

Nitrosyl Complexes of Molybdenum and Tungsten. Part 17.¹ Hydrazido(1-) Complexes of [Tris(3,5-dimethylpyrazolyl)borato]-molybdenum, Related Tungsten Compounds, and the Structures of *NN*-Dimethylhydrazido(1-)- and *N*-Methyl-*N*-phenylhydrazido(1-)-iodo(nitrosyl)[tris(3,5-dimethylpyrazol-1-yl)borato]molybdenum †

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The preparations of the compounds $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNRR}')]$ (Me_2pz = 3,5-dimethylpyrazolyl; $\text{R} = \text{R}' = \text{H}$ or Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$ or Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) and $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{N}_2)\}(\text{NO})\text{Br}(\text{NHNRR}')]$ ($\text{R} = \text{R}' = \text{H}$ or Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$) are described. The species with $\text{R} = \text{R}' = \text{H}$ react with acetone giving complexes containing the -NHN=CMe_2 group, and the hydrazido(1-) species react with acids causing cleavage of the $\text{M-NHNRR}'$ bond. The structures of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNRR}')]$ ($\text{R} = \text{R}' = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) have been determined crystallographically.

In an earlier paper in this series we described² the formation of a series of hydrazine, hydrazido(1-), and hydrazido(2-) complexes containing the group $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}$ (X = halide). These complexes are highly unusual in that they contain η^2 -hydrazine and hydrazido(1-) groups, and in that the binuclear species were bridged asymmetrically by a hydrazido(2-) group.

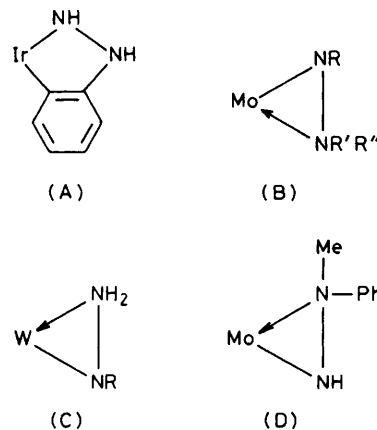
Our interest in hydrazido(1-) compounds was stimulated by the observation that acids reacted with our species $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NHNRR}')]$ reconstituting hydrazine complexes without degradation of the N-N group into ammonia and/or amines. These observations appeared to contrast markedly with those of Chatt and Richards,³ and others, who proposed that formation of ammonia by reduction of N_2 coordinated to tertiary phosphine complexes of Mo and W might proceed *via* monomeric hydrazido(2-) and hydrazido(1-) intermediates, and that protonation of M-NH-NH_2 species might give M-NH-NH_3^+ with subsequent loss of NH_3 . We concluded,² however, that these two sets of observations need not be mutually inconsistent because the electronic situation at the metal atoms in each system was likely to be totally different. Thus, in the nitrosyl complexes, because the metal is relatively 'electron-poor', being bound to NO and I , both N atoms of the hydrazido-group are required to relieve the electronic situation at Mo , thereby removing the accessibility of nitrogen atom lone pairs for protonation and subsequent detachment of NH_3 or amine. In the tertiary phosphine complexes, it is accepted³ that the metal is relatively 'electron-rich', and some of the surplus charge is back-donated to the hydrazido-group, thereby making it more susceptible to protonation and, presumably, to N-N bond cleavage.

In order to test this view, with respect to our nitrosyl system, we decided to prepare compounds as closely similar as possible to our original cyclopentadienyl complexes, but so constructed as to *prevent* chelation of the hydrazido(1-) group. At that time, not having easy access to $\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)$ systems, we considered that the tris(3,5-dimethylpyrazolyl)borato-

ligand, $\text{HB}(\text{Me}_2\text{pz})_3^-$, quite adequately fulfilled our requirements, as has been demonstrated by Trofimenko.⁴ We had found that simple alkoxides⁵ and, more recently, mono-alkylamides,^{6,7} of the type $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{XY}]$ (X = halide, $\text{Y} = \text{OR}$ or NHR) could be simply prepared, and we concluded that the species ($\text{X} = \text{I}$, $\text{Y} = \text{NHNRR}'$) should be reasonably straightforward to make.

We have described earlier our efforts to prepare hydrazido(1-) complexes^{6,8} and have reported briefly (and somewhat inaccurately) on two structures.⁶ In this paper we present a full report of our synthetic and spectroscopic studies of molybdenum complexes and also of some tungsten complexes derived from $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{N}_2)\}(\text{NO})\text{XY}]$ (2; $\text{X} = \text{Y} = \text{Br}$) (Me_2pz = 3,5-dimethylpyrazolyl).⁷ We also describe in detail the structures of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{XY}]$ (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNMe}_2$) and (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNMePh}$), which have been determined crystallographically.

There are relatively few classes of transition metal hydrazido(1-) complexes. Among the best characterised are the *o*-metallated species $[\text{Ir}(\text{CO})(\text{NHNHC}_6\text{H}_4)(\text{PPh}_3)_3][\text{BF}_4]$,⁹ $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NRNR}')]$ ($\text{R} = \text{H}$ or alkyl; $\text{R}' = \text{H}$, alkyl, or aryl; $\text{R}'' = \text{alkyl}$ or aryl),² $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NRNH}_2)]\text{-}[\text{BF}_4]$ ($\text{R} = p\text{-XC}_6\text{H}_4$; $\text{X} = \text{H}$, F , Me , or OMe),¹⁰ and $[\text{Mo}(\text{NNMePh})(\text{NHNMePh})(\text{S}_2\text{CNMe}_2)_2][\text{BPh}_4]$.¹¹ These compounds contain the hydrazido(1-) group attached in the modes (A), (B), (C), and (D), respectively (see below). The previously reported complex $[\text{WCl}_3(\text{NHNH}_2)(\text{PMe}_2\text{Ph})_2]$ ¹²



† Supplementary data available (No. SUP 23419, 39 pp.): observed structure amplitudes, calculated structure factors, anisotropic and isotropic thermal parameters, predicted hydrogen atom positional parameters, full bond lengths and angles, details of planar fragments. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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Table 1. Analytical and molecular weight data for $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{XY}]$ (1) and $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{N}_2)\}(\text{NO})\text{XY}]$ (2)

