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The Effect of Substituents on the Phenyl Portion of the Imido Ligand on the Structure and Properties of Molybdenum(VI) Imido Complexes

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Anilines with alkyl substituents on the phenyl ring ($ArNH_2$ = 2,4,6-trimethylaniline; 2,3-, 2,4-, 2,6-, and 3,4-dimethylaniline; and 2,6-diisopropylaniline) react with $MoO(X)_2(dtc)_2$ (X = Cl or Br; dtc = diethyldithiocarbamate) in methanol in the presence of 2 equiv of triethylamine to form ionic imido complexes of the type $[MoNAr(dtc)_3]_2[Mo_6O_{19}]$ or $MoNAr(dtc)_3]_4[Mo_8O_{26}]$. The same reaction in THF with butyllithium as base yields imido complexes of the type $MoNAr(X)_2(dtc)_2$. The structures of three ionic, five chloro, and two bromo complexes have been determined by X-ray crystallography. In all complexes, the molybenum center is a distorted pentagonal bipyramid. While the structures are similar, the angles of the imido linkages differ. The effect of the substituents on the phenyl ring of the imido ligand on the ^{95}Mo NMR chemical shifts was determined. The Mo nucleus becomes more deshielded with the substituents in the following order: 3,4-Me_2 < 2,3-Me_2 < 2,4-Me_2 < 2,6-Me_2 < 2,4,6-Me_3 < 2,6 isopropyl. Complexes with more deshielded ^{95}Mo centers tend to have angles of the imido linkage that are closer to 180°.

Introduction

Molybdenum imido complexes have been studied widely[1] because of their involvement in the activation of carbon–hydrogen bonds,[2] the oxidation, amination, and oxyamination of unsaturated organic compounds[3] and the catalysis of olefin metathesis.[4] The effect of slight modifications of the ligands can be important in the design of such compounds. We report here how a change of substituents on the phenyl group of the imido ligand influences the properties of molybdenum(VI) imido complexes. We reported previously that the reaction of 1,2-phenylenediamine with $MoO(Cl)_2(dtc)_2$ (dtc = diethyldithiocarbamate) in methanol in the presence of 2 equiv of triethylamine yields the imido complex $Mo(NC_6H_4^{(2-)}NH_2)Cl_2(dtc)_2$.[5] Although the structure of this complex is almost identical to $Mo(NC_6H_5)Cl_2(dtc)_2$,[6] the angles of the imido linkages differ by 12° and the ^{95}Mo NMR chemical shifts are 91 ppm apart. Hogarth and co-workers recently reported the synthesis of this type of complex with para-substituted anilines.[7] The varying properties of these complexes depending on the substituents on the phenyl ring of the imido ligand led us to study a number of complexes with methyl and isopropyl substituents in different positions on the phenyl ring to determine whether any systematic trends are evident.

Experimental Section

All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. The solvents

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Table 1. Elemental Analyses of Complexes **I**−**III**

	I(2,4,6)[a]		**II(2,4)**[a]		**III(2,6)**[b]	
	% calcd	% found	% calcd	% found	% calcd	% found
C	29.00	28.67	28.60	29.10	25.11	25.41
H	4.17	3.98	4.10	4.13	3.57	3.54
N	5.65	5.29	5.73	5.72	5.10	5.18

[a] $[\mathbf{III}]_4[Mo_8O_{26}]\cdot CH_2Cl_2$. [b] $[\mathbf{I}$ or $\mathbf{II}]_2[Mo_6O_{19}]$.

were dried and distilled prior to use. $MoO(Cl)_2(dtc)_2$,[8] $MoO(Br)_2(dtc)_2$,[8] and $[Mo(NC_6H_5)(dtc)_3]BF_4$[9] were synthesized according to literature methods. The $ArNH_2$ ligands (2,4,6-trimethylaniline, 2,3-, 2,4-, 3,4-, and 2,6-dimethylaniline, 2,6-diisopropylaniline) and butyllithium were purchased from Aldrich and used without further purification. Triethylamine was dried over sodium and distilled prior to use. The elemental analyses were carried out by Atlantic Microlab, Inc., in Norcross, GA.

Preparation of $[MoNAr(dtc)_3]_2[Mo_6O_{19}]$ or $[MoNAr(dtc)_3]_4[Mo_8O_{26}]$. $MoO(Cl)_2(dtc)_2$ (1.0 g; 2.1 mmol) was suspended in 20 mL of methanol to which 2.2 mmol of ligand, $ArNH_2$, dissolved in 10 mL of methanol, and 0.66 mL (5.0 mmol) triethylamine were added. Upon addition of the triethylamine, the yellow solution turned reddish-brown. The mixture was refluxed overnight and filtered to remove any solids; the filtrate was then evaporated to dryness. The crude green-brown residue was dissolved in CH_2Cl_2 and washed with water. Orange-brown crystals were grown by adding a layer of hexane to the solution. The yields after recrystallization ranged from 10% to 50%, based on the number of molybdenum atoms per formula unit of product. The elemental analyses for these complexes are listed in Table 1, and the ^1H NMR data are presented in Table 3.

