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Chemistry of Molybdenum and Tungsten Bis[hydrazido(2−)] Complexes. Preparations and X-ray Crystal Structures of $[Mo(NNMePh)_2(S_2CNMe_2)_2]$, $[Mo(NNPh_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$, $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4\cdot CH_2Cl_2$, and $[Mo(NNMe_2)_2(bpy)_2][BPh_4]_2\cdot CH_2Cl_2$

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Complexes of the type $[Mo(NNR_2)_2(S_2CNR'_2)_2]$ [R = MePh, Ph_2; $R'_2 = Me_2, Et_2, Ph_2, (CH_2)_5$] were prepared from $[MoO_2(S_2CNR'_2)_2]$ and R_2NNH_2. The structures of two derivatives were determined by X-ray diffraction. Crystal data: for $R_2 = Ph_2$ and $R'_2 = Me_2$, space group $P2/a$, $a = 17.054$ (3) Å, $b = 12.463$ (2) Å, $c = 14.030$ (4) Å, $\beta = 141.57$ (7)°, $V = 1853.34$ Å^3, $Z = 2$, $R = 0.074$ from 2905 reflections; for R_2 = MePh and $R'_2 = Me_2$, space group $A2/a$, $a = 10.563$ Å, $b = 16.990$ Å, $c = 14.269$ Å, $\beta = 87.78$ (8)°, $V = 2558.9$ Å^3, $Z = 4$, $R = 0.083$ from 1732 reflections. Both are pseudooctahedral with nearly linear cis hydrazido(2−) ligands. The complexes $[MCl(NNMe_2)_2(PR_3)_2]Cl$ (M = Mo, W, $PR_3 = PPh_3, PPh_2Me, PMe_2Ph$) were prepared from $[MCl_4(PR_3)_2]$ and $Me_3SiNHNMe_2$ in CH_3CN. The structure of the complex with M = Mo, $PR_3 = PPh_3$ was determined by X-ray diffraction. Crystal data: monoclinic space group, $P2_1/n$, $a = 20.996$ (2) Å, $b = 17.719$ (5) Å, $c = 16.409$ (3) Å, $\beta = 93.16$ (1)°, $V = 6095.1$ (3) Å^3, $Z = 4$, $R = 0.046$ from 4938 reflections. The cation is trigonal bipyramidal with apical PPh_3 groups and the hydrazido groups in the equatorial plane. The complex with M = Mo, $PR_3 = PPh_3$ reacts with bipyridyl to give $[Mo(NNMe_2)_2(bpy)_2]^{2+}$. The structure of the bis(tetraphenylborate) salt was determined by X-ray diffraction: space group $P2_1/c$, $a = 13.487$ (3) Å, $b = 13.875$ (3) Å, $c = 35.133$ (5) Å, $\beta = 100.18$ (1) Å, $V = 6471.00$ Å^3, $Z = 4$, $R = 0.069$ from 4253 reflections. The cation is pseudooctahedral again with nearly linear cis hydrazido groups.

Introduction

Hydrazido(2−) complexes are currently of considerable interest as they are proven intermediates in the protonation of dinitrogen coordinated to a molybdenum–tertiary phosphine site to ammonia.[1] Moreover dialkylhydrazido(2−) complexes can be prepared by the alkylation of molybdenum and tungsten bis(diphosphine)–dinitrogen complexes.[2] As part of a program aimed at defining the structural parameters and chemical reactivity of hydrazido(2−) complexes, we have synthesized such complexes with a range of different coligands. We here report the synthesis and structural characterization of bis[hydrazido(2−)] complexes with dithiocarbamato, tertiary phosphine, or bipyridyl coligands. Bis[hydrazido(2−)] derivatives represent a new type of complex, and we have determined several X-ray structures to explore the influence of coligands on the hydrazido ligands and the effects of the competition between two such electronically flexible, strongly π-bonding ligands. In view of the quite different synthetic routes employed, these complexes are discussed separately.

Experimental Section

Synthetic and Chemical Characterization of the Complexes. Reactions were carried out in dried solvents under an atmosphere of dinitrogen by using conventional Schlenk techniques. Unless otherwise indicated recrystallizations were performed in air at room temperature with use of reagent grade solvents. The following complexes were prepared by literature methods: $[MoO_2(S_2CNR_2)_2]$[12] ($R_2 = Me_2Et_2, (CH_2)_5$), $[Mo(NNMePh)O(S_2NMe_2)_2]$,[13] $[MoCl_4(PR_3)_2]$ (PR_3 = PPh_3, PPh_2Me), $[MoOCl_2(PMe_2Ph)_3]$.[14] $[WCl_4(PPh_3)_2]$ was prepared by a slight variation in the literature method described below. The hydrazines Me_2NNH_2, $PhMeNNH_2$, and $Ph_2NNH_2\cdot HCl$ were obtained commercially and used without purification.

Carbon, hydrogen, and nitrogen analyses were carried out by Mr. and Mrs. A. Olney at the University of Sussex or Mr. P. E. Meadows in the Unit of Nitrogen Fixation. Infrared spectra were recorded in the range 450–4000 cm^{-1} as Nujol or hexachlorobutadiene mulls on KBr plates with a Pye Unicam SP2000 spectrophotometer. ^{1}H NMR spectra were recorded at 100 MHz with a JEOL PS100 (at 90 MHz) or a JEOL FX 90Q instrument and with tetramethylsilane as internal standard.

Analytical data and proton NMR spectra are available as supplementary material.

Bis(dimethyldithiocarbamato)bis[diphenylhydrazido(2−)]molybdenum(VI) (I). $[MoO_2(S_2CNMe_2)_2]$ (0.5 g, 1.35 × 10^{-3} mol), $Ph_2NNH_2\cdot HCl$ (0.08 g, 3.61 × 10^{-3} mol), and triethylamine (0.35 g, 3.5 × 10^{-3} mol) were heated under reflux in methanol (40 mL) for 1 h. After the mixture cooled to room temperature, the complex was filtered off in air as a microcrystalline yellow solid. This was recrystallized as fine yellow needles from dichloromethane–methanol (yield 0.55 g, 78%). The complexes $[Mo(NNPh_2)_2(S_2CNEt_2)_2]$ (II), $[Mo(NNPh_2)_2(S_2CNMePh)_2]$ (III), $[Mo(NNMePh)_2(S_2CNMe_2)_2]$ (IV), $[Mo(NNMePh)_2(S_2CNEt_2)_2]$ (V), $[Mo(NNMePh)_2(S_2CNMePh)_2]$ (VI), and $[Mo(NNMe_2)(NNMePh)(S_2CNMe_2)_2]$ (VII) were prepared similarly by using the appropriate bis(dithiocarbamato)dioxomolybdenum complex and hydrazine.

Bis(dimethyldithiocarbamato)[dimethylhydrazido(2−)][methyl-

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Table I. Experimental Details of the X-ray Diffraction Studies of $[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$ and $[Mo(N_2PhMe)_2(S_2CNMe_2)_2]$[a]

(A) Crystal Parameters at 23 °C

compd	$[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$	$[Mo(N_2PhMe)_2(S_2CNMe_2)_2]$
a, Å	17.054 (3)	10.563
b, Å	12.463 (2)	16.990
c, Å	14.030 (4)	14.269
β, deg	141.57 (7)	87.78 (9)
V, Å^3	1853.34	2558.9
systematic absences	$h0l$, $h = 2n + 1$	hkl, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$
space group	$P2/a$	$A2/a$
Z	2	4
ρ(calcd), g/cm^3	1.36	1.50
ρ(obsd),[b] g/cm^3	1.35 (2)	1.51 (2)
F(000)	784.0	1184.0
mol wt	758.9	567.7

(B) Collection of Intensity Data

instrument: Seimens' AED diffractometer
radiation: Mo Kα, $\lambda = 0.7107$ Å
scan technique: coupled θ(cryst)-2θ(counter)
scan range: 170° (symmetric, plus Kα_1-Kα_2 dispersion)
scan rate: variable, 0.5°/min to 2.5°/min
2θ range: 1.5–43°
bkgd measmts: stationary cryst, stationary counter at each end of the 2θ scan range; time of bkgd count set equal to time of peak count
stds: 3 reflctns every 50 data

(C) Treatment of Intensity Data

compd	$[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$	$[Mo(N_2PhMe)_2(S_2CNMe_2)_2]$
	data corrected for background, attenuators, Lorentz, and polarization effects in the usual fashion	
abs coeff, cm^{-1}	5.94	8.33
abs cor	none ($T_{max}/T_{min} = 1.09$)	none ($T_{max}/T_{min} = 1.11$)
obsd data	3679 unique reflctns, of which 2905 having $I \geqslant 2.58\sigma(I)$ were used in the refinement	2210 unique reflctns, of which 1732 having $I \geqslant 2.58\sigma(I)$ were used in the refinement
structure soln	Mo position from a sharpened Patterson map; all other atoms located on subsequent Fourier maps	
atomic scattering factors	from ref 11	
anomalous dispersion	both the real and imaginary components of anomalous dispersion included for Mo and S	
final discrepancy factors	$R = 0.074$, $R_w = 0.095$	$R = 0.083$, $R_w = 0.104$
goodness of fit	1.75	1.83

[a] Footnotes are available as supplementary materials. See also ref 5.

phenylhydrazido(2−)]molybdenum(VI) (VII). $[MoO(NNMePh)(S_2CNMe_2)_2]$ (1.0 g, 2.1 × 10^{-3} mol) and dimethylhydrazine (1.0 g, 1.6 × 10^{-2} mol) were heated under reflux in methanol (40 mL) for 0.5 h. The volume of the reaction solution was reduced to 20 mL under reduced pressure and the product filtered off in air as a microcrystalline orange-yellow solid. This was recrystallized as orange-yellow rhombs from dichloromethane–diethyl ether (yield 0.7 g, 73%).