Complex		Analysis (%)								<i>M</i> ^a		
		Found				Calc.						
		C	H	N	X	C	H	N	X			
(1)	I	NHNH ₂	30.6	4.2	21.7	22.1	31.0	4.3	21.7	21.9	568	609
	I	NHNMe ₂	33.8	4.7	20.3	20.6	33.5	4.6	20.7	20.9		
	I	NHNHPh	38.4	4.4	19.0	19.3	38.4	4.4	19.2	19.3		
	I	NHNHC ₆ H ₄ Me- <i>p</i>	39.3	4.6	18.7	19.1	39.3	4.6	18.8	18.9		
	I	NHNHC ₆ F ₅	34.0	3.2	16.9	16.9	33.7	3.2	16.9	17.0	708	671
	I	NHNMePh	39.3	4.8	18.9	18.8	39.4	4.6	18.8	18.9		
	I	NHNHCSNH ₂ ^b	30.1	4.2	21.8	19.8	30.0	4.1	21.9	19.9		
	I	NHNHCO ₂ Me	31.9	4.3	19.7	18.9	32.0	4.2	19.8	19.9		
	I	NHNHCOPh	38.5	4.1	18.2	18.6	38.6	4.2	18.4	18.6	658	637
I	NHN=CMe ₂ ^c	35.0	4.7	20.0	20.6	34.8	4.7	20.3	20.5			
(2)	Br	NHNH ₂	25.6	3.5	17.7	22.9	25.7	3.4	18.0	22.8		
	Br	NHNMe ₂	28.1	3.5	17.3	24.9	28.0	3.8	17.3	24.9		
	Br	NHNHPh	32.9	3.3	15.8	19.7	32.4	3.7	16.2	20.5		
	Br	NHN=CMe ₂ ^c	31.3	4.0	15.7	22.0	31.6	4.3	15.8	22.0		

^a Determined osmotically in CHCl_3 . ^b S Analysis: Found 4.8, calc. 5.0%. ^c As monoacetone solvate.

has now been reformulated as containing hydrido and hydrazido(2-) groups: $[\text{WCl}_2\text{H}(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$.¹³

Experimental

All reactions were carried out under dry nitrogen, and all solvents were degassed immediately prior to use. Molecular weights were determined osmotically and i.r. spectra were measured using PE 457 and 180 spectrophotometers. Hydrogen-1 and ¹³C n.m.r. spectra were obtained using PE R34 and JEOL PFT 90 instruments. Microanalyses were performed by the Microanalytical Laboratory of this Department, and all yields are quoted relative to the metal-containing starting material. Data are in Tables 1 and 2.

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNH}_2)]$.—A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) and an excess of hydrazine hydrate (0.1 cm³) in dichloromethane was shaken for 3–4 min. MgSO_4 was added to the reaction mixture to remove traces of water. The solvent was concentrated *in vacuo* to ca. 5 cm³ and di-isopropyl ether (30 cm³) was added. The mixture was filtered under nitrogen and the solvent partially evaporated *in vacuo*. Addition of n-pentane caused the product to precipitate as a yellow powder which was washed with methanol (yield 0.2 g, 47%). The complex is stable indefinitely if stored as a solid under nitrogen at 0 °C.

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNHMe})]$.—A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) and an excess of methylhydrazine (0.1 cm³, 6 drops) in dichloromethane (40 cm³) was stirred at room temperature for 12–18 h until a yellow solution had formed. The solvent was removed *in vacuo* and the residue extracted with di-isopropyl ether. The extract was filtered and the filtrate was concentrated *in vacuo*. On addition of n-pentane the complex precipitated as a bright yellow powder (yield 0.21 g, 48%). This product was characterised by spectroscopic techniques alone.

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNMe}_2)]$.—*NN*-Dimethylhydrazine (0.2 cm³) was added to a solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) in dichloromethane (40 cm³) and the mixture was stirred for ca. 30 h at room temperature. The bright yellow solution was concentrated *in vacuo*, di-isopropyl

ether was added, and the mixture was filtered under nitrogen. Methanol was added to the filtrate and the solution further concentrated *in vacuo* upon which the product precipitated as a yellow crystalline solid. The compound can be recrystallised from freshly distilled n-pentane–tetrahydrofuran (thf) mixtures under nitrogen giving orange-green dichroic crystals (yield 0.25 g, 56%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNHPh})]$.—A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) and phenylhydrazine (0.15 cm³) was refluxed gently for ca. 15 h. The bright red solution was concentrated *in vacuo* and on addition of di-isopropyl ether a white precipitate of phenylhydrazinium iodide formed, which was filtered off. The filtrate was concentrated *in vacuo* and on addition of ethanol (10 cm³) this compound precipitated as dark red crystals (yield 0.30 g, 62%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNHC}_6\text{H}_4\text{Me-}p)]$.—*Method 1.* Fresh recrystallised *p*-tolylhydrazine (0.2 g) was added to a stirred solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) in dichloromethane (40 cm³) and the mixture left for ca. 2 h. The solvent was removed *in vacuo* and the product extracted from the residue into di-isopropyl ether. Addition of n-pentane to the extract followed by cooling to –10 °C over a number of days afforded the complex as a dark red-brown microcrystalline solid (yield 0.31 g, 61%).

Method 2. A mixture of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) and AgO_2CMe (0.14 g) was stirred overnight in dichloromethane. The emerald-green solution was filtered to remove AgI and treated with an excess of *p*-tolylhydrazine (0.2 g). The mixture was stirred for 30 min, filtered, and the solvent removed *in vacuo* giving a red-brown oil. The work-up procedure described above was used to give the product in similar yield.

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHNHC}_6\text{F}_5)]$.—A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.5 g) and an excess of pentafluorophenylhydrazine (0.3 g) in dichloromethane (50 cm³) was stirred at room temperature for ca. 30 h. The yellow-red solution was filtered and the filtrate was concentrated *in vacuo*. This caused the compound to precipitate as a brown-red powder which was recrystallised from methylcyclohexane (yield 0.4 g, 72%).

[Mo{HB(Me₂pz)₃}(NO)I(NHNMePh)].—*N*-Methyl-*N*-phenylhydrazine (0.2 g) was added to a stirred solution of [Mo{HB(Me₂pz)₃}(NO)I₂] (0.5 g) in dichloromethane (40 cm³) and the mixture was refluxed for 72 h. The dark brown-red solution was filtered and the filtrate concentrated *in vacuo*. On addition of a large excess of ethanol and further evaporation the complex precipitated as a chocolate-brown microcrystalline powder (yield 0.25 g, 51%).

