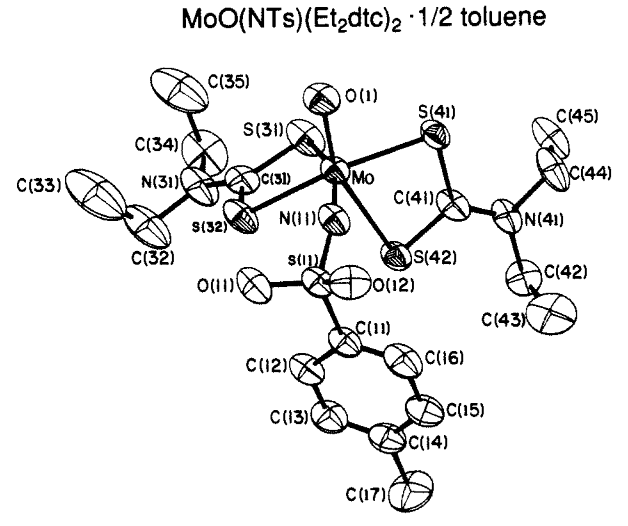

Figure 4. Structure of $MoO(NTs)(Et_2dtc)_2$ as its toluene hemisolvate, showing 50% probability ellipsoids and the atom numbering scheme.

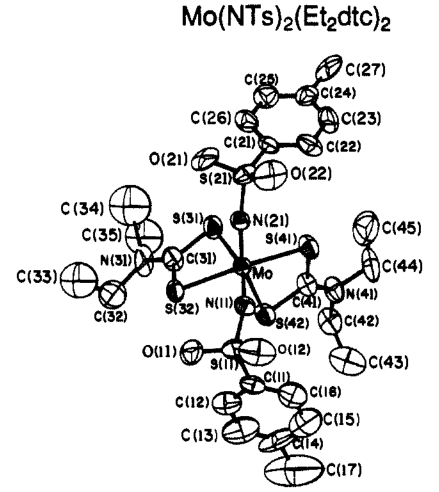

Figure 5. Structure of $Mo(NTs)_2(Et_2dtc)_2$, showing 50% probability ellipsoids and the atom numbering scheme.

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Table IV. Selected Interatomic Distances (Å) and Angles (deg)

	$MoO(NTs)(Et_2dtc)_2\cdot 0.5C_7H_8$	$Mo(NTs)_2(Et_2dtc)_2$
Mo–O(1)/N(21)	1.703 (6)	1.790 (8)
Mo–N(11)	1.801 (7)	1.797 (7)
Mo–S(31)	2.551 (3)	2.550 (3)
Mo–S(32)	2.432 (2)	2.452 (3)
Mo–S(41)	2.457 (2)	2.444 (3)
Mo–S(42)	2.642 (2)	2.559 (3)
N(11)–S(11)	1.624 (8)	1.617 (8)
N(21)–S(21)		1.611 (8)
C(31)–S(31)	1.72 (1)	1.72 (1)
C(31)–S(32)	1.73 (1)	1.72 (1)
C(41)–S(41)	1.743 (9)	1.74 (1)
C(41)–S(42)	1.706 (9)	1.70 (1)
O(1)/N(21)–Mo–N(11)	104.8 (3)	104.0 (4)
Mo–N(11)–S(11)	153.5 (4)	156.8 (5)
Mo–N(21)–S(21)		165.1 (5)
S(31)–Mo–S(32)	70.16 (8)	69.82 (9)
S(41)–Mo–S(42)	68.74 (8)	69.85 (9)

$Mo(NTs)_2(Et_2dtc)_2$. In the latter complex, the tosylimido groups are oriented so as to minimize interactions between them, and the two Mo═N distances differ by 0.047 Å.