Preparation of $MoNAr(X)_2(dtc)_2$ (X = Cl or Br). $MoO(Cl)_2(dtc)_2$ (1.0 g; 2.1 mmol) or $MoO(Br)_2(dtc)_2$ (1.2 g, 2.1 mmol) was dissolved in 20 mL of THF, and 2.2 mmol of ligand, $ArNH_2$, plus 0.46 mL (5.0 mmol) of butyllithium were added. The yellow solution turned brown after the addition of butyllithium. The solution was refluxed for 4 h. The reaction mixture was filtered and the filtrate evaporated to dryness. The resulting yellow solid was dissolved in CH_2Cl_2, and a layer of hexane was added over the solution. After several days, yellow crystals had formed, which were filtered off and dried under vacuum. Yields of approximately 30% were obtained for the recrystallized product. The elemental analyses for these complexes are listed in Table 2, and the ^1H NMR data are presented in Table 3.

For short and easy identification, the complexes will hereafter be referred to with Roman numerals.[10] In parentheses, the positions of the methyl groups or other substitutents on the phenyl ring of the imido ligand will be given. For substituents other than methyl groups, diiso will be added for diisopropyl, and NH_2 for the amine group. For the halogen complexes, the halogen will be noted in parentheses as well. For example, the cation $[Mo(2,6\text{-}(CH_3)_2C_6H_3N)(dtc)_3]^+$ will be abbreviated as **III(2,6)** and $Mo(2,6\text{-}(CH_3)_2C_6H_3N)Cl_2(dtc)_2$ as **VII(2,6,Cl)**.

NMR Spectroscopy. The NMR spectra were measured on a Bruker AC 300 MHz NMR spectrometer. For the ^1H spectra a 5 mm dual $^1H/^{13}C$ probehead was used. ^{14}N and ^{95}Mo NMR spectra were measured with a 10 mm broadband probehead ($^{109}Ag-^{31}P$) with digital tuning. For the ^1H NMR spectra the residual solvent was used as an internal reference. For the other nuclei external standards were used: nitromethane, neat (^{14}N NMR); 2 M Na_2MoO_4 in D_2O, basic (^{95}Mo NMR).

Table 2. Elemental Analyses of $MoNAr(X)_2(dtc)_2$ Complexes

	V(2,4,6,Cl)		**V(2,3,Cl)**		**VI(2,4,Cl)**	
	% calcd	% found	% calcd	% found	% calcd	% found
C	38.0	38.2	37.0	38.8	37.0	36.3
H	5.0	5.1	5.0	5.5	5.0	5.0
N	7.0	7.1	7.2	6.7	7.2	7.1
Cl	12.0	11.8	12.0	11.8	12.0	12.0

	VII(2,6,Cl)		**VIII(2,6,diiso,Cl)**	
	% calcd	% found	% calcd	% found
C	37.0	35.8	41.4	40.8
H	5.0	5.2	5.8	5.8
N	7.2	6.6	6.6	6.5
Cl	12.0	12.9	11.1	11.4

	XI(2,4,6,Br)		**XII(2,6,Br)**	
	% calcd	% found	% calcd	% found
C	33.4	33.2	33.2	33.2
H	4.1	4.3	4.3	4.3
N	6.2	6.0	6.2	6.1
Br	23.4	23.2	23.8	25.6

X-ray Structure Determination. The crystallographic data for all the new complexes are listed in Tables 4 and 5. All room temperature samples were glued onto glass fibers for diffraction analysis while all low-temperature samples were attached with viscous oil and instant-frozen to the end of glass fibers instead. Diffraction data were collected on various Siemens diffractometers (R3m/V (compounds **I**, **II**, **III**), P4 (compounds **IV**, **V**, **VI**, **VII**, **XI**, **XII**) or SMART/P4 (compound **VIII**)) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Space group determinations were first indicated by patterns of systematic absences ($P2_1/c$ and $P2/n$) or lacking any patterns ($P\bar{1}$) and confirmed with successful structural refinements. Empirical absorption corrections and Lp (Lorentz and polarization) corrections were applied onto the datasets. The structures were all solved by direct methods and refined by full-matrix least-squares techniques minimizing Δf^2.[11] Neutral atom scattering factors were taken from ref 12. All computations used the SHELXTL program package.[11] All non-hydrogen atoms were refined anisotropically, and all hydrogen

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(10) **I** = **I(2,4,6)**: tris(diethyldithiocarbamato)((2,4,6-trimethylphenyl)imido)molybdenum(VI) cation. **II** = **II(2,4)**: tris(diethyldithiocarbamato)((2,4-dimethylphenyl)imido)molybdenum(VI) cation. **III** = **III(2,6)**: tris(diethyldithiocarbamato)((2,6-dimethylphenyl)imido)molybdenum(VI) cation. **IV** = **IV(2,4,6,Cl)**: dichlorobis(diethyldithiocarbamato)((2,4,6-trimethylphenyl)imido)molybdenum(VI). **V** = **V(2,3,Cl)**: dichlorobis(diethyldithiocarbamato)((2,3-dimethylphenyl)imido)molybdenum(VI). **VI** = **VI(2,4,Cl)**: dichlorobis(diethyldithiocarbamato)((2,4-dimethylphenyl)imido)molybdenum(VI). **VII** = **VII(2,6,Cl)**: dichlorobis(diethyldithiocarbamato)((2,6-dimethylphenyl)imido)molybdenum(VI). **VIII** = **VIII(2,6,diiso,Cl)**: dichlorobis(diethyldithiocarbamato)((2,6-diisopropylphenyl)imido)molybdenum(VI). **IX** = **IX(Cl)**: dichlorobis(diethyldithiocarbamato)((phenyl)imido)molybdenum(VI). **X** = **X(2,NH₂)**: ((2-aminophenyl)imido)dichlorobis(diethyldithiocarbamato)molybdenum(VI). **XI** = **XI(2,4,6,Br)**: dibromobis(diethyldithiocarbamato)((2,4,6-trimethylphenyl)imido)molybdenum(VI). **XII** = **XII(2,6,Br)**: dibromobis(diethyldithiocarbamato)((2,6-dimethylphenyl)imido)molybdenum(VI).