(Trimethylsilyl)dimethylhydrazine. Dimethylhydrazine (60 g) in diethyl ether (1 L) was treated dropwise at room temperature with a mixture of trimethylchlorosilane (108 g) and diethyl ether (100 mL), with vigorous stirring over 2 h. The suspension was stirred overnight and filtered and the precipitate washed thoroughly with diethyl ether (250 mL). The filtrate and washup were distilled to remove diethyl ether, and the residue was distilled to give the hydrazine boiling point of 120 °C at atomosphere pressure (yield 57 g, 43%).

Bis[dimethylhydrazido(2−)]chlorobis(triphenylphosphine)molybdenum(VI) Chloride (VIII). $[MoCl_4(PPh_3)_2]$ (5.0 g, 6.5 × 10^{-3} mol) and $Me_3SiNHNMe_2$ (3.5 g, 10^{-2} mol) were stirred in dry acetonitrile (40 mL) for 3 h to give a yellowish brown solution. Evaporation of the reaction solution to 10 mL gave the complex as a pale yellow crystalline solid (3.5 g, 66%). Further less pure product can be obtained by addition of diethyl ether to the filtrate remaining after removal of the first crop of product.

Tetrachlorobis(triphenylphosphine)tungsten(IV). WCl_6 (10 g, 2.5 × 10^{-2} mol) was partially dissolved in dichloromethane (60 mL), and PPh_3 (20 g, 7.6 × 10^{-2} mol) was added in small portions. The complex precipitated from solution as small orange-yellow crystals (yield 11.5 g, 51%). Yields are lower than the literature method with amalgamated zinc, but the product does not have to be separated from excess reductant.

Bis[dimethylhydrazido(2−)]chlorobis(dimethylphenylphosphine)molybdenum(VI) Chloride (X). $[MoOCl_2(PMe_2Ph)_3]$ (1.0 g, 1.6 × 10^{-3} mol) and $Me_3SiNHNMe_2$ (0.43 g, 3.2 × 10^{-3} mol) were heated under reflux in acetonitrile (40 mL) to give a clear yellow solution. This was evaporated to 5 mL under reduced pressure and the complex precipitated by addition of diethyl ether. It was recrystallized from dichloromethane–diethyl ether as yellow needles in 50% yield.

Bis[dimethylhydrazido(2−)]bis(bipyridyl)molybdenum(VI) Tetraphenylborate. $[MoCl(NNMe_2)_2(PPh_3)_2]Cl$ (1.0 g, 1.24 × 10^{-3} mol) and bipyridyl (1.0 g, 6.4 × 10^{-3} mol) were stirred in methanol (40 mL) at 50 °C to give a clear orange solution. Addition of sodium tetraphenylborate (1.5 g, 3.4 × 10^{-3} mol) precipitated the complex as an orange solid which was recrystallized as orange rhombs from dichloromethane–methanol.

X-ray Crystal Structures of $[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]$, $[Mo(N_2MePh)_2(S_2CNMe_2)_2]$, $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4\cdot CH_2Cl_2$, and $[Mo(NNMe_2)_2(bpy)_2]BPh_4\cdot CH_2Cl_2$. The details of data collection and structure solutions and refinements are presented in Tables I, IV, and VIII. A full description of the experimental methodology may be found in ref 5 and 9. Final atomic positional parameters appear in Tables II, V, and IX for $[Mo(N_2R'_2)_2(S_2CNR_2)_2]$, $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4$, and $[Mo(bpy)_2(N_2Me_2)_2]BPh_4$, respectively.

Results and Discussion

Complexes of the Type $[Mo(NNR_2)_2(S_2CNR'_2)_2]$. (a) Preparations and Chemical Properties. We have previously reported that reaction of the complexes $[MoO_2(S_2CNR'_2)_2]$ with *N,N*-dimethylhydrazine generates the oxohydrazido complexes $[MoO(NNMe_2)(S_2CNR'_2)_2]$.[3] If however the N,N-disubstituted hydrazine bears a phenyl substituent, the second oxo group is also replaced to yield a bis[hydrazido(2−)] complex (eq 1).

$$[MoO_2(S_2CNR'_2)_2] + R_2NNH_2 \xrightarrow[\text{reflux}]{\text{MeOH}} [Mo(NNR_2)_2(S_2CNR'_2)_2] \quad (1)$$

$$R'_2 = Me_2, Et_2, (CH_2)_5;\ R_2 = MePh, Ph_2$$

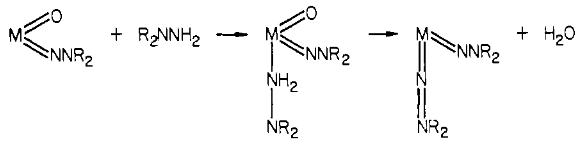
The oxo–hydrazido complex $[MoO(NNMe_2)(S_2CNMe_2)_2]$ does not give a bis(dimethylhydrazido) complex even on

Table II. Atomic Positional Parameters[a]

atom[b]	x	y	z	atom[b]	x	y	z
			(a) $[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$				
Mo	0.2500	−0.1303 (1)	0.0000	C7	0.0179 (9)	−0.1957 (8)	−0.6372 (9)
S1	0.0183 (1)	−0.0986 (2)	−0.2092 (2)	C8	−0.0046 (8)	−0.1433 (8)	−0.5748 (9)
S2	0.1956 (2)	0.0376 (2)	0.0603 (2)	C9	0.0564 (6)	−0.1736 (7)	−0.4332 (8)
N1	−0.0546 (5)	0.0625 (6)	−0.1638 (7)	C10	0.2477 (7)	−0.3981 (6)	−0.1481 (9)
N2	0.2238 (4)	−0.2152 (5)	−0.1259 (6)	C11	0.1723 (12)	−0.4862 (9)	−0.2448 (15)
N3	0.2004 (5)	−0.2904 (5)	−0.2108 (6)	C12	0.2237 (21)	−0.5927 (11)	−0.1751 (29)
C1	0.0430 (6)	0.0080 (7)	−0.1083 (8)	C13	0.3435 (27)	−0.5991 (19)	−0.0226 (32)
C2	−0.0372 (9)	0.1557 (8)	−0.0856 (12)	C14	0.4167 (22)	−0.5092 (18)	0.0672 (22)
C3	−1.873 (6)	0.0327 (11)	−0.3136 (10)	C15	0.3688 (10)	−0.4085 (11)	0.0021 (10)
C4	0.1370 (5)	−0.2621 (6)	−0.3575 (6)	C16	0.2500 (0)	0.3874 (16)	0.5000 (0)
C5	0.1612 (8)	−0.3187 (8)	−0.4179 (9)	C17	0.2911 (42)	0.3226 (27)	0.4576 (48)
C6	0.0982 (9)	−0.2849 (9)	−0.5608 (10)	O	0.2500 (0)	0.4860 (17)	0.5000 (0)
			(b) $[Mo(N_2PhMe)_2(S_2CNMe_2)_2]$				
Mo	0.25000	0.15645 (9)	0.00000	C3	0.036 (1)	0.1433 (8)	0.298 (1)
S1	0.0177 (2)	0.1795 (2)	0.0177 (2)	C4	0.347 (1)	0.0607 (8)	0.2435 (9)
S2	0.1944 (3)	0.2778 (2)	0.112 (2)	C5	0.326 (2)	0.0169 (9)	0.326 (1)
N1	0.0566 (9)	0.2081 (6)	0.3634 (7)	C6	0.400 (2)	0.043 (1)	0.406 (1)
N2	0.2720 (9)	0.0939 (6)	0.0991 (7)	C7	0.480 (2)	0.105 (1)	0.404 (1)
N3	0.2865 (9)	0.0410 (6)	0.1635 (7)	C8	0.497 (2)	0.148 (1)	0.323 (1)
C1	0.038 (1)	0.2548 (7)	0.0957 (8)	C9	0.431 (1)	0.1246 (9)	0.243 (1)
C2	0.189 (1)	0.231 (1)	0.378 (1)	C10	0.252 (2)	0.4609 (9)	0.356 (1)

[a] Estimated standard deviations are given in parentheses. [b] Numbering schemes are given in Figures 1 and 2. C16, C17, and O in I refer to the acetone molecule of crystallization.

Scheme I



R_2 = MePh or Ph_2

prolonged treatment with the hydrazine in a high-boiling solvent. However both the oxo and $NNMe_2$ groups are replaced on reaction with phenylmethylhydrazine with formation of $[Mo(NNMePh)_2(S_2CNMe_2)_2]$ and dimethylhydrazine (identified by GLC). However the mixed species $[Mo(NNMe_2)(NNMePh)(S_2CNMe_2)_2]$ can be prepared from reaction of $[MoO(NNMePh)(S_2CNMe_2)_2]$ with dimethylhydrazine. This indicates that the basicity of the hydrazine plays a crucial role in dictating the reaction pathway. The reactions presumably involve initial coordination of the hydrazine followed by proton transfer to the most basic site in the molecule which may be either oxygen or coordinated hydrazines (see Scheme I) depending on the substituents on the incoming hydrazine and the coordinated hydrazide.