Comparisons with dimensional parameters of $MoO_2(Et_2dtc)_2$ and certain molybdenum(VI,V) imido complexes, summarized in Table V, provide several interesting results. $MoO(NTs)(Et_2dtc)_2$ is only the second Mo complex containing both an oxo and an imido ligand whose structure has been determined. The first is $MoO(NH)Cl_2(EtPh_2PO)_2$;[25c] parameters of the MoO(NH) group are comparable with those of $MoO(NTs)(Et_2dtc)_2$. The Mo═O distance of the latter is indistinguishable from that in $MoO_2(Et_2dtc)_2$. Its Mo═N distance is the same as those in $Mo(NTs)_2(Et_2dtc)_2$ and is among the longest known, but the entire range covers only 0.1 Å. The O/N–Mo–O/N angles in these three compounds are essentially identical. In $Mo(NTs)_2(Et_2dtc)_2$, the two Mo–N–S angles differ by only 8°. The virtually equal values of the smaller angle and that in $MoO(NTs)(Et_2dtc)_2$ indicate that both angles are not strongly affected by steric effects. Also, these angles are closely comparable to that in seven-coordinate $[Mo(NSO_2Ph)(Et_2dtc)_3]^+$. The situation is very different from that of $Mo(NPh)_2(Et_2dtc)_2$, where the two Mo–N–C angles differ by 30°. Further, the correlation in this molecule of the shorter Mo═N distance with the larger angle does not hold in $Mo(NTs)_2(Et_2dtc)_2$, where the two Mo═N distances are indistinguishable from each other and from the distance associated with the smaller angle in $Mo(Ntol)_2(Et_2dtc)_2$. The trans influence on Mo–S bond lengths by the tosylimido group in $MoO(NTs)(Et_2dtc)_2$ and $Mo(NTs)_2(Et_2dtc)_2$ is appreciable and nearly equal in the two compounds (ca. 0.1 Å) and is half as large as the effect of an oxo ligand in the former compound. Examination of all comparative structural data leads to the principal conclusion that the structural features of the Mo═O and M═NTs groups are independently manifested in $MoO(NTs)(Et_2dtc)_2$. The Mo–N–S bond angles of 154–165° suggest that the tosylimido group is acting as an electron donor intermediate between the four-electron (ca. 120°) and six-electron (ca. 180°) limits.

Imido Transfer from Mo(VI) and Formation of Mo(V) Dimers. Having established imido group transfer to Mo(IV) with certain reagents (**9**, **10**, and **15**–**17**), the reverse process has been examined using *tert*-phosphines as substrates. Reactions 13–17 are pertinent

$$MoO(NTs)(Et_2dtc)_2 + R_3P \rightarrow Mo(NTs)(Et_2dtc)_2 + R_3PO \quad (13)$$

$$MoO(NTs)(Et_2dtc)_2 + R_3P \rightarrow MoO(Et_2dtc)_2 + R_3PNTs \quad (14)$$

$$MoO(NTs)(Et_2dtc)_2 + Mo(NTs)(Et_2dtc)_2 \rightleftharpoons Mo_2O(NTs)_2(Et_2dtc)_4 \quad (15)$$

$$MoO(NTs)(Et_2dtc)_2 + MoO(Et_2dtc)_2 \rightleftharpoons Mo_2O_2(NTs)(Et_2dtc)_4 \quad (16)$$

$$MoO_2(Et_2dtc)_2 + MoO(Et_2dtc)_2 \rightleftharpoons Mo_2O_3(Et_2dtc)_4 \quad (17)$$

here and were carried out in chloroform or dichloromethane solutions, in which the results were the same. Phosphorus reaction products with the indicated chemical shifts were identified by ^{31}P NMR.

Reaction 13 with excess Ph_3P led to an intermediate deep violet solution (λ_{max} 538 nm), which slowly decayed to a red–brown solution with an essentially featureless visible spectrum. One equivalent of Ph_3PO (+25.0 ppm) was formed. The immediate product of this reaction is interpreted to be $Mo(NTs)(Et_2dtc)_2$, which is captured in reaction 15 to afford a binuclear purple chromophore. The latter is identified as the indicated μ-oxo Mo(V) complex on the basis of its spectral similarity to $Mo_2O(Ntol)_2(Et_2dtc)_4$ (λ_{max} 533 nm in toluene), which has been isolated and characterized by Devore and Maatta.[52a] Attempts to isolate $Mo_2O(NTs)_2(Et_2dtc)_4$ by similar means led to a red–brown solution. Its ^1H NMR spectrum revealed an envelope of dithiocarbamate ethyl signals corresponding to several metal-containing products that were not identified.