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(12) *International Tables for X-ray Crystallography*; Kluwer: Boston, 1992; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2.

Table 3. ^{1}H NMR Data (ppm)[a]

	CH_3(dtc)	CH_2(dtc)	H (Ar)	CH_3 (Ar)
I(2,4,6)	1.31−1.47 (m, 18)	3.81−4.00 (m, 12)	6.85 (s, 2)	2.40 (s, 3) 2.57 (s, 6)
II(2,4)	1.31−1.49 (m, 18)	3.80−4.03 (m, 12)	7.03 (s, 1) 7.07 (d, 1) 7.44 (d, 1)	2.53 (s, 3) 2.45 (s, 3)
III(2,6)	1.39−1.50 (m, 18)	3.75−4.04 (m, 12)	6.70 (t, 1) 7.00 (d, 1) 7.07 (d, 1)	2.25 (s, 3) 2.62 (s, 3)
IV(2,4,6,Cl)	1.32 (t, 12)	3.65−4.00 (m, 8)	6.70 (s, 2)	2.30 (s, 3) 2.72 (s, 6)
V(2,3,Cl)	1.32 (t, 12)	3.65−4.00 (m, 8)	7.05 (d, 2) 7.50 (t, 1)	2.20 (s, 3) 2.50 (s, 3)
VI(2,4,Cl)	1.30 (t, 12)	3.65−3.95 (m, 8)	6.85 (s, 1) 7.55 (d, 1) 6.90 (d, 1)	2.35 (s, 3) 2.55 (s, 3)
VII(2,6,Cl)	1.30 (t, 12)	3.65−3.95 (m, 8)	6.88 (d, 2) 7.00 (t, 1)	2.72 (s, 6)
VIII(2,6,diiso,Cl)	1.39 (q, 12)	3.74−4.35 (m, 8)	7.13 (d, 2) 7.20 (t, 1)	1.27 (d, 12)
XI(2,4,6,Br)	1.35 (t, 12)	3.60−4.00 (m, 8)	6.65 (s, 2)	2.25 (s, 3) 2.65 (s, 6)
XII(2,6,Br)	1.35 (t, 12)	3.60−4.00 (m, 8)	6.82 (d, 2) 6.95 (t, 1)	2.70 (s, 6)

[a] In $CDCl_3$.

Table 4. Crystallographic Data for [MoNAr(dtc)$_3$]$_2$[Mo$_6$O$_{19}$] and [MoNAr(dtc)$_3$]$_4$[Mo$_8$O$_{24}$] Compounds

	[**I(2,4,6)**]$_2$[Mo$_6$O$_{19}$]	[**II(2,4)**]$_4$[Mo$_8$O$_{26}$]	[**III(2,6)**]$_2$[Mo$_6$O$_{19}$]
chem formula	$C_{48}H_{82}N_8O_{19}S_{12}Mo_8\cdot 4CH_2Cl_2$	$C_{92}H_{156}N_{16}O_{26}S_{24}Mo_{12}\cdot CH_2Cl_2$	$C_{46}H_{78}N_8O_{19}S_{12}Mo_8$
fw	2567.2	3908.0	2199.4
space group	$P2/n$ (No. 13)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell dimens			
a, Å	15.279(4)	16.073(3)	10.377(4)
b, Å	12.131(9)	16.838(4)	29.151(11)
c, Å	24.748(10)	16.948(4)	12.696(5)
β, deg	93.88(2)	93.86(2)	91.29(3)
α, deg		108.55(2)	
γ, deg		116.33(2)	
vol, Å^3	4577(4)	3778.3(14)	3840(3)
Z	2	1	2
T, °C	−100	22	22
λ, Å	0.71073	0.71073	0.71073
ρ_{calcd}, g/cm^3	1.863	1.718	1.902
μ, mm^{-1}	1.627	1.388	1.610
final R indices (obsd)			
R, %	5.45	5.25	3.36
R_w, %	9.36	8.02	4.34

atoms were placed at their idealized positions for the last cycle of least-squares refinement but not refined.

Results

The ORTEP drawings of the cation **III(2,6)** and of **VII(2,6,Cl)** are shown in Figures 1 and 2. Figures 3 and 4 show [**II(2,4)**]$_4$[Mo$_8$O$_{26}$] and [**III(2,6)**]$_2$[Mo$_6$O$_{19}$], respectively. Selected bond lengths and bond angles for compounds **I**−**XII** are listed in Tables 6 and 7. All atoms in Tables 6 and 7 are numbered according to Figures 1 and 2. The^{14}N and ^{95}Mo NMR chemical shifts of the compounds are listed in Table 8.