[Mo{HB(Me₂pz)₃}(NO)I(NHNHCOPh)].—A solution of [Mo{HB(Me₂pz)₃}(NO)I₂] (0.5 g) and benzohydrazide (0.2 g) in dichloromethane (40 cm³) was stirred at room temperature for 4 h. The red-brown solution was filtered and concentrated to ca. 15 cm³ *in vacuo*. Di-isopropyl ether was added causing the compound to precipitate as an orange-brown powder; this could be recrystallised from dichloromethane-di-isopropyl ether giving red-brown crystals (yield 0.39 g, 77%).

[Mo{HB(Me₂pz)₃}(NO)I(NHNHCO₂Me)].—To [Mo{HB(Me₂pz)₃}(NO)I₂] (0.5 g) in dichloromethane (30 cm³) solution was added methoxycarbonylhydrazine (0.2 g) and the mixture was stirred at room temperature for ca. 1 h, giving a dark red solution. Most of the solvent was removed *in vacuo*, di-isopropyl ether was added, and the solution was then filtered. An excess of methanol was added to the filtrate and on careful evaporation, deposition of the complex occurred as bright red microcrystals (yield 0.31 g, 66%).

[Mo{HB(Me₂pz)₃}(NO)I(NHNHCSNH₂)].—Thiosemicarbazide (0.2 g) was added to a solution of [Mo{HB(Me₂pz)₃}(NO)I₂] (0.5 g) in 1,2-dimethoxyethane (40 cm³) and the mixture was stirred at room temperature for 48 h. During this time the solution changed from black to a deep red colour. The mixture was filtered and concentrated *in vacuo*, and an excess of di-isopropyl ether was added to the filtrate causing precipitation of the dark red microcrystalline compound, which was washed with ethanol (yield 0.3 g, 61%).

[Mo{HB(Me₂pz)₃}(NO)I(NHN=CMe₂)]·Me₂CO.—Acetone (30 cm³) was added to a pure dry sample of [Mo{HB(Me₂pz)₃}(NO)I(NHNH₂)] (0.3 g) and the solution stirred at room temperature for 30 min. During this time the solution changed from yellow to a deep orange-red colour; it was concentrated *in vacuo* to afford the compound as dark red-brown crystals (yield 0.18 g, 56%).

[W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br(NHNH₂)].—To a solution of [W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br₂] (0.25 g) in dichloromethane (20 cm³) was added hydrazine hydrate (0.1 g), and the mixture was stirred at room temperature for 3 h. During this time the colour of the mixture changed from deep green to bright yellow. The solvent was then evaporated *in vacuo* and the yellow residue recrystallised from methanol, affording the complex as yellow crystals (yield ca. 20%).

[W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br(NHNMe₂)].—To a solution of [W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br₂] (0.2 g) in dichloromethane (0.5 cm³) was added *NN*-dimethylhydrazine (0.5 cm³). The mixture was stirred for 1 h during which time it changed in colour from green to brown-red. The solvent was evaporated *in vacuo* and the residue was recrystallised from methanol affording the complex as a bright yellow powder (yield ca. 35%).

[W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br(NHNHPh)].—To a solution of [W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br₂] (0.3 g) in dichloromethane (25 cm³) was added phenyl-

hydrazine (0.2 g). After stirring for 1 h, the mixture became red and a white precipitate had formed. After filtration, the filtrate was concentrated *in vacuo* and, on addition of diethyl ether, red crystals of the complex formed. These were collected by filtration, washed with ether, and dried *in vacuo* (yield ca. 55%).

[W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br(NHN=CMe₂)]·Me₂CO.—The complex [W{HB(Me₂pz)₂(3,5-Me₂-4-BrC₃N₂)}(NO)Br(NHNH₂)] was prepared as described above. The yellow compound was dissolved in acetone (30 cm³) and stirred for 30 min. The solution became red and an orange solid precipitated. This was collected by filtration, and the filtrate partially evaporated *in vacuo* when more orange solid formed. The two batches were combined, washed with *n*-pentane and dried *in vacuo*, affording the complex as fine orange microcrystals (yield ca. 40%).

X-Ray Crystallographic Studies.—[Mo{HB(Me₂pz)₃}(NO)I(NHNMePh)]. The complex was obtained from dichloromethane as elongated, brown crystals; a crystal of dimensions 0.07 × 0.17 × 0.47 mm was used.

Crystal data. C₂₂H₃₁BIMoN₉O·0.5CH₂Cl₂, *M* = 713.7, Monoclinic, *a* = 20.11(18), *b* = 19.67(17), *c* = 15.75(19) Å, β = 99.65(18)°, *U* = 6 141(108) Å³, *D_m* = 1.58, *Z* = 8, *D_c* = 1.54 g cm⁻³, space group *B*₂/c (a non-standard setting of *P*₂₁/c, no. 14, *C*_{2h}²), Mo-*K*_α radiation (λ = 0.710 69 Å), μ(Mo-*K*_α) = 16.2 cm⁻¹, *F*(000) = 2 840.

Three-dimensional X-ray diffraction data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 diffractometer by the omega-scan method; 1 474 independent reflections for which *I*/σ(*I*) > 3.0 were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were detected in electron-density difference syntheses and were placed in calculated positions [C-H 0.95, N-H 0.90, B-H 1.14 Å; X-C-H (methyl) 112°, X = N or C]; their contributions were included in structure factor calculations (*B* = 10 Å²) but no refinement of positional parameters was permitted. The geometries of one pyrazolyl ring and of a half-occupancy dichloromethane solvent molecule were constrained during final refinement which converged at *R* 0.1065 with allowance for the anomalous scattering and anisotropic thermal motion of molybdenum and iodine only. Table 3 lists atomic positional parameters with estimated standard deviations in parentheses.

[Mo{HB(Me₂pz)₃}(NO)I(NHNMe₂)]. The complex was obtained from thf-*n*-pentane as small, orange-green dichroic elongated crystals which were twinned.

Crystal data. C₁₇H₂₉BIMoN₉O, *M* = 609.1, Monoclinic, *a* = 14.231(13), *b* = 20.648(9), *c* = 8.116(6) Å, β = 86.968(5)° *U* = 2 386(3) Å³, *D_m* = 1.65, *Z* = 4, *D_c* = 1.69 g cm⁻³, space group *P*₂₁/n (a non standard setting of *P*₂₁/c, no. 14, *C*_{2h}²), Mo-*K*_α radiation (λ = 0.710 69 Å), μ(Mo-*K*_α) = 18.4 cm⁻¹, *F*(000) = 1 208.