Treatment of $MoO(NTs)(Et_2dtc)_2$ with excess Ph_2MeP resulted in the formation of Ph_2MePO (+30.0 ppm) and $Ph_2MePNTs$ (+14.6 ppm) in a ca. 2:1 ratio; i.e., reactions 13 and 14 both proceed. A deep violet intermediate is also observed and is due to combined products of reactions 15 and 16. When $MoO(NTs)(Et_2dtc)_2$ is reacted with stoichiometric Et_3P, only reaction 14 occurs to a detectable extent, affording Et_3PNTs (+37.8 ppm) and $MoO(Et_2dtc)_2$, which was detected spectrophotometrically (λ_{max} 385, 508 nm). Here again a violet intermediate is generated (λ_{max} 514 nm). Reaction 16 was confirmed by combining equimolar quantities of the authentic Mo(IV) and Mo(VI) complexes, which produced the identical chromophore. This is the same reaction that produces the violet intermediate in imido group transfer to Mo(IV).

Reactions of $Mo(NTs)_2(Et_2dtc)_2$ with phosphines were not encouraging. With 30 mM complex and 5 equiv of Ph_3P, the formation of Ph_3PNTs (+10.5 ppm) is less than 5% complete after 24 h. With 1 equiv of Ph_2MeP, the reaction affords quantitative formation of $Ph_2MePNTs$ in 5 h. The ^1H NMR spectrum indicated the presence of several Mo-containing products and no evidence, from a visible color or absorption band, was found for a μ-NTs product. A reaction system containing 5 equiv of Ph_2MeP resulted in bleaching.

The formation of a bridged intermediate in reactions 13 and 14 is entirely analogous to the intervention of purple $Mo_2O_3(Et_2dtc)_4$ (λ_{max} 512 nm in 1,2-dichloroethane[54]) in oxo transfer

Table V. Comparison of Selected Bond Lengths (Å) and Angles (deg) for Molybdenum Oxo/Imido Complexes

complex	Mo═O	Mo═N	Mo—S[a] cis O/N	Mo—S[a] trans N	Mo—S[a] trans O	O/N—Mo—O/N	Mo—N—C/S	ref
$MoO_2(Et_2dtc)_2$	1.703 (2)		2.450 (1)		2.639 (1)	105.8 (1)		12
$MoO(NTs)(Et_2dtc)_2$	1.703 (6)	1.801 (7)	2.44 (1)	2.551 (3)	2.642 (2)	104.8 (3)	153.5 (4)	*c*
$Mo(NPh)_2(Et_2dtc)_2$		1.754 (4) 1.789 (4)	2.457 (6)	2.602 (2) 2.755 (2)		103.5 (2)	169.4 (4) 139.4 (4)	13
$Mo(NTs)_2(Et_2dtc)_2$		1.790 (8) 1.797 (7)	2.448 (6)	2.559 (3) 2.550 (3)		104.0 (4)	165.1 (5) 156.8 (5)	*c*
$Mo(NPh)Cl_2(Et_2dtc)_2$		1.734 (4)	2.508 (6)				166.8 (3)	23
$[Mo(NSO_2Ph)(Me_2dtc)_3]^+$		1.70 (2)	2.49 (2)[b]				161 (1)	24
$[Mo(NCPh_3)(Me_2dtc)_3]^+$		1.731 (2)	2.498 (9)	2.606 (2)			175.1 (5)	24
$Mo(Ntol)(S_2P(OEt)_2)_3$		1.732 (4)	2.49 (3)	2.645 (2)			168.4 (4)	27b

[a] Distances cis or trans to the indicated atoms; mean values given where appropriate. [b] Irregular structure; mean of all values. [c] This work.

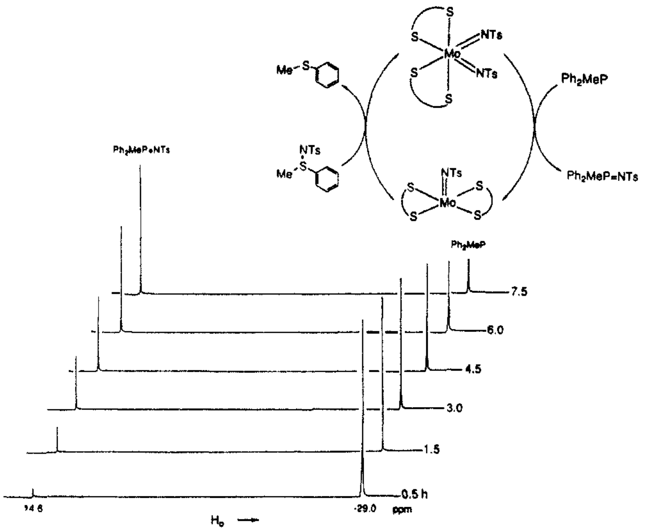

Figure 6. Time course (to 7.5 h and 29 turnovers) of the Mo-catalyzed tosylimido group transfer between PhMeSNTs and Ph_2MeP in chloroform solution at 35 °C as observed by ^{31}P NMR spectroscopy. Initial concentrations were [PhMeSNTs] = 700 mM, $[Ph_2MeP]$ = 350 mM, and $[Mo(NTs)_2(Et_2dtc)_2]$ = 9.0 mM. Chemical shifts and signal assignments are indicated.