Discussion

Synthesis and Structure. Depending on the reaction conditions, MoO(X)$_2$(dtc)$_2$ (X = Cl, Br) will form different products when reacted with anilines that contain alkyl subsitituents on the phenyl ring (Figure 5). When the molybdenum starting material is refluxed in methanol with the aniline and 2 equiv of triethylamine, imido complexes of the type [MoNAr(dtc)$_3$]$_2$[Mo$_6$O$_{19}$] or [MoNAr(dtc)$_3$]$_4$[Mo$_8$O$_{26}$] are formed. The structures of three of these complexes, [**III(2,4,6)**]$_2$[Mo$_6$O$_{19}$], [**II(2,4)**]$_4$[Mo$_8$O$_{26}$], and [**III(2,6)**]$_2$[Mo$_6$O$_{19}$], were determined by X-ray crystallography. The cations have distorted pentagonal-bipyramidal molybdenum centers with five sulfur atoms in the equatorial plane and the imido nitrogen and one sulfur in the axial positions. There are no significant differences in the lengths of the molybdenum imido bonds, Mo(4)−N(4) (1.74 Å). The angles of the imido linkage range from 169° to 178°. The axial Mo(4)−S(5) bond is slightly longer than the Mo−S bonds in the equatorial positions. In the case of [**II(2,4)**]$_4$[Mo$_8$O$_{26}$], all averaged distances obtained from two independent cations are comparable to those of the corresponding bond distances of the other two compounds. We have not detected any systematic trends for the formation of the [Mo$_6$O$_{19}$]$^{2-}$ or [Mo$_8$O$_{26}$]$^{4-}$ anions during these reactions, but [Mo$_6$O$_{19}$]$^{2-}$ is the more commonly found anion.

Table 5. Crystallographic Data for [MoNAr(X)$_2$(dtc$_2$] Compounds[a]

	IV(2,4,6,Cl)	**V(2,3,Cl)**	**VI(2,4,Cl)**	**VII(2,6,Cl)**
chem formula	$C_{19}H_{31}N_3S_4Cl_2Mo$	$C_{18}H_{29}N_3S_4Cl_2Mo$	$C_{18}H_{29}N_3S_4Cl_2Mo$	$C_{18}H_{29}Cl_2N_3S_4Mo$
fw	596.55	582.52	582.52	582.5
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit cell dimens				
a, Å	13.8410(10)	12.843(2)	13.2424(11)	7.741(2)
b, Å	13.8499(7)	13.6179(12)	13.677(2)	14.865(4)
c, Å	13.8845(12)	14.696(2)	14.615(2)	24.845(9)
β, deg	100.082(6)	100.382(13)	96.141(9)	95.74(3)
vol, Å^3	2620.5(3)	2528.2(5)	2631.8(5)	2844.7(15)
Z	4	4	4	4
T, °C	−160	−160	23	23
λ, Å	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}, g/cm^3	1.512	1.530	1.470	1.360
μ, mm^{-1}	0.9038	0.9353	1.029	0.952
final *R* indices (obsd)				
R, %	3.31	4.93	3.94	6.0
R_w, %	8.22	10.55	9.55	14.92

	VIII(2,6, diiso,Cl)	**XI(2,4,6,Br)**	**XII(2,6,Br)**
chem formula	$C_{22}H_{37}Cl_2N_3S_4Mo$	$C_{19}H_{31}Br_2N_3S_4Mo$	$C_{18}H_{29}Br_2N_3S_4Mo\cdot0.5(C_6H_6)$
fw	638.63	685.47	710.50
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell dimens			
a, Å	17.9468(2)	13.8497(13)	10.1653(9)
b, Å	9.2198(2)	14.345(4)	10.6198(10)
c, Å	18.3413(2)	14.330(3)	13.8730(11)
β, deg	92.379(2)	99.567(12)	74.744(7)
α, deg	88.920(9)°		
γ, deg	85.898(9)		
vol, Å^3	3032.24(8)	2807.4(9)	1441.2(2)
Z	4	4	2
T, °C	−140	25	25
λ, Å	0.71073	0.71073	0.71073
ρ_{calcd}, g/cm^3	1.399	1.622	1.637
μ, mm^{-1}	0.900	1.059	1.085
final *R* indices (obsd)			
R, %	2.10	5.49	3.95
R_w, %	5.26	12.27	10.17

[a] Crystallographic data for **IX**[6] and **X**[5] have been published previously.

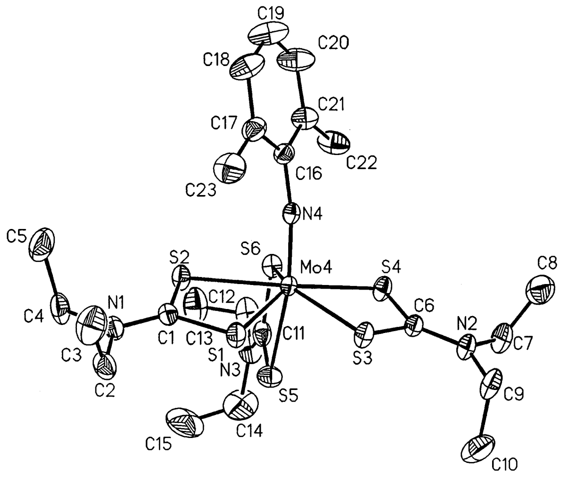

Figure 1. ORTEP drawing of [Mo(2,6-(CH$_3$)$_2$C$_6$H$_3$N)(dtc)$_3$]$^+$, **III(2,6)**.