The data were collected (6.5 < 2θ < 50°) as for the methylphenylhydrazido-complex above. The nature of the twinning caused overlap of diffraction maxima only for *hk*0 and *hk*5 data and allowed the direct measurement of the twinning factor (0.60); *hk*0 data were appropriately scaled and *hk*5 data were eventually excluded from structure refinement after only partially successful attempts to include de-twinned values had been abandoned. The final data set comprised 1 385 independent reflections which were processed, and the structure solved, and refined (*R* 0.0662) as for the methylphenylhydrazido-complex above. No constraints were applied to the molecular geometry during refinement. Table 4 lists atomic positional parameters and estimated standard deviations.

Table 2. I.r. and ^1H n.m.r. spectral data for $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{XY}]$ (1) and $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{N}_2)\}(\text{NO})\text{XY}]$ (2)

Complex			I.r. data ^a (cm^{-1})		^1H n.m.r. data			
	X	Y	$\nu(\text{NO})$	Other	δ ^b /p.p.m.	A ^c		Assignment
(1)	I	NHNH_2	1 635	3 390 (NH) 3 250 (NH)	12.70 5.86 5.82 5.80 2.60 2.55 2.44 2.39 2.33 2.32	1 3 18 (+2?)	(s,br) (s) (s) (s) (s) (s) (s) (s) (s) (s)	NHNH_2 $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$ (+ NHNH_2)
(1)	I	NHNHMe	1 635	3 400 (NH) 3 250 (NH)	12.22 5.88 5.85 5.83 4.07 2.65 2.58 2.40 2.37 2.32 2.22	1—2 3 3 18	(s,br) (s) (s) (s) (s) (s) (s) (s) (s) (s) (s)	NHNHMe $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{NHNH}(\text{CH}_3)$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$
(1)	I	NHNMe_2	1 634 1 640 ^d	3 276 (NH) 3 268 ^d (NH)	12.00 5.86 5.82 5.81 3.50 2.64 2.53 2.40 2.37 2.35 2.28 3.75 ^e 3.33 ^e	1 3 6 18 6	(s,br) (s) (s) (s) (s) (s) (s) (s) (s) (s) (s) (s,br) (s,br)	NHNMe_2 $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{NHN}(\text{CH}_3)_2$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$ $\text{NHN}(\text{CH}_3)_2$
(1)	I	NHNHPh	1 630	3 350 (NH)	11.22 7.00 5.88 5.84 5.77 2.63 2.54 2.41 2.35 2.34 2.23	2 5 3 18	(s) (m) (s) (s) (s) (s) (s) (s) (s) (s) (s)	AB pair, NHNHPh , $\delta(\text{A})$ 12.41, $\delta(\text{B})$ 10.03, $J(\text{AB})$ 11.8 Hz NHNHC_6H_5 $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$
(1)	I	$\text{NHNHC}_6\text{H}_4\text{Me-}p$	1 640	3 270 (NH)	11.25 7.04 5.89 5.85 5.78 2.66 2.56 2.44 2.36 2.26	2 4 18	(s) (s) (s) (s) (s) (s) (s) (s) (s) (s)	AB pair, $\text{NHNHC}_6\text{H}_4\text{Me}$, $\delta(\text{A})$ 12.47, $\delta(\text{B})$ 10.03, $J(\text{AB})$ 12.2 Hz AB pair, $\text{NHNHC}_6\text{H}_4\text{Me}$, $\delta(\text{A})$ 7.29, $\delta(\text{B})$ 6.79, $J(\text{AB})$ 7.3 Hz $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$
(1)	I	NHNHC_6F_5	1 630	3 400 (NH) 3 340 (NH)	11.0 1.67 5.89 5.84 5.81 2.60 2.53 2.40 2.34 2.28	3 2 3 18	(s) (s) (s) (s) (s) (s) (s) (s) (s) (s)	$\text{NHNHC}_6\text{H}_4\text{CH}_3$ AB pair, NHNHC_6F_5 , $\delta(\text{A})$ 12.63, $\delta(\text{B})$ 9.37, $J(\text{AB})$ 12.2 Hz $\text{C}_3\text{N}_2\text{HMe}_2$ $\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2$

Table 2 (continued)

Complex			I.r. data ^a (cm ⁻¹)		¹ H n.m.r. data			
	X	Y	$\nu(\text{NO})$	Other	$\delta^b/\text{p.p.m.}$	A^c	Assignment	
(1)	I	NHNHMePh	1 636 1 644 ^d	3 260 (NH) 3 260 (NH) ^d	12.53 7.00 5.86 5.79 4.31 2.72 2.42 2.44 2.38 2.19	1 (s) 5 (m) 3 (s + sh) (s) (s) (s) (s) (s) (s) (s)	NHNHMePh NHNHMe(C ₆ H ₅) C ₃ N ₂ HMe ₂	
(1)	I	NHNHCSNH ₂	1 654 1 654 ^d	3 284 (NH) 3 168 (NH) 3 120 (NH) 3 300 ^d (NH) 3 100 ^d (NH)	12.62 6.43 5.89 5.86 5.80 2.60 2.59 2.40 2.37 2.35 2.20	2 2 (s) 3 (s) (s) (s) (s) (s) (s) (s) (s) (s)	AB pair, NHNHCSNH ₂ , $\delta(\text{A})$ 13.32, $\delta(\text{B})$ 11.92, $J(\text{AB})$ 12.2 Hz NHNHCSNH ₂ C ₃ N ₂ HMe ₂ C ₃ N ₂ H(CH ₃) ₂	
(1)	I	NHNHCO ₂ Me	1 652 1 658 ^d	3 330 (NH) 3 220 (NH) 1 720 (CO) 3 410 ^d (NH) 3 250 ^d (NH)	11.48 5.88 5.83 5.79 2.60 2.55 2.40 2.34 2.33 2.26	2 3 (s) (s) (s) (s) (s) (s) (s) (s) (s)	AB pair, NHNHCO ₂ Me, $\delta(\text{A})$ 12.64, $\delta(\text{B})$ 10.32, $J(\text{AB})$ 12.2 Hz C ₃ N ₂ HMe ₂ C ₃ N ₂ H(CH ₃) ₂ + NHNHCO ₂ CH ₃	
(1)	I	NHNHCOPh	1 623	3 320 (NH) 3 200 (NH) 1 664 (CO)	12.59 7.75 5.91 5.87 5.80 2.59 2.57 2.42 2.35 2.33 2.26	2 5 (m) 3 (s) (s) (s) (s) (s) (s) (s) (s) (s)	AB pair, NHNHCOPh, $\delta(\text{A})$ 13.42, $\delta(\text{B})$ 11.35, $J(\text{AB})$ 10.7 Hz NHNHCOC ₆ H ₅ C ₃ N ₂ HMe ₂ C ₃ N ₂ H(CH ₃) ₂	
(1)	I	NHN=CMe ₂	1 658	3 160 (NH)	13.66 5.91 5.81 5.79 2.60 2.58 2.50 2.43 2.33 2.21 2.15	1 (s) 3 (s) (s) (s) (s) (s) (s) (s) (s) (s) (s)	NHN=CMe ₂ C ₃ N ₂ HMe ₂ C ₃ N ₂ H(CH ₃) ₂ NHNC(CH ₃) ₂	
(2)	Br	NHNH ₂	1 615	3 400 (NH) 3 260 (NH)	11.04 5.86 2.61 2.59 2.56 2.41 2.32	1 (s) 2 (s) (s) (s) (s) (s) (s)	NHNH ₂ C ₃ N ₂ HMe ₂ C ₃ N ₂ H(CH ₃) ₂ + NHNH ₂ ?	
(2)	Br	NHNMe ₂	1 615	3 210 (NH)	10.69 5.86 3.33 2.68 2.62 2.49 2.43 2.34 2.32	1 (s) 2 (s) 6 (s) (s) (s) (s) (s) (s) (s)	NHNMe ₂ C ₃ N ₂ HMe ₂ NHN(CH ₃) ₂ C ₃ N ₂ H(CH ₃) ₂	