The mechanism of reaction of monosubstituted hydrazines with $[MoO_2(S_2CNR_2)_2]$ to give the bis(diazenido) complexes $[Mo(N_2Ph)_2(S_2CNR_2)_2]$ has been briefly discussed earlier.[4] It differs considerably from the disubstituted hydrazines above, in that the bis[hydrazido(2−)] complexes $[Mo(NNHR)_2(S_2CNR_2)_2]$ are not formed as isolable intermediates. Instead the diazenido–hydrazido(1−) species $[Mo(NHNHR)(N_2R)(S_2CNR_2)_2]$ is the intermediate that undergoes aerobic oxidation to the bis(diazenido) complex for R = aryl. The X-ray crystal structure of the derivative with R = CO_2Me has been determined and will be reported in detail elsewhere.

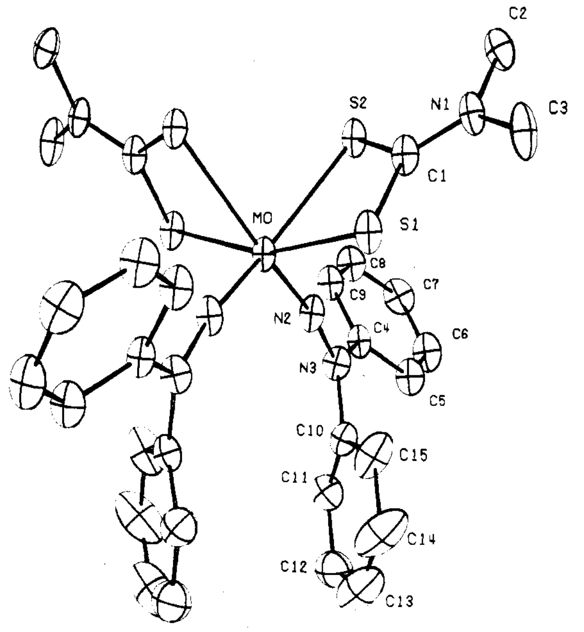


Figure 1. Perspective view of the molecule $[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]$, I, showing the atom-labeling scheme.

The disubstituted hydrazido(2−) complexes prepared as above are isolated as air-stable yellow crystalline solids, which are monomeric and nonconducting in 1,2-dichloromethane solution. The ^1H NMR spectra at room temperature of complexes I, IV, and VII consist of singlets for the dimethyldithiocarbamato groups, indicating that the complexes are fluxional in solution. In complex IV at 0 °C the dithiocarbamate methyls are resolved into two singlets, consistent with the cis arrangement of the hydrazido(2−) ligands, confirmed by X-ray structure (see below). Increasing the bulk of the hydrazido substituents in complex I raises the coalescence temperature for the dithiocarbamato alkyls from 0 to 20 °C.

The bis[hydrazido(2−)] complexes react rapidly with acids (eq 2) analogously to the oxo–hydrazido(2−) complexes as

$$[Mo(NNR_2)_2(S_2CNR'_2)_2] + 3HX \rightarrow [MoX_2(NNR_2)(S_2CNR_2)_2] + R_2NNH_3X \quad (2)$$

already reported.[5] The hydrazine hydrochloride can be isolated from reaction 2 in nearly quantitative yield. The bis(hydrazido) complexes react with 1 equiv of acid to give hydrazido(1−)–hydrazido(2−) complexes, to be described elsewhere.

(b) Structures of $[Mo(N_2R_2)_2(S_2CNR'_2)_2]$ Complexes. Final positional and thermal parameters for complexes I and IV are given in Table II and the supplementary material. Table III contains the relevant bond lengths and valence angles for the complexes, Table V presents the coefficients of selected

Table III. Selected Bond Lengths (Å) and Angles (Deg)[a]

(a) $[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]\cdot Me_2CO$

Mo–S1	2.493 (2)	C5–C6	1.40 (2)
Mo–S2	2.680 (3)	C6–C7	1.40 (1)
Mo–N2	1.790 (8)	C7–C8	1.37 (2)
S1–C1	1.74 (1)	C8–C9	1.39 (2)
S2–C1	1.691 (6)	C10–C11	1.40 (1)
C1–N1	1.34 (1)	C10–C15	1.380 (9)
N1–C2	1.46 (1)	C11–C12	1.45 (2)
N1–C3	1.492 (8)	C12–C13	1.38 (3)
N2–N3	1.31 (1)	C13–C14	1.39 (3)
N3–C4	1.43 (1)	C14–C15	1.40 (1)
N3–C10	1.45 (1)	O–C16	1.23 (3)
C4–C5	1.39 (1)	C16–C17	1.47 (3)
C4–C9	1.40 (1)		

S1–Mo–S2	68.08 (6)	S1–C1–S2	115.6 (6)
S1–Mo–S2′	97.21 (7)	S1–C1–N1	121.0 (4)
S1–Mo–S1′	161.75 (8)	S2–C1–N1	123.4 (5)
S2–Mo–S2′	77.3 (1)	C1–N1–C2	122.4 (5)
S1–Mo–N2	89.5 (2)	C1–N1–C3	116.6 (7)
S1–Mo–N2′	101.3 (2)	C2–N1–C3	121.0 (8)
S2–Mo–N2	153.2 (2)	N2–N3–C4	118.8 (5)
S2–Mo–N2′	91.8 (3)	N2–N3–C10	118.7 (7)
N2–Mo–N2′	107.5 (3)	C4–N3–C10	122.3 (7)
Mo–N2–N3	169.9 (8)	C–C–C, ring I, av	120.0 (13)
Mo–S1–C1	90.7 (2)	C–C–C, ring II, av	120.0 (13)
Mo–S2–C1	85.6 (4)		

(b) $[Mo(N_2PhMe)_2(S_2CNMe_2)_2]$

Mo–S1	2.488 (3)	N3–C4	1.37 (1)
Mo–S2	2.662 (4)	N3–C10	1.45 (2)
Mo–N2	1.790 (9)	C4–C5	1.41 (2)
S1–C1	1.72 (1)	C4–C9	1.40 (2)
S2–C1	1.7[illegible] (1)	C5–C6	1.42 (2)
N1–C1	1.30 (2)	C6–C7	1.38 (2)
N1–C2	1.47 (2)	C7–C8	1.36 (3)
N1–C3	1.48 (2)	C8–C9	1.45 (2)
N2–N3	1.30 (1)		

S1–Mo–S2	67.9 (1)	Mo–S2–C1	86.1 (4)
S1–Mo–S2′	97.7 (1)	S1–C1–S2	113.8 (6)
S1–Mo–S1′	161.9 (1)	S1–C1–N1	122.5 (9)
S2–Mo–S2′	78.4 (1)	S2–C1–N1	123.7 (10)
S1–Mo–N2	90.9 (3)	C1–N1–C2	121.3 (10)
S1–Mo–N2′	99.8 (3)	C1–N1–C3	122.1 (11)
S2–Mo–N2	154.4 (3)	C2–N–C3	116.6 (11)
S2–Mo–N2′	91.0 (3)	N2–N3–C4	119.5 (10)
N2–Mo–N2′	107.2 (5)	N2–N3–C10	112.9 (11)
Mo–N2–N3	172.6 (8)	C4–N3–C10	122.4 (12)
Mo–S1–C1	91.9 (4)	C–C–C, ring, av	120.0 (17)

[a] Estimated standard deviations are given in parentheses.

least-squares planes, and the dihedral angles between planes are available as supplementary material. Perspective views of the molecular geometries of I and IV are given in Figures 1 and 2, respectively.

In each structure, I and IV, the molecule lies on a site of crystallographic 2-fold symmetry, the axis passing through the Mo atom to produce C_{2v} molecular point symmetry. The atoms of the basic asymmetric unit are labeled in Figures 1 and 2; atoms in the remaining half are related to the basic unit via rotation about the crystallographic axes at $(^1/_4, y, 0)$ in each case and are not labeled in the figures. The coordinates of the halves of the molecules are related via the transformation $[x', y', z'] = [^1/_2 - x, y, -z]$.

The stereochemistries of the Mo atoms of the two structures are identical; both I and IV exhibit cis configuration of the hydrazido ligands, and examination of Table III reveals identical Mo–ligand bond distances and valence angles, within the experimental error of the analyses.

The Mo–N distances in I and IV are relatively short, (1.790 (8) Å in both) and are very similar to those observed for other hydrazido and diazenido complexes where Mo–N multiple bonding has been postulated. Further evidence for Mo–N multiple bonding may be drawn from the significantly longer Mo–S bond distance for the S donor trans to the hydrazido group, suggesting a considerable trans influence similar to that observed in other Mo complexes where multiply bonded donor groups are present. The Mo–S distances for the sulfur trans to the hydrazido group are ca. 0.2 Å longer than those observed for cis Mo–S bond lengths, and the $Mo–S_4$ geometry is most similar to that observed for $[MoO_2(S_2CN\text{-}n\text{-}Pr_2)_2]$, a complex also displaying local C_{2v} point symmetry.