reactions.[6] This compound exists in equilibrium 17,[58] whose reversibility may be expected to extend to reactions 15 and 16. While an imido-bridged product may not be formed in these reactions, there are precedents for the unsupported μ-NR group, among them $[Fe(salen)]_2(Ntol)$.[15,59] It should be noted that $Mo_2O_2(NTs)(Et_2dtc)_4$ could dissociate into $MoO_2(Et_2dtc)_2$ and $Mo(NTs)(Et_2dtc)_2$ as well as the species in reaction 16. In this event, $Mo(NTs)_2(Et_2dtc)_2$ and R_3PO (with all phosphines) would be expected upon imido transfer to and from Mo, respectively. These species were not observed. In the only previous example of imido group transfer to a phosphine, Cr(Ntol)(TPP) and Ph_3P yielded Cr(TPP) and Ph_3PNtol.[60] While one of the immediate products of reaction 13 is $Mo(NTs)(Et_2dtc)_2$, this compound could not be isolated because of its instability, despite a number of attempts to do so. Indeed, Devore and Maatta[52a] were unable to isolate pure $Mo(Ntol)(Et_2dtc)_2$ from the reaction of $MoO(Ntol)(Et_2dtc)_2$ and excess Ph_3P. The compound was ultimately trapped and crystallographically characterized as the dimethylacetylene dicarboxylate adduct.[52] Our inability to isolate $Mo_2O(NTs)_2(Et_2dtc)_4$ is a likely consequence of the instability of $Mo(NTs)(Et_2dtc)_2$, whose decomposition would remove the binuclear complex from the system.

Catalytic Imido Transfer. Successful imido group transfer to and from Mo suggests the coupling of reactions 18 and 19 to form a catalytic cycle with net reaction 20. In the catalytic system,

$$Mo(NTs)_2(Et_2dtc)_2 + R_3P \rightarrow Mo(NTs)(Et_2dtc)_2 + R_3PNTs \quad (18)$$

$$Mo(NTs)(Et_2dtc)_2 + XNTs \rightarrow Mo(NTs)_2(Et_2dtc)_2 + X \quad (19)$$

$$XNTs + R_3P \rightarrow X + R_3PNTs \quad (20)$$

reaction 19, rendered sufficiently rapid by a large excess of substrate, should arrest decomposition of the unstable imidomolybdenum(IV) complex. This expectation has been realized.

The system in Figure 6, initially containing the mole ratio $PhMeSNTs{:}Ph_2MeP{:}Mo(NTs)_2(Et_2dtc)_2$ = 78:39:1, was maintained at 35 °C and was monitored periodically by ^{31}P NMR. After 7.5 h, the reaction was 72% complete, representing 28 turnovers of sulfilimine substrate relative to the Mo complex. No other signals were observed in the range −40 to +50 ppm. The final solution was examined by ^1H NMR and found to contain equimolar amounts of PhSMe (δ 2.46) and $Ph_2MePNTs$ (δ 2.29, d), with the indicated methyl shifts. Other than unreacted PhMeSNTs (δ 2.81) and Ph_2MeP (δ 1.59, d), no additional species were observed. The catalytic reaction could have been continued for longer periods inasmuch as there was no sign of degradation at 7.5 h. A similar system containing Ph_3P evidenced reaction but at a very much slower rate. The system in Figure 6 without the Mo complex showed no reaction after 24 h. Earlier, a number of phosphines, including Ph_3P, had been demonstrated to reduce quantitatively arylalkyl-*N*-tosylsulfilimines at 120 °C in DMF solutions.[61]

A chloroform solution containing initially 450 mM Ph_3SbNTs, 400 mM Ph_2MeP, and 9.0 mM $Mo(NTs)_2(Et_2dtc)_2$ was maintained at 25 °C and monitored by ^{31}P NMR. After 6 h, formation of $Ph_2MePNTs$ was 79% complete, equivalent to 35 turnovers. Again, no degradation of the system was observed. A control reaction in the absence of the Mo complex revealed a slower reaction, with 22% conversion of phosphine to phosphinimine at 24 h. It is clear that the Mo complex catalyzes the reaction.