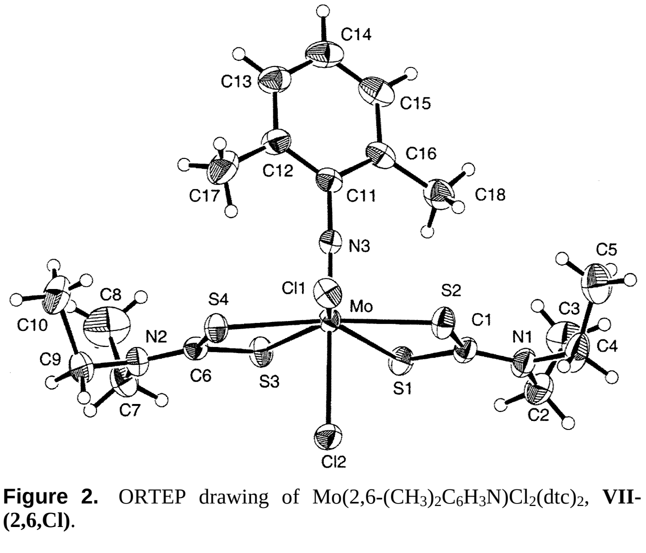

Figure 2. ORTEP drawing of Mo(2,6-(CH$_3$)$_2$C$_6$H$_3$N)Cl$_2$(dtc)$_2$, **VII-(2,6,Cl)**.

To get more insight into the formation of these salts, the reactions of MoO(Cl)$_2$(dtc)$_2$, MoO(Br)$_2$(dtc)$_2$, and MoO$_2$-(dtc)$_2$, with 2,6-dimethylaniline were performed in evacuated 10 mm NMR tubes using one-tenth of the amounts described in the Experimental Section. The progress of each reaction was monitored by ^{95}Mo and ^{14}N NMR spectroscopy. In all three cases, the first new peak to appear in the ^{95}Mo NMR spectrum was that of [MoO(dtc)$_3$]$^+$. After approximately 5 h, the peaks for the polymolybdate anion and the imido cations could be detected. In a separate experiment, each molybdenum starting material was mixed with triethylamine in methanol without the aniline, and the cation [MoO(dtc)$_3$]$^+$ was also formed. In the ^{14}N NMR spectrum, one broad peak for 2,6-dimethylaniline and triethylamine around −330 ppm was observed at the beginning; after several hours, the imido

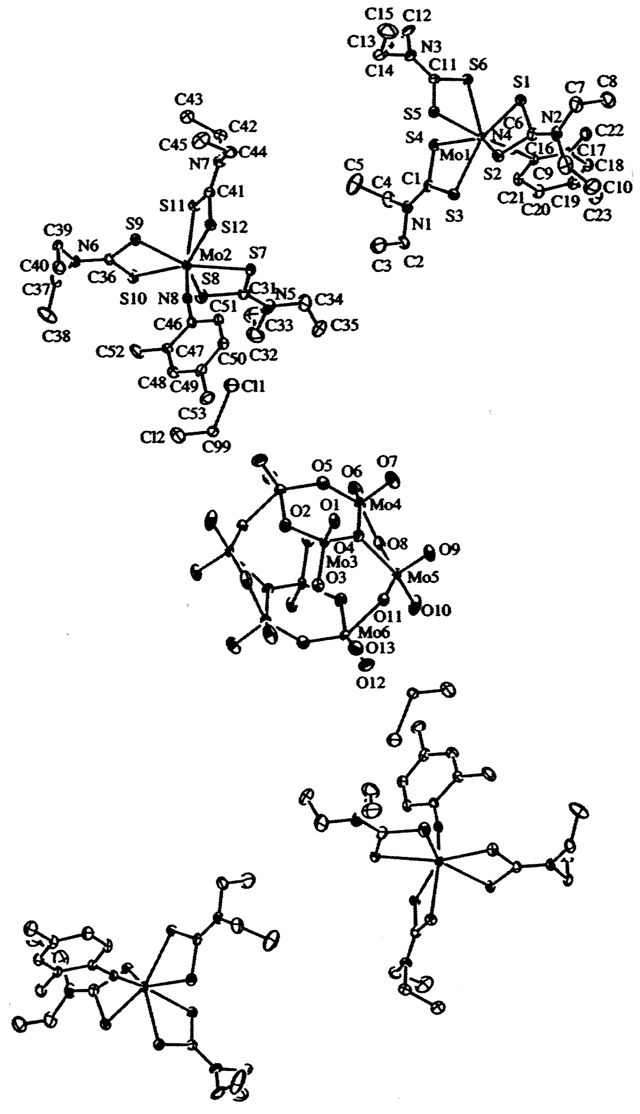

Figure 3. ORTEP drawing of $[Mo(2,4\text{-}(CH_3)_2C_6H_3N)(dtc)_3]_4[Mo_8O_{26}]$, [**II(2,4)**]$_4$[$Mo_8O_{26}$].