Table 2 (continued)

Complex			I.r. data ^a (cm ⁻¹)		¹ H n.m.r. data		
	X	Y	v(NO)	Other	δ ^b /p.p.m.	<i>A</i> ^c	Assignment
(2)	Br	NHNHPh	1 615	3 220 (NH)	10.07	2	AB pair, NHNHPh, δ (A) 12.14, δ (B) 8.99, <i>J</i> (AB) 11.0 Hz
					7.00	5 (m)	NHNHC ₆ H ₅
					5.88	2 (s)	C ₃ N ₂ HMe ₂
					5.84		
					2.66	(s)	C ₃ N ₂ H(CH ₃) ₂
					2.58	(s)	
					2.46	(s)	
					2.35	(s)	
					11.77	1 (s)	NHNHMe ₂
(2)	Br	NHNHMe ₂	1 630	3 150 (NH) 1 715 (CO)	5.85	2 (s)	C ₃ N ₂ HMe ₂
					5.83	(s)	C ₃ N ₂ H(CH ₃) ₂
					2.62	(s)	
					2.57	(s)	
					2.44	(s)	
					2.32	(s)	
					2.22	(s)	NHNH(CH ₃) ₂
					2.21	(s)	OC(CH ₃) ₂
					2.16	(s)	

^a In KBr discs unless otherwise stated. ^b In CDCl₃ unless otherwise stated. ^c Relative area (multiplicities in parentheses). ^d In CHCl₃ solution. ^e At -75 °C.

Table 3. Atomic positional parameters for [Mo{HB(Me₂pz)₃}(NO)I(NHNMePh)]·0.5CH₂Cl₂ * with estimated standard deviations in parentheses

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
I	0.370 32(14)	0.378 56(13)	0.212 6(3)	C(8)	0.438 5(18)	0.244 0(19)	-0.030(3)
Mo	0.270 00(15)	0.312 79(14)	0.098 4(3)	C(9)	0.406 5(16)	0.184 3(17)	-0.009(3)
O	0.251 8(14)	0.430 5(14)	-0.018 0(20)	C(10)	0.427 7(22)	0.113 4(23)	-0.019(3)
N(1)	0.259 7(14)	0.383 2(15)	0.035 2(22)	C(11)	0.110 3(18)	0.322 1(19)	-0.042(3)
N(2)	0.282 0(12)	0.217 2(9)	0.184 0(17)	C(12)	0.148 4(17)	0.254 8(17)	-0.038(3)
N(3)	0.292 6(11)	0.156 8(13)	0.143 7(13)	C(13)	0.128 7(17)	0.194 3(18)	-0.085(3)
N(4)	0.348 2(12)	0.267 9(12)	0.035 7(20)	C(14)	0.180 1(17)	0.149 9(17)	-0.051(3)
N(5)	0.352 7(13)	0.198 9(13)	0.028 4(20)	C(15)	0.188 2(22)	0.078 3(22)	-0.090(3)
N(6)	0.207 0(12)	0.247 3(13)	0.007 4(20)	C(16)	0.170 0(20)	0.450 4(21)	0.145(3)
N(7)	0.229 7(12)	0.179 7(12)	0.002 4(19)	C(17)	0.087 4(18)	0.369 7(18)	0.187(3)
N(8)	0.194 9(12)	0.332 4(13)	0.151 4(20)	C(18)	0.060 4(17)	0.303 2(18)	0.177(3)
N(9)	0.151 5(14)	0.382 8(15)	0.167 7(22)	C(19)	-0.003 0(24)	0.287 4(24)	0.202(3)
C(1)	0.269 7(19)	0.254 8(20)	0.323 4(29)	C(20)	-0.034 6(24)	0.336 0(24)	0.237(3)
C(2)	0.281 3(10)	0.202 5(8)	0.267 6(15)	C(21)	-0.007 9(23)	0.401 2(23)	0.243(3)
C(3)	0.291 3(8)	0.133 6(9)	0.284 3(13)	C(22)	0.054 2(19)	0.419 4(19)	0.220(3)
C(4)	0.298 0(10)	0.107 6(8)	0.204 2(15)	B	0.293 6(19)	0.154 7(19)	0.059(3)
C(5)	0.312 0(20)	0.034 9(20)	0.177(3)	Cl(1)	0.093(4)	0.034 7(14)	0.083 2(18)
C(6)	0.409 2(20)	0.372 0(21)	0.000(3)	Cl(2)	0.098(4)	0.127 4(14)	0.229 7(18)
C(7)	0.399 2(17)	0.294 5(17)	0.001(3)	C(23)	0.115(3)	0.116 8(19)	0.124 1(23)

* Atoms Cl(1), Cl(2), and C(23) comprise the half-occupancy dichloromethane solvent molecule. The geometries of the dichloromethane and of one pyrazolyl ring [N(2), N(3), C(2)—C(4)] were constrained during refinement; the estimated standard deviations for the positional parameters of these atoms were derived from the e.s.d.s of the translational and rotational parameters of the group which were refined.