The overall linear geometry of both the hydrazido ligands in I and IV is similar to that in other hydrazido complexes such as $[MoO(NNMe_2)(S_2CNMe_2)_2]$[3] and [Mo(NNEtPh)(S₂CN-

Table IV. Summary of Crystal Data and Experimental Details for the Structural Study of $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4\cdot CH_2Cl_2$

(A) Crystal Parameters[a] at 23 °C

$a = 20.996$ (2) Å	$V = 6095.1$ (3) Å^3
$b = 17.718$ (5) Å	space group: $P2_1/n$
$c = 16.409$ (3) Å	$Z = 4$
$\alpha = 90.00°$	$\rho_{calcd} = 1.28$ g/cm^3
$\beta = 93.16$ (1)°	$\rho_{obsd} = 1.29$ g/cm^3 (flotation)

(B) Measurement of Intensity Data

cryst dimens: 0.21 × 0.24 × 0.18 mm
instrument: Nonius CAD4 automated diffractometer
radiation: Mo Kα (λ = 0.710 73 Å)
scan mode: ω
scan rate: variable, within the limits of 2 and 28°/min
scan range: $3° \leqslant 2\theta \leqslant 40°$
bkgd measmt: 10 s at either end of the 2θ scan range
no. of reflctns collected: 6835

(C) Reduction of Intensity Data and Summary of Structure Solution and Refinement

data corrected for background, attenuators, Lorentz and polariztion effects in the usual fashion
abs coeff: 4.22 cm^{-1}
abs cor: none ($T_{max}/T_{min} = 1.16$)
obsd data: 4328 with $F_o \geqslant 2.58\sigma(F_o)$
structure soln: Mo atomic position from sharpened Patterson map; all other nonhydrogen atoms located from subsequent difference Fourier maps
atomic scattering factors: from ref 11
anomalous dispersion: both real and imaginary components of the anomalous scattering included for Mo, P, and Cl
final discrepancy factors: $R = 0.046$, $R_w = 0.048$
goodness of fit: 1.21

[a] All experimental conditions were similar to those described in ref 5.

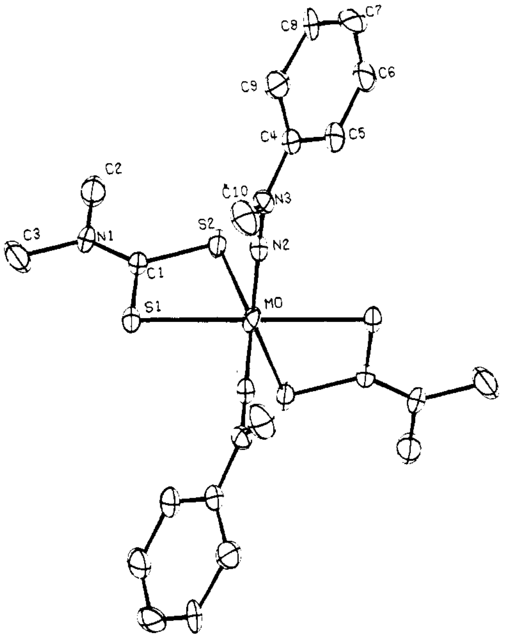


Figure 2. Perspective view of the molecule $[Mo(N_2MePh)_2(S_2CNMe)_2]$, IV, showing the atom-labeling scheme.

Table V. Final Positional Parameters for $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4 \cdot CH_2Cl$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	0.28429 (2)	0.30052 (2)	0.33032 (2)	C33	0.0681 (6)	0.1485 (9)	0.3811 (8)
Cl1	0.29978 (7)	0.43031 (8)	0.29510 (10)	C34	0.0772 (6)	0.0902 (7)	0.3294 (11)
P1	0.40304 (6)	0.29986 (7)	0.36398 (8)	C35	0.1092 (4)	0.0972 (6)	0.2640 (8)
P2	0.16973 (6)	0.31418 (8)	0.27650 (9)	C36	0.1359 (3)	0.1661 (4)	0.2443 (5)
N1	0.2639 (2)	0.2818 (2)	0.4304 (3)	C37	0.2387 (3)	0.1818 (4)	0.5179 (6)
N2	0.2496 (2)	0.2599 (3)	0.5022 (4)	C38	0.2463 (4)	0.3160 (5)	0.5668 (4)
N3	0.2927 (2)	0.2172 (2)	0.2731 (3)	C39	0.3166 (5)	0.1333 (8)	0.1701 (8)
N4	0.2956 (2)	0.1484 (4)	0.2508 (4)	C40	0.2853 (4)	0.0871 (3)	0.3062 (7)
C1	0.4464 (2)	0.3396 (3)	0.2823 (3)	B	0.7731 (3)	0.4871 (3)	0.2582 (4)
C2	0.4994 (3)	0.3850 (3)	0.2964 (4)	C41	0.7173 (3)	0.5080 (3)	0.1911 (4)
C3	0.5316 (3)	0.4123 (4)	0.2301 (6)	C42	0.7172 (4)	0.4904 (4)	0.1105 (6)
C4	0.5131 (4)	0.3953 (4)	0.1532 (5)	C43	0.6661 (7)	0.5121 (5)	0.0535 (6)
C5	0.4611 (4)	0.3505 (4)	0.1389 (4)	C44	0.6180 (6)	0.5523 (7)	0.0774 (9)
C6	0.4276 (3)	0.3241 (3)	0.2036 (4)	C45	0.6170 (4)	0.5721 (5)	0.1562 (8)
C7	0.4340 (2)	0.2042 (3)	0.3761 (3)	C46	0.6642 (3)	0.5512 (3)	0.2119 (4)
C8	0.4086 (2)	0.1582 (3)	0.4332 (4)	C47	0.8207 (2)	0.4208 (3)	0.2254 (3)
C9	0.4275 (3)	0.0834 (4)	0.4406 (4)	C48	0.8123 (3)	0.3445 (4)	0.2432 (4)
C10	0.4724 (4)	0.0563 (4)	0.3913 (5)	C49	0.8538 (4)	0.2898 (4)	0.2150 (4)
C11	0.4990 (4)	0.1022 (4)	0.3370 (5)	C50	0.9028 (3)	0.3074 (4)	0.1703 (4)
C12	0.4787 (3)	0.1758 (3)	0.3282 (4)	C51	0.9125 (3)	0.3815 (4)	0.1521 (4)
C13	0.4310 (2)	0.3472 (3)	0.4573 (3)	C52	0.8716 (3)	0.4360 (3)	0.1793 (4)
C14	0.3964 (3)	0.4028 (4)	0.4897 (4)	C53	0.7398 (2)	0.4580 (3)	0.3393 (4)
C15	0.4169 (3)	0.4381 (4)	0.5608 (5)	C54	0.6914 (3)	0.4027 (3)	0.3331 (4)
C16	0.4726 (3)	0.4172 (4)	0.6001 (4)	C55	0.6644 (3)	0.3720 (3)	0.3998 (5)
C17	0.5081 (3)	0.3622 (4)	0.5689 (4)	C56	0.6817 (3)	0.3958 (4)	0.4770 (5)
C18	0.4877 (3)	0.3277 (4)	0.4975 (4)	C57	0.7274 (3)	0.4515 (4)	0.4863 (4)
C19	0.1590 (2)	0.3308 (3)	0.1671 (3)	C58	0.7547 (3)	0.4810 (3)	0.4199 (4)
C20	0.1015 (3)	0.3223 (4)	0.1248 (4)	C59	0.8175 (2)	0.5634 (3)	0.2761 (3)
C21	0.0942 (3)	0.3398 (4)	0.0430 (4)	C60	0.8703 (3)	0.5617 (3)	0.3308 (4)
C22	0.1424 (4)	0.3625 (5)	0.0016 (4)	C61	0.9073 (3)	0.6250 (4)	0.3489 (4)
C23	0.1982 (5)	0.3739 (6)	0.0426 (6)	C62	0.8932 (4)	0.6917 (4)	0.3096 (6)
C24	0.2061 (3)	0.3583 (5)	0.1258 (5)	C63	0.8435 (4)	0.6955 (3)	0.2538 (5)
C25	0.1218 (2)	0.3851 (3)	0.3241 (4)	C64	0.8056 (3)	0.6324 (3)	0.2370 (4)
C26	0.1437 (3)	0.4218 (3)	0.3908 (4)	C65[b]	0.9031 (15)	0.3197 (14)	0.4251 (10)
C27	0.1050 (4)	0.4730 (4)	0.4284 (4)	C65′[c]	0.8572 (13)	0.3166 (12)	0.4508 (10)
C28	0.0461 (4)	0.4873 (4)	0.4016 (5)	Cl2[b]	0.8444 (5)	0.2401 (5)	0.4408 (4)
C29	0.0238 (4)	0.4508 (7)	0.3346 (6)	Cl3[b]	0.9507 (3)	0.3232 (4)	0.4960 (4)
C30	0.0627 (4)	0.4017 (6)	0.2948 (5)	Cl2′[c]	0.9228 (9)	0.3039 (12)	0.4677 (15)
C31	0.1277 (2)	0.2267 (3)	0.2938 (4)	Cl3′[c]	0.8217 (5)	0.2445 (5)	0.4859 (7)
C32	0.0945 (4)	0.2183 (5)	0.3616 (5)				

[a] Estimated standard deviations in the least significant digits given are in parentheses. [b] Population parameter set at 0.6. [c] Population parameter set at 0.4.