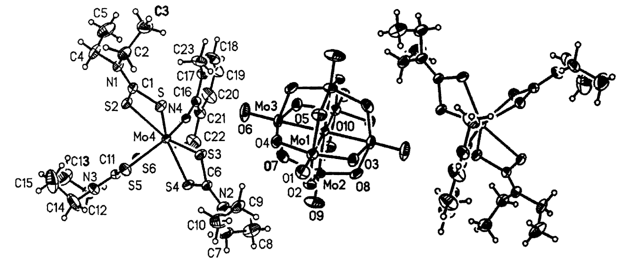

Figure 4. ORTEP drawing of $[Mo(2,6\text{-}(CH_3)_2C_6H_3N)(dtc)_3]_2[Mo_6O_{19}]$, [**III(2,6)**]$_2$[$Mo_6O_{19}$].

peak around +12 ppm could be detected. It is interesting to note that under the same conditions the reaction of MoO(Cl)$_2$(dtc)$_2$ with 1,2-phenylenediamine produces the complex MoNAr(Cl)$_2$(dtc)$_2$.[5] This indicates that 2-aminoaniline reacts faster than the anilines used here so that the imido complex forms before the oxo cation [MoO(dtc)$_3$]$^+$.

When the reaction of MoO(X)$_2$(dtc)$_2$ with anilines containing alkyl subsitituents on the phenyl ring is performed in THF with 2 equiv of butyllithium as base, imido complexes of the type MoNAr(X)$_2$(dtc)$_2$ are formed. The structures of five new chloro complexes, **IV(2,4,6,Cl)**, **V(2,3,Cl)**, **VI(2,4,Cl)**, **VII(2,6,Cl)**, and **VIII(2,6,diiso,Cl)**, and two new bromo complexes, **XI(2,4,6,Br)** and **XII(2,6,Br)**, were determined by X-ray crystallography. The coordination sphere of the Mo is distorted pentagonal-bipyramidal with four sulfurs and one halogen in the equatorial positions and the imido nitrogen and the second halogen along the axis. The length of the molybdenum−imido nitrogen bonds for **IV(2,4,6,Cl)**, **V(2,3Cl)**, **VI(2,4,Cl)**, **VII(2,6,Cl)** is the same (about 1.73 Å). The axial Mo−Cl(2) bonds are longer than the equatorial Mo−Cl(1) bonds due to the trans influence. The angles of the imido linkages vary from 166° to 179°. The structures of the bromo complexes are identical to the chloro complexes. In each category (cations, chloro and bromo complexes), the complex with methyl groups in the 2,4,6 positions has the angle of the imido linkage closest to 180°.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for [MoNAr(dtc)$_3$]$^+$

	I(2,4,6)	II(2,4)	III(2,6)
Mo(4)−N4	1.737(8)	1.737(7) 1.726(8)	1.736(3)
Mo(4)−S1	2.481(3)	2.508(3) 2.520(2)	2.494(1)
Mo(4)−S2	2.520(3)	2.485(3) 2.486(4)	2.519(1)
Mo(4)−S3	2.499(3)	2.498(3) 2.511(2)	2.496(1)
Mo(4)−S4	2.509(3)	2.504(3) 2.485(2)	2.505(2)
Mo(4)−S5	2.581(3)	2.586(3) 2.587(3)	2.576(2)
Mo(4)−S6	2.491(3)	2.496(3) 2.489(3)	2.493(1)
N4−C16	1.369(13)	1.383(12) 1.369(14)	1.387(5)
C16−N4−Mo(4)	177.8(6)	172.4(5) 170.5(6)	168.6(3)
N4−Mo(4)−S6	98.4(2)	100.2(3) 93.3(3)	93.9(1)
N4−Mo(4)−S5	167.0(2)	169.6(3) 162.8(3)	162.3(1)

NMR. The cations and the halogen complexes can be easily distinguished by their ^{1}H NMR spectra (Table 3). The methyl groups of the dithiocarbamate ligand in the cations form a multiplet of overlapping triplets, while only one triplet is seen in the ^{1}H spectrum of the halogen complexes. An exception is **VIII(2,6,diiso,Cl)**, which has two overlapping methyl triplets, forming a quadruplet. This indicates that the rotation of the ethyl groups of the dithiocarbamate ligand about the N−C bond may be hindered by the isopropyl substituents on the imido ligand.

The formation of an imido complex can be easily monitored by ^{14}N NMR spectroscopy. A signal between −20 and +80 ppm indicates the presence of an imido nitrogen. The starting materials, anilines and triethylamine, as mentioned above, appear around −330 ppm. The imido nitrogens of **I(2,4,6)**, **II(2,4)**, and **III(2,6)** absorb around +10 ppm and are more deshielded than the imido nitrogens in the halide complexes, which are found around −10 ppm.