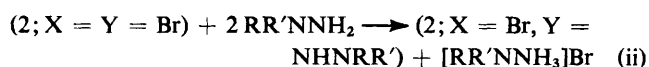
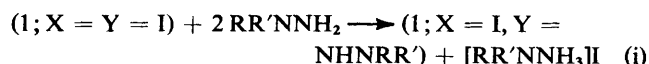
Table 4. Atomic positional parameters for [Mo{HB(Me₂pz)₃}(NO)I(NHNMe₂)] with estimated standard deviations in parentheses

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
I	0.163 01(13)	0.205 07(9)	0.190 5(3)	C(4)	0.066 9(16)	0.011 2(11)	-0.218(3)
Mo	0.286 82(14)	0.122 94(10)	0.008 6(3)	C(5)	0.028 7(18)	-0.054 7(13)	-0.244(3)
O	0.435 8(12)	0.172 5(9)	0.217(2)	C(6)	0.280 1(19)	0.086 9(13)	0.464(3)
N(1)	0.380 3(15)	0.152 4(10)	0.129(3)	C(7)	0.254 5(14)	0.032 1(10)	0.347(3)
N(2)	0.165 5(12)	0.089 4(9)	-0.138(2)	C(8)	0.232 5(15)	-0.030 8(12)	0.385(3)
N(3)	0.148 8(12)	0.023 2(9)	-0.145(2)	C(9)	0.214 9(15)	-0.061 0(11)	0.245(3)
N(4)	0.247 9(12)	0.040 5(9)	0.181(2)	C(10)	0.194 8(20)	-0.131 1(15)	0.204(4)
N(5)	0.223 7(12)	-0.018 8(9)	0.118(2)	C(11)	0.523 3(19)	0.093 3(14)	-0.178(4)
N(6)	0.361 8(12)	0.044 0(9)	-0.118(2)	C(12)	0.450 2(17)	0.039 0(12)	-0.181(3)
N(7)	0.317 8(12)	-0.013 5(8)	-0.151(2)	C(13)	0.461 6(17)	-0.021 5(13)	-0.259(3)
N(8)	0.310 9(11)	0.181 7(8)	-0.182(2)	C(14)	0.379 6(17)	-0.053 7(13)	-0.240(3)
N(9)	0.358 9(15)	0.235 9(11)	-0.223(3)	C(15)	0.351 7(18)	-0.121 9(14)	-0.283(3)
C(1)	0.092 2(19)	0.190 1(14)	-0.256(4)	C(16)	0.413 5(19)	0.264 3(13)	-0.094(4)
C(2)	0.096 8(16)	0.118 4(13)	-0.222(3)	C(17)	0.383 0(21)	0.247 0(15)	-0.394(4)
C(3)	0.037 5(17)	0.068 8(12)	-0.275(3)	B	0.218 1(18)	-0.026 5(13)	-0.070(4)

Scattering factors were taken from ref. 14; unit weights were used throughout the refinement. Computer programs formed part of the Sheffield X-ray system.

Results and Discussion

Synthetic Studies.—The complexes $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{XY}]$ (1) ($\text{X} = \text{I}$, $\text{Y} = \text{NHNRR}'$; $\text{R} = \text{H}$, $\text{R}' = \text{H}$, Me , Ph , $\text{C}_6\text{H}_4\text{Me-}p$, C_6F_5 , COPh , CO_2Me , or CSNH_2 ; $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$ or Ph) and $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{N}_2)\}(\text{NO})\text{XY}]$ (2) ($\text{X} = \text{Br}$, $\text{Y} = \text{NHNRR}'$; $\text{R} = \text{R}' = \text{H}$ or Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$) were prepared by treating (1; $\text{X} = \text{Y} = \text{I}$) and (2; $\text{X} = \text{Y} = \text{Br}$) with an excess of the appropriate hydrazine in dichloromethane, the precise conditions being dependent on the particular hydrazine. The excess of hydrazine facilitated removal of HI or HBr generated in the reactions (i) and (ii). On occasions the hydrazinium salts could be



isolated and characterised. Analytical and molecular weight data for the new complexes are given in Table 1.

The hydrazido(1-) species (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNH}_2$) and (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNH}_2$) were prepared at room temperature and were found to be unstable in solution, decomposition occurring over about 10 min in air. The species (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNHMe}$) was also rather unstable. However, the remainder of the complexes proved to be relatively stable towards air, the species containing electron-withdrawing substituents being formed quite quickly at room temperature whereas those containing $\text{Y} = \text{NHNRR}'$ ($\text{R} = \text{H}$, $\text{R}' = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me-}p$; $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$ or Ph) were obtained after quite long periods of refluxing in dichloromethane.

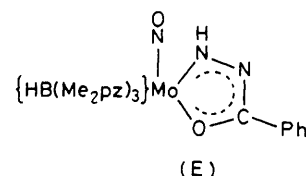
The molybdenum complexes could also be prepared by prior treatment of (1; $\text{X} = \text{Y} = \text{I}$) with AgO_2CMe in dichloromethane followed by addition of the hydrazine, the time for isolation of the desired complexes being reduced by about half. The intermediate in this reaction is probably (1; $\text{X} = \text{I}$, $\text{Y} = \text{O}_2\text{CMe}$), and the overall synthesis parallels the behaviour of $[\text{Mo}(\eta^2\text{-C}_3\text{H}_5)(\text{NO})\text{I}(\text{O}_2\text{CMe})]$ which we have described previously.²

The M-N bond in these hydrazido(1-) complexes is readily susceptible to acidolysis, in a manner entirely similar to the closely related monoalkylamides (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHR}$) and (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHR}$).⁷ Thus treatment of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNH}_2$) with HCl afforded a mixture of (1; $\text{X} = \text{I}$, $\text{Y} = \text{Cl}$) and (1; $\text{X} = \text{Y} = \text{Cl}$), and hydrazine (as hydrochloride) but apparently no ammonia (p -dimethylamino-benzaldehyde-indophenol tests;¹⁵ vapour phase chromatography). Similarly, treatment of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNHPh}$) with HI afforded (1; $\text{X} = \text{Y} = \text{I}$) and $[\text{PhNHNH}_3]\text{I}$ which was isolated and identified by i.r. spectroscopy and mixed melting point comparison with an authentic sample of the salt.