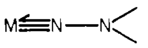
Table VI. Selected Bond Lengths (Å) for $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4 \cdot CH_2Cl_2$

Mo–Cl1	2.398 (1)	N4–C39	1.444 (9)
Mo–P1	2.524 (1)	N4–C40	1.440 (11)
Mo–P2	2.528 (1)	P–C, av	1.815 (5)
Mo–N1	1.752 (5)	C–C, ring, av	1.363 (7)
Mo–N3	1.763 (4)	P–C, av	1.815 (5)
N1–N2	1.291 (7)	C–C, ring, av	1.363 (7)
N2–C37	1.427 (9)	B–C, av	1.635 (8)
N2–C38	1.458 (9)	C–C, ring, av	1.364 (11)
N3–N4	1.276 (8)		

Table VII. Selected Interatomic Angles (Deg) for $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4 \cdot CH_2Cl_2$

P1–Mo–Cl1	84.93 (4)	C1–P1–C13	107.1 (2)
P1–Mo–N1	94.8 (1)	C7–P1–C13	103.9 (2)
P1–Mo–N3	89.2 (1)	Mo–P1–C1	111.6 (1)
P2–Mo–Cl1	87.88 (5)	Mo–P1–C7	111.7 (2)
P2–Mo–N1	93.9 (1)	Mo–P1–C13	116.9 (2)
P2–Mo–N3	90.9 (1)	Mo–P2–C19	115.1 (2)
P1–Mo–P2	170.55 (5)	Mo–P2–C25	117.1 (2)
Cl1–Mo–N1	116.8 (1)	Mo–P2–C31	109.0 (2)
Cl1–Mo–N3	131.0 (2)	C41–B–C47	111.8 (4)
N1–Mo–N3	112.2 (2)	C41–B–C53	107.9 (4)
Mo–N1–N2	173.4 (4)	C41–B–C59	108.4 (4)
C37–N2–C38	120.9 (6)	C47–B–C59	109.6 (4)
Mo–N3–N4	163.8 (4)	C47–B–C59	107.0 (4)
C39–N4–C40	120.2 (8)	C53–B–C59	112.3 (4)
C1–P1–C7	104.6 (2)	C–C–C, ring, av	120.0 (9)

$(CH_2)_5)_3]^+$.[6] The N–N distances of 1.31 (1) Å in I and 1.30 (1) Å in IV indicate considerable multiple bonding between the nitrogens. The linearity and short N–N distance suggest a significant contribution from the two canonical forms **1** and **2** with the hydrazido ligands each formally acting as four-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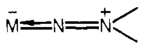
2

electron donors to the molybdenum. The near planarity of the Mo–N2–N3–C4–C10 moieties in both complexes is also consistent with participation of canonical form **2**.

These two structures can be compared to that of $[Mo(NPh)_2(S_2CNEt_2)_2]$.[7] Phenylimido and hydrazido(2–) ligands are analogous in being able in principle to function as four-electron, linear or two-electron, bent donor ligands. However both hydrazido(2–) complexes contain linear hydrazido ligands whereas in the bis(phenylimido) complex one of the arylimido ligands is bent with Mo–N–C = 139.4 (4)°. The imido or hydrazido ligands differ in the ability of the latter to be much more electronically flexible, donating or withdrawing electrons from the N–N bonding system while retaining linearity of the M–N–N system.

A consequence of the linearity of the hydrazido ligands is that the complex formally has a 20-electron count. A simple symmetry-based molecular orbital scheme presented in Figure 3 can be used to rationalize this. With the assumption that the metal uses essentially d^2sp^3 hybrid orbitals in the σ-bonding backbone of the molecule, the d_{xz}, d_{yz}, and d_{xy} orbitals remain for π interaction with the hydrazido ligands. It it is assumed that N_2 is sp hybridized, N2 will have, after σ bonding to Mo

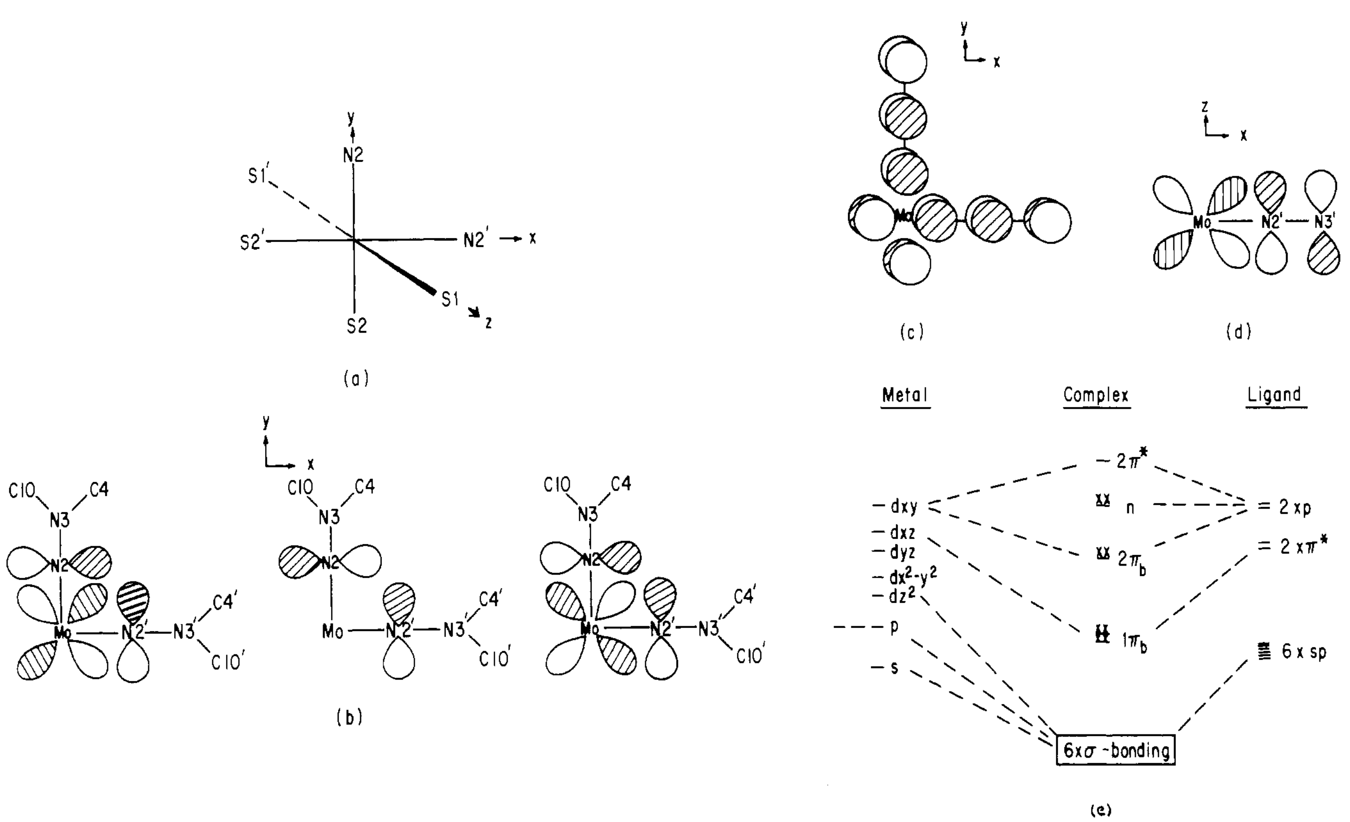

Figure 3. Schematic representation of the bonding in $[Mo(N_2R_2)_2(S_2CNR_2)_2]$ complexes. (a) Reference coordinate system. (b) Overlap combinations in xy plane between the metal d_{xy} orbital and the appropriate ligand p-type orbitals. As illustrated, the Mo–N2–N3–N2′–N3′–C4–C10–C4′–C10′ atom grouping is nearly planar, constraining the ligand p orbitals to this plane. (c) Bonding interaction between the ligand π^* orbitals and the metal d_{xz} and d_{yz} orbitals, viewed along the molecular z axis. The resultant bonding orbital is labeled $1\pi_b$. (d) Orbital interaction as in (c), viewed along the y axis. (e) Schematic of the relative ordering of the molecular orbitals. A 20-electron structure will populate the σ-bonding, π-bonding, and nonbonding orbitals. The $1\pi_b$ orbital is bonding with respect to the N2–N2′ and N3–N3′ atoms, suggesting that this orbital should be further stabilized by small changes in the Mo–N2–N3 angles in the xy plane so as to move N3 and N3′ closer together.