Benzenethiol was examined as an alternative electron donor in the catalytic sulfilimine reduction, reaction 21. A system initially containing 150 mM PhMeSNTs, 200 mM PhSH, and

$$PhMeS{=}NTs + 2PhSH \rightarrow PhSMe + PhSSPh + TsNH_2 \quad (21)$$

10 mM $Mo(NTs)_2(Et_2dtc)_2$ in chloroform at room temperature was monitored by ^1H NMR. After 56 h, all the thiol had been consumed, as evidenced by the disappearance of the SH resonance at δ 3.40, a 67% conversion to the sulfilimine to the sulfide had occurred, and equal quantities of the sulfide and sulfonamide had been produced. The reaction proceeds because $Mo(NTs)_2(Et_2dtc)_2$ is reduced to $Mo(NTs)(Et_2dtc)_2$ by the thiol.[62] A chloroform solution of the sulfilimine and PhSH, both at 200 mM, showed no reaction after 3 days at 25 °C.[63] Earlier, we have demonstrated the Mo-catalyzed reduction of sulfoxides using benzenethiol as an electron source.[64]

Lastly, $MoO(Ntol)(Et_2dtc)_2$ has been shown to catalyze the oxidation of Ph_3P by Me_2SO, presumably by the intermediacy of $Mo(Ntol)(Et_2dtc)_2$.[28b,52a] Similar reactivity of $MoO(NTs)(Et_2dtc)_2$ was tested in a system initially containing 150 mM Me_2SO, 100 mM Ph_3P, and 10 mM complex in chloroform. After 24 h at room temperature, all Ph_3P had been converted to Ph_3PO, indicating the ability of $Mo(NTs)(Et_2dtc)_2$ to react with oxo as well as imido donors.

Summary. The following are the principal findings and conclusions from this investigation.

1. *N*-Tosylimido group transfer reactions to Mo(II) (reactions 11 and 12) and oxomolybdenum(IV) in high yield using reagents **9**, **10**, and **15**–**17** have been developed.
2. Oxygen atom and *N*-tosylimido group transfer reactions from (oxoimido)molybdenum(VI) to *tert*-phosphines proceed, but with the more basic phosphines[65] favoring imido rather than oxo transfer (reactions 13 and 14).
3. The comparative structures of the set $MoXY(Et_2dtc)_2$ with X = Y = O, X = Y = NTs, and X = O, Y = NTs show that the metric features of the MoXY unit are almost independent of X and Y; tosylimido is a nearly isostructural replacement for oxo.
4. Reactions 1 and 2 involve the purple intermediates with probable bridge units $Mo_2O(NTs)(\mu\text{-}O)$ and $Mo_2(NTs)_2(\mu\text{-}O)$, respectively, analogous to the structurally established $Mo_2O_2(\mu\text{-}O)$ bridge in $Mo_2O_3(Pr_2dtc)_4$[66] and that present in isolated Mo_2O-

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[58] Matsuda, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1979**, *18*, 454.

[59] For an example of an imido/oxo-bridged Mo structure, cf. ref 51a.

[60] Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191.

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[62] The analogous reduction of $MoO_2(Et_2dtc)_2$ to $MoO(Et_2dtc)_2$ by PhSH has been demonstrated: McDonald, J. W.; Corbin, J. L.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2056.

[63] In a different, uncatalyzed transformation, RR'SNTs with ArS^- yields RSSAr and $TsNH_2$: Oae, S.; Aida, T.; Nakajima, M.; Furukawa, N. *Tetrahedron* **1974**, *30*, 947.

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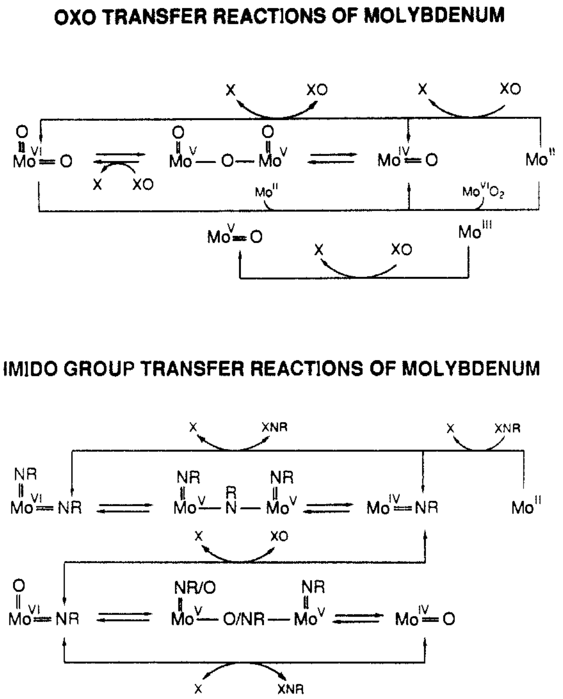
OXO TRANSFER REACTIONS OF MOLYBDENUM