Treatment of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNH}_2$) with acetone afforded (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHN=CMe}_2$); isolated as an acetone solvate. It was not necessary to use either NEt_3 or acid to catalyse this reaction. This contrasts with the behaviour of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NH}_2$) which gives (1; $\text{X} = \text{I}$, $\text{Y} = \text{N=CMe}_2$) in the presence of NEt_3 ,⁷ and with the reactions of the hydrazido(2-) complexes $\text{trans-}[\text{MX}(\text{=NNH}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{-PPh}_2)_2]^+$ and $[\text{WX}_2(\text{=NNH}_2)(\text{PR}_3)_3]$ in the presence of acetone, when the group M=N=N=CMe_2 is formed.¹⁶

In the reaction between (1; $\text{X} = \text{Y} = \text{I}$) and potentially chelating 'hydrazines', e.g. NH_2NHCOPh , thiosemicarbazide, etc., only the hydrazido(1-) species (1; $\text{X} = \text{I}$, $\text{Y} =$

NHNHR) were formed, and we could obtain no evidence for the formation of species such as (E). This behaviour contrasts



with the reaction of $[\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3]$ with NH_2NHCOPh ,

when $[\text{MoCl}(\text{N}_2\text{COPh})(\text{NHNCOPh})(\text{PMe}_2\text{Ph})_2]$, containing a chelating N -benzoyldiazene- N',O group is formed.¹⁷

Spectral Studies.—The i.r. spectra of the new complexes (Table 2) exhibit the expected absorptions due to the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand [*ca.* 2 500 cm^{-1} due to $\nu(\text{BH})$ and 1 400 cm^{-1} associated with the pyrazolyl ring]. The NO stretching frequencies of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNRR}'$) occur between 1 623 and 1 658 cm^{-1} , comparable to the related amido-species (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHR}$),⁷ whereas $\nu(\text{NO})$ in the related tungsten complexes (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNRR}'$) occurs at 1 615 cm^{-1} . This drop in NO stretching frequency of the W complexes relative to their Mo analogues presumably reflects greater back-donation from W to NO. This could be brought about possibly by the greater size of the tungsten atom relative to molybdenum which facilitates closer approach of the $\text{-NHNRR}'$ group to W (the whole system would be slightly less sterically hindered than the Mo analogues) thereby enhancing $\text{N} \rightarrow \text{M } p\pi\text{-}d\pi$ donation. There would also be increased overlap between the more diffuse d orbitals in W and the π^* orbitals on NO. The NO stretching frequencies of (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHN=CMe}_2$) and (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHN=CMe}_2$) are *ca.* 20 cm^{-1} higher than those in the related complexes with $\text{Y} = \text{NHNH}_2$, reflecting the reduction of the donating powers of the -NHNH group by introduction of a C=N bond.

The hydrazido-complexes containing $\text{-NHNRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) exhibit one $\nu(\text{NH})$ in the expected position between 3 100 and 3 400 cm^{-1} . The species containing -NHNHR ($\text{R} = \text{Me}$, C_6F_5 , CO_2Me , and COPh) exhibit two $\nu(\text{NH})$, as do the unsubstituted hydrazido(1-) complexes (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNH}_2$) and (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNH}_2$). It may be noted that (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHN=CMe}_2$) and (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHN=CMe}_2$) also show only one NH stretching mode. Those complexes containing NHNHCOPh , NHNHCO_2Me , and NHNHCSNH_2 groups exhibited bands typical of their group frequencies, suggesting that the O or S atoms are *not* co-ordinated to the metal.

The ^1H n.m.r. spectra of the new compounds are summarised in Table 2. Generally, the complexes exhibit a group of signals around δ 2.5 p.p.m. due to the methyl groups of the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand. Resonances due to the proton attached to C^4 of the pyrazolyl groups occur between δ 5.0 and 6.0 p.p.m., and in the Mo complexes these signals usually appear as three singlets. This multiplicity in the asymmetric series (1; $\text{X} = \text{I}$, $\text{Y} = \text{NHNRR}'$) is due to the lack of a plane of symmetry in these six-co-ordinate complexes. In the compounds (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNRR}'$) there are only two C^4 protons, one of the three pyrazolyl rings being brominated at this position. Accordingly, because of the asymmetric nature of these compounds, we could expect to see two H^4 signals, as found in the spectra of (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNHPh}$ and NHN=CMe_2). However, in the spectra of (2; $\text{X} = \text{Br}$, $\text{Y} = \text{NHNH}_2$ and NHNMe_2), only one signal was observed, and we presume this is due to accidental degeneracy.

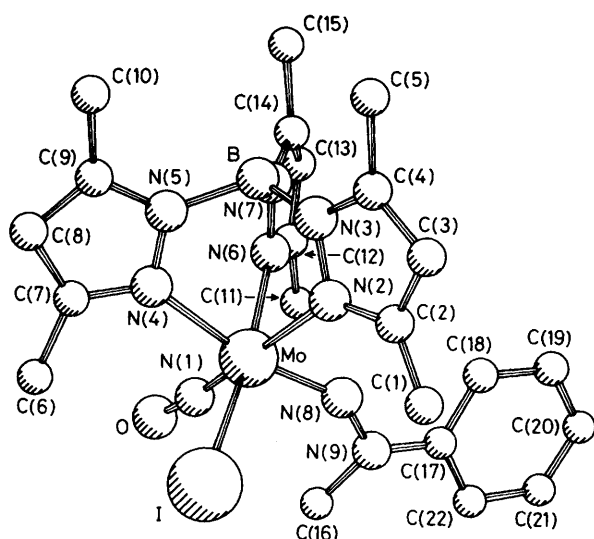


Figure 1. Molecular structure of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NH-NMePh})]$ showing the atom labelling

The signals associated with the N-H protons are generally sharp and well resolved. To a first approximation, the α -NH protons resonate in the range 11.00–12.70 p.p.m. in the Mo complexes, values which are broadly comparable with their monoalkylamido-analogues, (1; X = I, Y = NHR).⁷ The α -NH signals in the hydrazidotungsten complexes appear in the range 10.00–11.00 p.p.m. However, the proton signals in the species containing -NHNHR appear as AB pairs, with the exception of the simple hydrazido(1-) species (1; X = I, Y = NHNH_2) and (2; X = Br, Y = NHNH_2), and of (1; X = I, Y = NHNHMe). The occurrence at low field of these signals is consistent with the strong electron-withdrawing properties of the metal atom.