Table VIII. Experimental Details for the X-ray Diffraction Study of $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2][BPh_4]_2 \cdot CH_2Cl_2$

(A) Crystal Parameters[a] at 23 °C

$a = 13.487$ (3) Å space group: $P2_1/c$
$b = 13.875$ (3) Å $Z = 4$
$c = 35.133$ (5) Å ρ(calcd) = 1.28 g/cm³
$\beta = 100.18$ (1) Å ρ(obsd) = 1.30 (2) g/cm³ (flotation)
$V = 6471.00$ Å³

(B) Measurement of Intensity Data

cryst dimens: 0.15 × 0.35 × 0.20 mm
instrument: Nicolet R3/m automated diffractometer
radiation: Mo Kα (λ = 0.710 69 Å); graphite monochromator
scan mode: coupled θ(cryst)-2θ(counter)
scan rate: variable, within limits of 0.5–30.0°/min
scan length: 1.0°
bkgd measmts: 10 min at each end of the 2θ scan range
stds: 3 reflctns measd every 100 data
no. of reflctns collected: 4253

(C) Reduction of Data

Data corrected for background, attenuators, Lorentz, and polarization effects in the usual fashion
obsd data: 3541 with $F_o \geq 6\sigma(F_o)$
abs coeff: 3.35 cm⁻¹
abs corr: none ($T_{max}/T_{min} = 1.17$)
structure soln: Mo atomic position from a sharpened Patterson map; all other nonhydrogen positions from subsequent difference Fourier maps
atomic scattering factors and anomalous dispersion as above
final discrepancy factors: $R = 0.069$, $R_w = 0.071$

and π bonding to N3, a p orbital of appropriate symmetry to overlap with the d_{xy} orbital, giving the bonding, nonbonding, and antibonding combinations in Figure 3b. As a result the Mo–N–NR$_2$ systems are planar and the ligand π^* orbitals can overlap with the metal d_{xz} and d_{yz} orbitals to produce the degenerate set of Mo–N π-bonding orbitals shown in Figure 3c,d. This simple scheme can then accommodate the 20 electrons in σ-bonding, π-bonding, and nonbonding orbitals (Figure 3e). The scheme also suggests that the $1\pi_b$ orbital should provide some bonding interaction between N2 and N2′. This is reflected in the contact distance of 2.88 Å between N2 and N2′ in the two structures.

Steric interactions between the hydrazido substituents limit the bonding interaction between these two nitrogens. In complex I two of the phenyl substituents are arranged parallel with an average spacing of about 3.8 Å. The constraint imposed on the phenyl substituents rotates both out of the plane of the hydrazido ligand and prevents them from participating in electron delocalization. The methyl groups of complex IV offer less steric bulk and the phenyl group can twist toward the plane of the hydrazido ligand. Here the N–phenyl distance of 1.37 Å is considerably shorter than the average of 1.44 Å found for the diphenyl-substituted complex I.

Complexes of the Type $[MCl(NNMe_2)_2(PR_3)_2]^+$. (a) Preparation. The synthetic route used for the complexes $[Mo(NNR'_2)_2(S_2CNR_2)_2]$ is restricted in scope by the availability of suitable oxo complex precursors. Accordingly a method utilizing silylated hydrazines was developed and is summarized in eq 3. The reaction involves loss of the α-nitrogen hydrogen as well as elimination of trimethylchloro-

$$[MoCl_4(PR_3)_2] + 2Me_3SiNHNMe_2 \xrightarrow{CH_3CN} [MCl(NNMe_2)_2(PR_3)_2]Cl + 2Me_3SiCl \quad (3)$$

$$M = Mo, W; PR_3 = PPh_3, PMe_2Ph, PPh_2Me$$

Table IX. Atomic Positional Parameters for $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2][BPh_4]_2 \cdot CH_2Cl_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	0.20602 (9)	0.78946 (9)	0.85585 (3)	C30	0.3148 (6)	0.1987 (8)	−0.0774 (2)
N1	0.658 (1)	0.297 (1)	0.1469 (6)	C31	0.0678 (5)	0.2822 (7)	−0.0624 (2)
N2	0.6697 (7)	0.1509 (7)	0.0991 (3)	C32	0.0517 (5)	0.3172 (7)	−0.1003 (2)
N3	0.9040 (8)	0.1002 (9)	0.1360 (3)	C33	−0.0463 (5)	0.3262 (8)	−0.1209 (2)
N4	0.7473 (7)	0.0727 (6)	0.1712 (3)	C34	−0.1280 (6)	0.3003 (7)	−0.1037 (2)
N5	0.856 (1)	0.253 (1)	0.1907 (7)	C35	−0.1118 (5)	0.2654 (6)	−0.0658 (2)
N6	0.9014 (8)	0.2999 (9)	0.2199 (3)	C36	−0.0139 (4)	0.2563 (7)	−0.0452 (2)
N7	0.8345 (7)	0.2860 (8)	0.1086 (3)	C37	0.2061 (6)	0.3648 (5)	−0.0025 (2)
N8	0.8726 (9)	0.3417 (9)	0.0859 (4)	C38	0.1293 (6)	0.4223 (5)	0.0071 (2)
C1	0.667 (1)	0.064 (1)	0.1885 (4)	C39	0.15522 (6)	0.4961 (5)	0.0342 (3)
C2	0.637 (1)	−0.022 (1)	0.2003 (4)	C40	0.2519 (5)	0.5124 (5)	0.0517 (2)
C3	0.687 (1)	−0.103 (1)	0.1952 (4)	C41	0.3287 (6)	0.4548 (5)	0.0422 (2)
C4	0.771 (1)	−0.098 (1)	0.1783 (5)	C42	0.3058 (5)	0.3810 (5)	0.0151 (2)
C5	0.795 (1)	−0.009 (1)	0.1668 (4)	C43	0.1911 (6)	0.1671 (4)	−0.0110 (3)
C6	0.891 (1)	0.010 (1)	0.1449 (4)	C44	0.1492 (6)	0.0855 (5)	−0.0307 (2)
C7	0.948 (1)	−0.069 (1)	0.1583 (4)	C45	0.1509 (6)	−0.0026 (4)	−0.0115 (2)
C8	1.026 (1)	−0.047 (1)	0.1200 (4)	C46	0.1946 (5)	−0.0091 (5)	0.0275 (2)
C9	1.047 (1)	0.045 (1)	0.1104 (5)	C47	0.2365 (6)	0.0725 (5)	0.0473 (2)
C10	0.983 (1)	0.118 (1)	0.1195 (4)	C48	0.2347 (4)	0.1606 (5)	0.0280 (2)
C11	0.661 (1)	0.3738 (9)	0.1701 (4)	C49	0.4229 (5)	0.1766 (6)	0.2355 (3)
C12	0.574 (1)	0.427 (1)	0.1707 (4)	C50	0.4698 (5)	0.2666 (6)	0.2399 (2)
C13	0.487 (1)	0.402 (1)	0.1481 (4)	C51	0.5640 (4)	0.2764 (5)	0.2634 (2)
C14	0.482 (1)	0.3261 (9)	0.1245 (4)	C52	0.6114 (4)	0.1963 (6)	0.2826 (2)
C15	0.571 (1)	0.278 (1)	0.1245 (4)	C53	0.5646 (5)	0.1064 (6)	0.2782 (2)
C16	0.579 (1)	0.187 (1)	0.0967 (4)	C54	0.4703 (4)	0.0965 (5)	0.2547 (3)
C17	0.493 (1)	0.156 (1)	0.0719 (5)	C55	0.3171 (5)	0.0601 (5)	0.1820 (2)
C18	0.508 (1)	0.079 (1)	0.0491 (5)	C56	0.3901 (6)	0.0629 (5)	0.1584 (3)
C19	0.600 (1)	0.044 (1)	0.0500 (5)	C57	0.4038 (6)	−0.0164 (5)	0.1355 (3)
C20	0.679 (1)	0.080 (1)	0.0749 (4)	C58	0.3445 (5)	−0.0985 (4)	0.1361 (2)
C21	0.870 (1)	0.290 (1)	0.2567 (11)	C59	0.2715 (6)	−0.1014 (5)	0.1597 (2)
C22	0.992 (1)	0.351 (1)	0.2177 (5)	C60	0.2578 (6)	−0.0221 (5)	0.1826 (2)
C23	0.918 (1)	0.429 (1)	0.1004 (5)	C61	0.2521 (11)	0.1374 (6)	0.2797 (2)
C24	0.868 (1)	0.312 (1)	0.0458 (4)	C62	0.2235 (4)	0.1380 (6)	0.2395 (2)
B1	0.185 (1)	0.274 (1)	−0.0349 (6)	C63	0.1231 (5)	0.1223 (6)	0.2228 (3)
B2	0.307 (2)	0.156 (2)	0.2095 (6)	C64	0.0513 (4)	0.1059 (6)	0.2462 (2)
C73	0.439 (1)	0.691 (1)	0.0184 (5)	C65	0.0799 (4)	0.1053 (6)	0.2863 (2)
C11	0.4050 (4)	0.6368 (5)	−0.0275 (2)	C66	0.1803 (4)	0.1210 (6)	0.3031 (2)
C12	0.3694 (4)	0.7880 (5)	0.0256 (2)	C67	0.2625 (6)	0.2542 (5)	0.1820 (2)
C25	0.2723 (6)	0.2809 (8)	−0.0650 (2)	C68	0.2410 (6)	0.2508 (4)	0.1417 (2)
C26	0.3001 (6)	0.3721 (8)	−0.0751 (2)	C69	0.2055 (5)	0.3329 (5)	0.1207 (3)
C27	0.3704 (6)	0.3811 (8)	−0.0996 (2)	C70	0.1915 (6)	0.4183 (6)	0.1399 (2)
C28	0.4130 (6)	0.2990 (8)	−0.1130 (12)	C71	0.2130 (6)	0.4217 (5)	0.1802 (2)
C29	0.3852 (6)	0.2078 (8)	−0.1019 (2)	C72	0.2485 (5)	0.3397 (5)	0.2013 (2)

silane. The fate of this hydrogen is at present unclear, although experiments carried out in sealed flasks in vacuo indicate that it does not appear as dihydrogen. The elimination of hydrogen from the complexes $[WHCl_3(NNH_2)(PMe_2Ph)_2]$ to give $[WCl_3(NNH_2)(PMe_2Ph)_2]$, which has been characterized by an X-ray crystal structure, occurs very rapidly.[8] This suggests that in reaction 3 the hydrogen loss may well involve its prior migration to the metal. An analogous reaction occurs with 1 equiv of the silylhydrazine to give the complexes $[MCl_3(NNR_2)(PR_3)_2]$.[9]