IMIDO GROUP TRANSFER REACTIONS OF MOLYBDENUM

Figure 7. Generalized representations of the established oxo and imido group transfer reactions of Mo. Double-headed curved arrows indicate that transformations between species connected with joined straight line segments are bidirectional (but not with the same reagent); single-headed arrows indicate a unidirectional transformation. Allowance is made for the possible existence of bridged units $Mo_2(NR)_3$ and bridging groups μ-NR, although neither has yet been proven.

$(Ntol)_2(Et_2dtc)_4$.[52a] The Mo(IV) complex $Mo(NTs)(Et_2dtc)_2$, produced in reactions 11 and 13 and implicated in equilibrium 15, proved too unstable for isolation in the pure form.

5. The catalytic reactions 20 with XNR = PhMeSNTs or Ph_3SbNTs and R_3P = Ph_2MeP and reaction 21 in which a thiol serves as an electron donor—all initiated by the catalyst $Mo(NTs)_2(Et_2dtc)_2$—were demonstrated. Systems are robust and could have been operated for much longer times than those used here.

All known oxygen atom and imido group transfer reactions of Mo are summarized in Figure 7 as transformations between oxidation states and oxo/imido Mo groups. Here XO/X and XNR/X are oxo and imido donors/acceptors, single- and double-headed curved arrows represent uni- and bidirectional transformations between species connected by joined straight-line segments, and double arrows link species in known or potential equilibrium. The schemes are generalized; not all transformations are spontaneous with a given Mo complex or donor/acceptor. Oxo transfer reactions are presented and discussed at length elsewhere.[6,10] Imido group transfer reactions are drawn from this work and previously cited references. Schemes such as those in Figure 7 provide a unified presentation of all known transformations by the processes of atom or group transfer. They represent a desirable goal in the evolvement of the atom or group transfer chemistry of a given element, for they summarize known reactions and imply possible reactions of other compounds of the element.

The imido group transfer reactions to and from Mo demonstrated here show more clearly than heretofore that a significant body of such reactions is possible for Mo and, by implication, for other elements. Further, catalytic imido group transfer can be improved and expanded using the results here as a base. Earlier, catalytic amidation of cyclohexane and alkenes, primarily using manganese and iron porphyrins, had been achieved but with limited turnovers.[17-21] The active intermediate imidometal species have not been isolated or otherwise detected.[67] Lastly, inspection of Figure 1 reveals untouched areas for investigation. For example, given the extensive oxo chemistry of Ru,[6] imido-Ru complexes are especially conspicuous by their absence. The most recent addition to the table of imidometal groups is the highly reactive Zr=NR[68,69] and Ir=NR.[70] One example of each has been structurally characterized.[68,70] In an inverted contrast, the Zr=O and Ir=O groups remain elusive. Metal-imido multiple bonds have very recently been extended to the actinides, in compounds such as $(MeCp)_3UNPh$[71] and Cp_3MNPPh_3 (M = Th, U).[72]

Other metal-ligand multiply bonded units collected at the outset remain attractive subjects for investigations of atom and group transfer reactions. For example, the first instance of nitrogen atom transfer, from a Mn^V=N porphyrin to metal(II,III) porphyrins, has been reported.[73] There is also at least one example of what might be termed an alkylidene group transfer reaction. Treatment of $Cp_2TaMe(Me_3P)$ with the ylide Et_3PCHMe results in the transfer of a carbene equivalent to the metal, yielding $Cp_2TaMe(CHMe)$.[74] The availability of sulfonium[75] and iodonium[76] ylides suggests extensions of this reaction type.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, and calculated hydrogen atom positions for $MoO(NTs)(Et_2dtc)_2$ and $Mo(NTs)_2(Et_2dtc)_2$, and details of the data collection (13 pages); table of calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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