In the ^{95}Mo NMR spectrum, the [Mo_6O_{19}]$^{2-}$ cluster absorbs at +125 ppm, the [Mo_8O_{26}]$^{4-}$ cluster at +20 ppm. The imido cations are found below −200 ppm. Compared to the oxo

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for $MoNAr(X)_2(dtc)_2$

	IV(2,4,6,Cl)	**V(2,3,Cl)**	**VI(2,4,Cl)**	**VII(2,6,Cl)**
Mo−N3	1.739(3)	1.735(4)	1.731(4)	1.734(5)
Mo−X1	2.4347(9)	2.4288(13)	2.4370(14)	2.431(2)
Mo−X2	2.5322(8)	2.5020(3)	2.502(2)	2.525(2)
Mo−S1	2.5244(10)	2.4990(14)	2.5013(14)	2.518(2)
Mo−S2	2.4877(8)	2.5217(14)	2.5295(14)	2.493(2)
Mo−S3	2.4880(9)	2.5027(13)	2.493(2)	2.519(2)
Mo−S4	2.5188(9)	2.514(2)	2.515(2)	2.493(2)
N3−C11	1.383(4)	1.364(12)	1.375(6)	1.379(8)
Mo−N3−C11	178.9(3)	166.4(7)	169.2(4)	177.7(4)
N3−Mo−X1	93.35(10)	95.06(13)	94.64(14)	94.3(2)
N3−Mo−X2	176.95(10)	175.54(13)	174.29(14)	177.6(2)

	VIII(2,6,diiso,Cl)	**IX(Cl)**[a]	**X(2,NH_2,Cl)**[b]	**XI(2,4,6,Br)**	**XII(2,6,Br)**
Mo−N3	1.7630(12)	1.734	1.700	1.736(10)	1.738(5)
Mo−X1	2.4600(4)	2.469(1)	2.442(14)	2.5936(13)	2.5946(8)
Mo−X2	2.5267((4)	2.467(1)	2.497(12)	2.710(2)	2.7012(8)
Mo−S1	2.5385(4)	2.512(1)	2.507(19)	2.488(3)	2.502(2)
Mo−S2	2.5359(4)	2.508(1)	2.516(24)	2.521(3)	2.517(2)
Mo−S3	2.5334((4)	2.499(1)	2.514(27)	2.494(3)	2.489(2)
Mo−S4	2.5395(4)	2.512(1)	2.515(6)	2.524(3)	2.524(2)
N3−C11	1.401(2)	1.377(6)	1.375(19)	1.391(14)	1.388(7)
Mo−N3−C11	173.83(11)	166.8(3)	178.0(11)	178.8(7)	173.5(4)
N3−Mo−X1	91.18(4)	88.6(1)	94.3(5)	92.8(2)	95.23(14)
N3−Mo−X2	176.13(4)	173.9(1)	177.8(5)	177.1(2)	176.07(14)

[a] Reference 6. [b] Reference 5.

Table 8. ^{95}Mo and ^{14}N NMR Data

compd	δ ^{95}Mo, (ppm; LW, Hz)	δ ^{14}N (ppm; LW, Hz)
I(2,4,6)	+125 (100) −218 (500)	+10 (450)
II(2,4)	+20 (250) −258 (600)	+11 (470)
III(2,6)	+123 (100) −235 (400)	+12 (400)
(2,3)	+123 (100) −271 (650)	+12 (400)
IV(2,4,6,Cl)	−174 (500)	−2 (350)
V(2,3,Cl)	−230 (500)	−8 (300)
VI(2,4,Cl)	−211 (250)	−11 (400)
VII(2,6,Cl)	−176 (500)	−6 (300)
(3,4,Cl)	−242 (800)	−21 (300)
VIII(2,6,diiso,Cl)	−163 (500)	−5 (300)
IX(Cl)	−254 (480)	−14 (200)
X(2NH_2,Cl)	−164 (400)	−19 (360)
XI(2,4,6,Br)	−129 (300)	+2 (300)
XII(2,6,Br)	−139 (350)	−5 (250)
(2,3,Br)	−196 (450)	−11 (300)
$[Mo(NC_6H_5)dtc_3]^+$	−294 (450)	−12 (300)

complex, $[MoO(dtc)_3]^+$, the molybdenum nuclei in these cations are shielded by about 300 ppm.[13]

The ^{95}Mo NMR chemical shifts for the chloro compounds range from −163 ppm for **VIII(2,6,diiso,Cl)** to −254 ppm for **IX(Cl)**; i.e., the molybdenum nuclei are less shielded than in the cations. The Mo nuclei in the bromo complexes are less shielded than the chloro complexes due to the inverse halogen dependence which has generally been observed for Mo(VI) complexes.[13] The chemical shift difference between $MoO(Cl)_2(dtc)_2$ and $MoO(Br)_2(dtc)_2$ is about 50 ppm, the same order of magnitude as observed here for the imido complexes.[13]

The ^{95}Mo NMR chemical shifts of the chloro complexes are clearly influenced by the substituents on the benzene ring of the imido ligands. **IX(Cl)**, with no substituents, has the most shielded molybdenum nucleus (−254 ppm). Methyl groups in the 3,4 (−242 ppm) and 2,3 (−230 ppm) positions cause a slight deshielding, methyl groups in the 2,4 (−211 ppm) position deshield more, and methyl groups in the 2,6 (−176 ppm) and 2,4,6 (−174 ppm) positions deshield most among the methyl groups. Isopropyl substituents in the 2,6 (−163 ppm) positions deshield more than the methyl groups. An amino group in the 2 position (−164 ppm) in **X(2,NH_2,-Cl)** has a similar effect. The same trends are found for the cations and the bromo complexes. For $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4R)]$, the effects of the substituents on the aryl ring with σ-bonding to the molybdenum have been studied earlier.[14] Electron-donating substituents like methyl groups cause shielding of the ^{95}Mo nucleus in these Mo(II) complexes, the opposite effect of what we observe for the Mo(VI) imido complexes here. This is consistent with the fact that molybdenum complexes in lower oxidation states generally show opposite responses to changes in the ligand field when compared to molybdenum complexes in the +VI oxidation state, i.e., Mo(VI) complexes show a inverse halogen dependence (chloro species more deshielded than bromo species) while Mo(II) complexes show a normal halogen dependence.[13]