Preliminary data on the preparation and structures of the molybdenum and tungsten complexes prepared in this manner have already appeared.[9] The reaction proceeds readily for molybdenum or tungsten with a range of tertiary phosphines. No characterizable products could be isolated by reaction of $[MCl_4(Ph_2PCH_2CH_2PPh_2)]$ or $[MCl_4(bpy)]$ with excess of the silylated hydrazine. The preparative reaction is carried out in acetonitrile at room temperature, and the products crystallize as the chloride salts on reduction in volume of the solution. Tetraphenylborate salts can be obtained by metathesis in methanol solution. The complex $[MoCl(NNMe_2)_2(PMe_2Ph)_2]Cl$ was most conveniently prepared from $[MoOCl_2(PMe_2Ph)_3]$ and the silylated hydrazine, the reaction in this instance presumably involving elimination of $(Me_3Si)_2O$ rather than Me_3SiCl.

The IR spectra of the complexes show medium-intensity, sharp IR bands at about 1580 cm^{-1}, which are associated with the Me_2NN ligands. No bands assignable to metal–nitrogen stretching frequencies could be identified in the range 1000–1200 cm^{-1} probably due to the intervention of ligand bands. The ^1H NMR spectra indicate that the hydrazido methyl groups are equivalent. The appearance of a triplet for the PMe_2Ph methyls in complex X suggests a trans geometry for the phosphines with a plane of symmetry along the P–M–P axis.

(b) X-ray Study of $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4$. Atomic positional and thermal parameters for $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4 \cdot CH_2Cl_2$ are collected in Table V. Intramolecular bond distances and angles are given in Tables VI and VII, respectively. The deviations of atoms from selected least-squares planes are collected in a supplementary table. The calculated hydrogen atom positions are available as supplementary material. An ORTEP representation of the molecular structure with the atom labeling scheme is shown in Figure 4.

The coordination polyhedron about the formally 6+ molybdenum atom is distorted trigonal bipyramidal (tpb). The triphenylphosphine ligands occupy the axial positions with a P1–Mo–P2 angle of 170.6°. The chloride and the two dimethylhydrazido ligands occupy the positions in the equatorial plane. The bond angles between the donor atoms forming the equatorial plane deviate substantially from the 120° expected for an ideal tpb with N1–Mo–N3 = 112.2°, Cl1–Mo–N1 = 116.8°, and Cl1–Mo–N3 = 131.0°. The source of this distortion is not obvious from the symmetry of the molecule but can be rationalized on the basis of nonbonding intramolecular

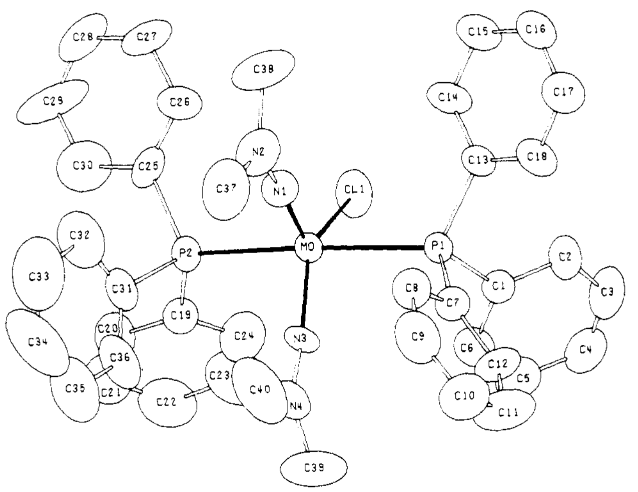

Figure 4. Perspective view of the cation $[MoCl(NNMe_2)_2(PPh_3)_2]^+$, showing the atom-labeling scheme.

interactions between the equatorial ligands and the bulky triphenylphosphine ligands occupying the axial positions. The C40 methyl group of the hydrazido ligand has the shortest nonbonding contact distance with the phenyl ring carbons, 3.47 Å with C8 and 3.53 Å with C36. The other hydrazido methyl groups have no significant contact distances with the phenyl-ring carbons, the shortest being 3.79 Å between C37 and C14. The closest distance between methyl carbons on the adjacent hydrazido ligands is 4.03 Å between C37 and C40. The chloride ligand, Cl1, also makes several short nonbonding contact distances with C1, 3.49 Å, and C24, 3.55 Å. These nonbonding interactions have the effect of forcing the N3 hydrazido ligand away from Cl1 and closer to the N1 hydrazido ligand with Cl1–N3 = 3.79 Å, compared to Cl1–N1 = 3.55 Å, and increasing the angle between Cl1 and N3 to 131.0° while decreasing the angle between N1 and N3 to 112.2°.

The molybdenum atom is not significantly displaced from the equatorial plane as is expected due to the pseudosymmetry of the molecule. The phosphorus donor atoms are equally distant from the molybdenum, within a 3σ criterion 2.524 (1) and 2.528 (1) Å for P1 and P2, respectively, as are the hydrazido nitrogen donor atoms, 1.752 (5) and 1.763 (4) Å for N1 and N3, respectively. The dimethylhydrazido ligands are very nearly in the equatorial plane with the dihedral angle between the Mo,N1,N2,C37,C38 plane and the equatorial plane being 4.92° and that between the Mo,N3,N4,C39,C40 plane and the equatorial plane being 2.60°. The dihedral angle between the hydrazido planes is 7.50°. This configuration is undoubtedly stabilized by the nonbonding contact interactions between the hydrazido methyl groups and phenyl rings of the bulky triphenylphosphine ligands.

Distortion of the tetrahedral geometry about the triphenylphosphine ligands is due to the bending of phenyl rings slightly away from the equatorial plane. Thus the internal valency angles of the phosphorus atom, those that include the molybdenum atom, are larger, with an average of 113.6°, than the external valence angles between the carbons of the phenyl rings, with an average of 105.0°.

The Mo–N1 and Mo–N3 distances of 1.752 (5) and 1.763 (4) Å are very similar to those of the bis(dithiocarbamato)-bis(hydrazido) derivatives despite the differences in coordination number and formal electron count. The N1–N2 and N3–N4 distances of 1.291 (7) and 1.276 (8) Å are also very close to values found in other hydrazido(2–) complexes and reflect the relative insensitivity of these bond lengths to variation in ligand environment of the metal. There is a significant difference in the Mo–N–N angles for the two hydrazido ligands, Mo–N–N1–N2 being 173.4° while Mo–N3–N4 is 163.8°. These variations are ascribable to the steric interactions with the triphenylphosphine and chloride ligands discussed earlier. In common with the other bis(hydrazido) complexes described in this paper, the bending of the hydrazido ligands is such as to move N2 and N4 toward each other. This is indicated by the N2–Mo–N4 angle of 102.6° compared to the N1–Mo–N3 angle of 112.2°.

Table X. Selected Bond Lengths (Å) and Angles (Deg) for $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2][BPh_4]_2 \cdot CH_2Cl_2$

(a) $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2]^{2+}$ Cation

Mo–N1	2.21 (1)	N3–C10	1.33 (2)
Mo–N2	2.25 (1)	N4–C1	1.33 (2)
Mo–N3	2.19 (1)	N4–C5	1.33 (2)
Mo–N4	2.27 (1)	C–C, av (C1–C10)	1.35 (2)
Mo–N5	1.80 (1)	C–C, av (C11–C20)	1.34 (2)
Mo–N7	1.79 (1)	N5–N6	1.27 (2)
N1–C11	1.34 (2)	N6–C21	1.43 (3)
N1–C15	1.32 (2)	N6–C22	1.42 (2)
N2–C16	1.31 (2)	N7–N8	1.28 (2)
N2–C20	1.33 (2)	N8–C23	1.42 (2)
N3–C6	1.31 (2)	N8–C24	1.46 (2)

N1–Mo–N2	73.2 (6)	Mo–N2–C16	118.6 (7)
N1–Mo–N3	167.2 (7)	Mo–N2–C20	125.4 (6)
N1–Mo–N4	98.5 (7)	C16–N2–C20	116.0 (7)
N1–Mo–N5	92.1 (6)	Mo–N3–C6	120.9 (6)
N1–Mo–N7	94.0 (6)	Mo–N3–C10	123.3 (7)
N2–Mo–N3	95.1 (7)	C6–N3–C10	115.6 (6)
N2–Mo–N4	76.0 (6)	Mo–N4–C1	124.8 (6)
N2–Mo–N5	158.3 (6)	Mo–N4–C5	119.9 (8)
N2–Mo–N7	90.3 (7)	C1–N4–C5	115.0 (7)
N3–Mo–N4	73.1 (6)	Mo–N5–N6	168.2 (7)
N3–Mo–N5	97.6 (7)	Mo–N7–N8	173.5 (8)
N3–Mo–N7	91.2 (7)	N5–N6–C21	120.2 (24)
N4–Mo–N5	91.0 (6)	N5–N6–C22	120.2 (24)
N4–Mo–N7	157.8 (6)	C21–N6–C22	119.1 (30)
N5–Mo–N7	106.9 (6)	N7–N8–C23	119.3 (26)
Mo–N1–C11	121.8 (6)	N7–N8–C24	118.8 (30)
Mo–N1–C5	121.6 (6)	C23–N8–C24	121.9 (22)
C11–N1–C15	116.5 (7)		

(b) BPh_4^- Anions

B1–C25	1.69 (2)	B2–C55	1.67 (3)
B1–C31	1.71 (2)	B2–C62	1.69 (2)
B1–C37	1.69 (2)	B2–C67	1.72 (3)
B1–C43	1.70 (3)	C–C, av (C25–C72)	1.40 (3)
B2–C49	1.69 (3)		

C25–B1–C31	109.1 (18)	C49–B2–C55	106.6 (28)
C25–B1–C37	108.6 (24)	C49–B2–C62	110.0 (30)
C25–B1–C43	111.8 (22)	C40–B2–C67	111.6 (22)
C31–B1–C37	111.2 (24)	C55–B2–C62	112.2 (24)
C31–B1–C43	107.0 (24)	C62–B2–C67	105.3 (26)
C37–B1–C43	109.1 (27)	C–C–C, av (C25–C72)	120.0 (28)

(c) CH_2Cl_2 Group

C73–Cl1	1.76 (3)	Cl1–C73–Cl2	114.2 (27)
C73–Cl2	1.69 (3)		

(c) Reactions of the Complexes $[MoCl(NNMe_2)_2(PPh_3)_2]Cl$. The cationic bis[hydrazido(2–)] complexes react rapidly with a range of nucleophiles including bipyridyl. Thus the complex $[MoCl(NNMe_2)_2(PPh_3)_2]Cl$ reacts readily with bipyridyl in warm methanol to give the orange complex $[Mo(NNMe_2)_2(bpy)_2]Cl_2$, which is isolated as the tetraphenylborate salt. Spectroscopy was not sufficient to indicate whether the hydrazido ligands were cis or trans, and accordingly an X-ray crystal structure was undertaken.

(d) Structural Study of $[Mo(NNMe_2)_2(bpy)_2][BPh_4]_2 \cdot CH_2Cl_2$. The atomic positional parameters for $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2][BPh_4]_2 \cdot CH_2Cl_2$ are presented in Table IX. A perspective view of the $[Mo(C_{10}H_8N_2)_2(NNMe_2)_2]^+$ cation and the atom-labeling scheme are shown in Figure 5. The relevant bond lengths and angles are summarized in Table X.

The overall geometry of the mononuclear dication [Mo-

Table XI. Crystallographic Data for Hydrazido(2–) Complexes

complex	M-N, Å	N-N<, Å	M-N-N<, deg	ref
$[Mo(NNMePh)_2(S_2CNMe_2)_2]$	1.790 (9)	1.30 (1)	172.6 (8)	this work
$[Mo(NNPh_2)_2(S_2CNMe_2)_2]$	1.790 (8)	1.31 (1)	169.9 (8)	this work
$[MoCl(NNMe_2)_2(PPh_3)_2]^+$	1.752 (5)	1.291 (7)	163.8 (4)	this work
	1.763 (2)	1.276 (8)	173.4 (4)	
$[Mo(NNMe_2)_2(bpy)_2]^{2+}$	1.80 (1)	1.27 (2)	168.2 (7)	this work
	1.79 (1)	1.28 (2)	173.5 (8)	
$[Mo_2S_4(NNMe_2)_2(PPh_3)]$	1.78 (3)	1.30 (4)	165.0 (3)	15
	1.85 (3)	1.27 (4)	178.2 (3)	
$[MoO(NNMe_2)(S_2CNMe_2)_2]$	1.85 (2)	1.24 (2)	168 (2)	3
$[MoO(NNMe_2)(oxine)_2]^a$	1.800 (9)	1.28 (1)	155.5 (9)	5
$[Mo(NNEtPh)(S_2CN(CH_2)_5)_3]^+$	1.715 (16)	1.37 (2)	170 (2)	6
$[MoF(NNH_2)(dppe)_2]^{+\,b}$	1.76 (1)	1.33 (2)	176.4 (13)	16
$[(\eta\text{-}C_5H_5)_2WH(NNHC_6H_4F)]^+$	1.838	1.31	146.3	17, 21

[a] Oxine = 8-hydroxyquinoline. [b] dppe = $Ph_2PCH_2CH_2PPh_2$.

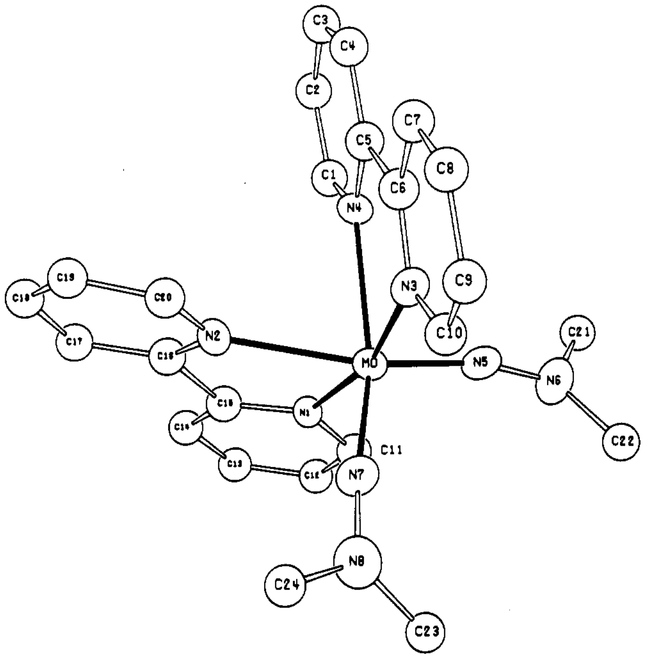

Figure 5. Perspective view of the cation $[Mo(NNMe_2)_2(bpy)_2]^{2+}$, showing the atom-labeling scheme.

$(C_{10}H_8N_2)_2(NNMe_2)_2]^{2+}$ is similar to that observed for the complexes $[Mo(NNR_2)_2(S_2CNMe_2)_2]$ described earlier. The geometry about the molybdenum is pseudooctahedral, the coordination polyhedron being generated by the nitrogen donors of the two bipyridyl ligands and N5 and N7 from the hydrazido(2–) ligands. The strongly multiply bonded hydrazido(2–) groups adopt the usual cis configuration, thus minimizing overlap with the metal t_2 type orbitals. The significantly different Mo–bipyridyl nitrogen bond distances reflect the trans influence of the multiply bonded hydrazido(2–) ligands. Thus, the Mo–N bond distance for the pair of bonds cis to the hydrazido ligands averages 2.20 (1) Å, while the trans pair averages 2.26 (1) Å. The molybdenum–nitrogen bonds for the hydrazido ligands, 1.80 (1) Å average, are consistent with the multiple-bond character of the interaction and are similar to Mo–N distances in other Mo–hydrazido(2–) species. The Mo–N–N angles are nearly linear, 170.9 (8) Å average, consistent with the description of the hydrazido(2–) groups as formal four-electron donors.

Conclusions

The bond length data for the hydrazido(2–) ligands in these and other complexes are collected together in Table XI for comparison. The bond lengths for all the bis(hydrazido) complexes are remarkably similar and are clearly largely independent of the coordination number and nature of the coligands. The very strongly π-bonded hydrazido ligands adopt a cis configuration in both pseudooctahedral and trigonal-bipyramidal geometries, thereby maximizing π overlap with molybdenum d orbitals.

The structure of $[MoO(NNMe_2)(S_2CNMe_2)_2]^3$ reveals longer Mo–N and shorter N–N distances than in the bis(hydrazido) derivatives. This is consistent with the more electrogenative oxyen being a stronger electron-withholding ligand and reducing the electron density available for the π bonding to the hydrazido ligand, thereby lengthening Mo–N. In the absence of any π-bonding competition as in $[Mo(NNEtPh)(S_2CN(CH_2)_5)_3]^+$, the M–N bond shortens to 1.715 (6) Å and the N–N bond is correspondingly long at 1.37 (2) Å. In valence-bond terms this represents increasing contributions from the canonical form **1** and less from form **2**.

There are several features of the hydrazido complex structures that are difficult to rationalize at this stage. In all the bis(hydrazido) structures the hydrazide ligands are bent so as to move the terminal nitrogens toward one another, despite thereby increasing steric interactions. The hydrazido ligands, although best described as linear, show considerable variation in the Mo–N–N angles from 146.3 to 176.4°. Simple arguments based on the 18-electron rule fail to explain these, and ab initio calculations are in progress to try to shed further light on the problem.

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Supplementary Material Available: Footnotes to Table I, detailing conditions of the data collection, and tables listing analytical and NMR data, least-squares planes and dihedral angles, thermal parameters, observed and calculated structure factors, and calculated H atom positions (94 pages). Ordering information is given on any current masthead page.