In Figure 6, the ^{95}Mo NMR chemical shifts for the chloro complexes (**IV**−**X**) are plotted versus the bond angles of their imido linkages. The complexes with imido linkages close to 180° have the least shielded molybdenum nuclei. With the possible exception of **VIII(2,6,diiso,Cl)**, where the methyl protons of the dithiocarbamate ligand are not

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(13) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

(14) Brownlee, R. T. C.; Masters, A. F.; O'Connor, M. J.; Wedd, A. G.; Kimlin, H. A.; Cotton, J. D. *Org. Magn. Reson.* **1982**, *20*, 73.

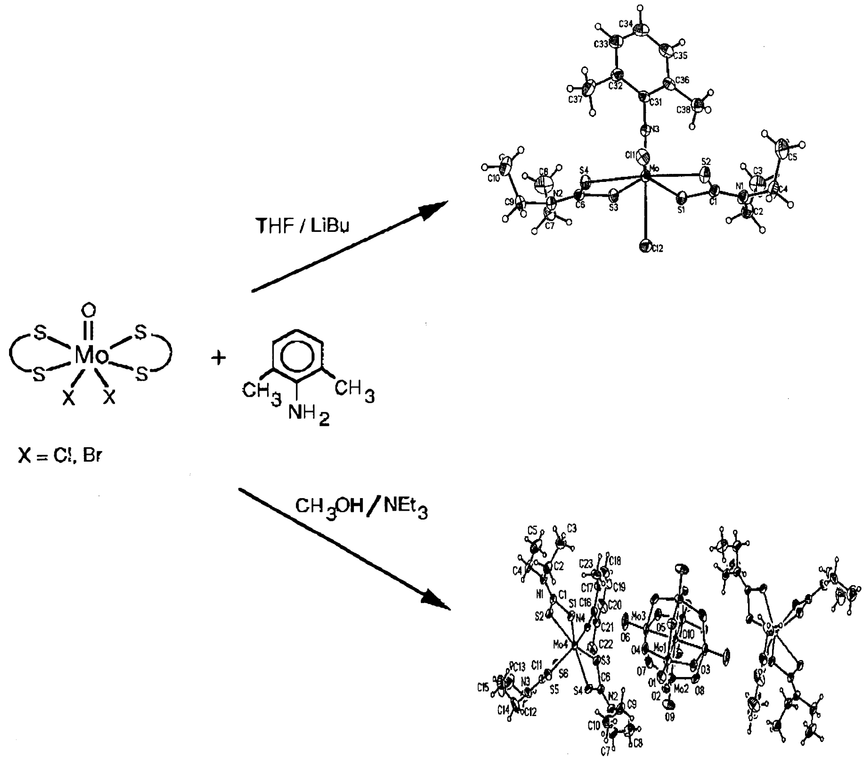

Figure 5. Synthetic routes for the $[MoNAr(dtc)_3]_2[Mo_6O_{19}]$ and $MoNAr(X)_2(dtc)_2$ complexes.

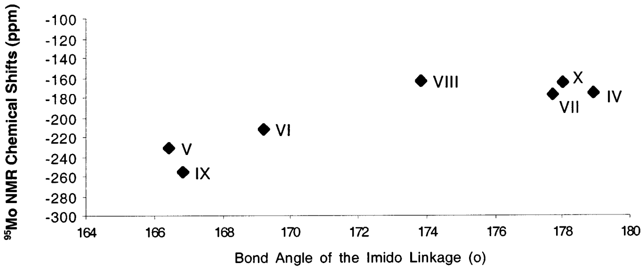

Figure 6. Angles of the imido linkages vs ^{95}Mo NMR chemical shifts.

equivalent, steric hindrance due to the substituents on the aromatic ring of the imido ligand does not seem to be a determining factor for the angle of the imido linkage. All chloro complexes have the same space group, $P2_1/c$, with four molecules per unit cell, so packing does not seem to be the main factor responsible for the difference in the bond angles of the imido linkages, i.e., in these compounds the angles of the solid structures correlate with the ^{95}Mo NMR chemical shifts in solution.

Conclusions

Depending on the solvent and base used, the reaction of $MoO(X)_2(dtc)_2$ compounds with anilines that contain alkyl substituents on the phenyl ring yields ionic complexes of the type $[MoNAr(dtc)_3]_2[Mo_6O_{19}]$ and $MoNAr(dtc)_3]_4$-$[Mo_8O_{26}]$ or halogen complexes of the type $MoNAr(X)_2$-$(dtc)_2$. The position of the alkyl groups on the aryl group of the imido ligand influences the ^{95}Mo NMR chemical shift and the angle of the imido linkage. Alkyl groups in the 2,6 and 2,4,6 positions have the most deshielding effect on the ^{95}Mo nucleus. The deshielded nuclei generally have bond angles of the imido linkage that are close to 180°.

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Supporting Information Available: Tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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