The spectra of (1; X = I, Y = NHNH_2) and (2; X = Br, Y = NHNH_2) revealed, in addition to the normal pyrazolyl ligand resonances, only one signal due to the α -NH group. We concluded that the β -NH₂ signals might occur under those of the 3,5-Me₂ protons, but we were unable to establish this unequivocally using integration techniques or *via* exchange with D₂O.

Variable-temperature ¹H n.m.r. spectral studies were carried out using (1; X = I, Y = NHNMe_2). At probe temperature (26 °C), the methyl signals of the hydrazido-group appeared as a sharp line at δ 3.50 p.p.m. On cooling to -75 °C, however, two separate signals, at δ 3.33 and 3.75 p.p.m., were observed. This is consistent with the cessation of rotation about the N-N bond of the hydrazido-group at low temperatures, given that the molecule as a whole has no plane of symmetry and that the -NHNMe_2 group is unidentate. We calculated, on the basis of coalescence temperatures, that ΔG for the N-N bond rotation was of the order of 39 kJ mol⁻¹, significantly lower than for the related process in $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NMeNMe}_2)]$ (59 kJ mol⁻¹).² However, in the latter system, the MoNMeNMe_2 chelate ring has to open and there must be inversion at the NMe₂ group for methyl group site exchange to occur. This N-N bond rotational effect was not detected in the other new hydrazido(1-) species described here, so that the ¹H n.m.r. spectrum of (1; X = I, Y = NHNMePh) showed only one sharp methyl signal over the temperature range -70 °C (below which the compound crystallised) to +50 °C (above which it decomposed).

The ¹H n.m.r. spectra of (1; X = I, Y = NHN=CMe_2) and

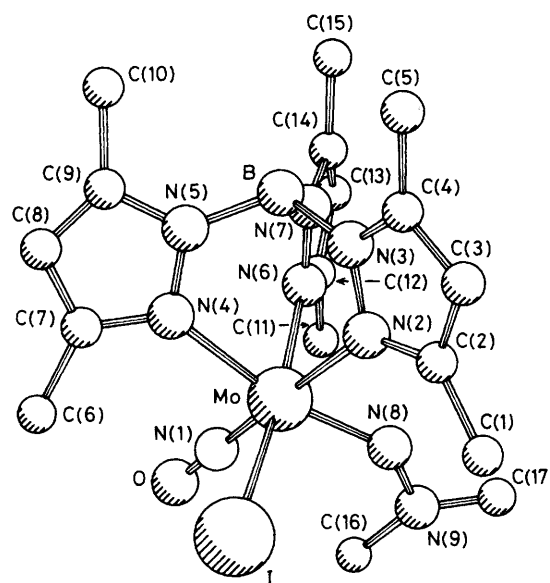
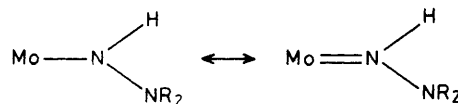


Figure 2. Molecular structure of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NH-NMe}_2)]$ showing the atom labelling

(2; X = Br, Y = NHN=CMe_2) exhibited $\delta(\text{NH})$ at lower field than that in the precursors containing -NHNH_2 , and two signals due to the CH₃ group of NHN=CMe_2 ; the acetone of solvation was also detected.

Crystallographic Studies.—The structure of the methylphenylhydrazido(1-) complex and of the dimethylhydrazido(1-) complex are illustrated in Figures 1 and 2 respectively, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) are given in Table 5.

In both (1; X = I, Y = NHNMePh) and (1; X = I, Y = NHNMe_2), the co-ordination geometry of the molybdenum is distorted octahedral; the molybdenum-nitrosyl fragments are linear, although that of the less well determined methylphenylhydrazido-complex shows ill distributed bond lengths: the molybdenum-iodine bond lengths are slightly short, reflecting some small degree of π -donor bonding. The pyrazolyl rings are essentially planar with small deviations of the substituent methyl groups and larger deviations of molybdenum and boron atoms from their mean planes. As noted in the case of related arylamido-complexes,¹ the angular distortions of the tris(pyrazolyl)borato-fragments from C₃ symmetry reflect the bulk of the adjacent unidentate ligands. The molybdenum-nitrogen and nitrogen-nitrogen bonds of the hydrazido-molybdenum fragments are intermediate in length between single and double bonds, suggesting some redistribution of electron density of the form shown below. The two molyb-



denum-nitrogen bond lengths differ markedly and although this difference may simply reflect the associated high estimated standard deviations, particularly in the methylphenylhydrazido-complex, a contributing factor may be an apparently greater π -donor capacity of this methylphenylhydrazido-ligand, as evidenced by its extended π -electron delocalisation.

Table 5. Bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses, for [Mo{HB(Me₂pz)₃}(NO)I-(NHNMePh)]·0.5CH₂Cl₂ * (A) and [Mo{HB(Me₂pz)₃}(NO)I(NHNMe₂)] (B)

	A	B		A	B
Mo-N(2)	2.30(2)	2.261(18)	I-Mo-N(6)	168.9(7)	168.3(5)
Mo-N(4)	2.18(3)	2.253(18)	I-Mo-N(8)	99.5(8)	96.8(5)
Mo-N(6)	2.17(3)	2.178(18)	N(1)-Mo-N(2)	179.0(12)	177.6(8)
Mo-N(1)	1.70(3)	1.80(2)	N(1)-Mo-N(4)	95.2(13)	94.8(8)
N(1)-O	1.24(4)	1.17(3)	N(1)-Mo-N(6)	95.5(13)	98.7(8)
Mo-I	2.787(5)	2.810(3)	N(1)-Mo-N(8)	93.7(13)	96.5(8)
Mo-N(8)	1.88(3)	1.980(17)	N(2)-Mo-N(4)	85.5(9)	85.8(7)
N(8)-N(9)	1.37(4)	1.34(3)	N(2)-Mo-N(6)	83.9(9)	83.8(7)
N(9)-C(16)	1.44(5)	1.46(4)	N(2)-Mo-N(8)	85.4(10)	83.3(7)
N(9)-C(17)	1.39(5)	1.43(4)	N(4)-Mo-N(6)	81.2(10)	80.0(7)
C(17)-C(18)	1.42(5)		N(4)-Mo-N(8)	167.6(11)	166.9(7)
C(18)-C(19)	1.43(6)		N(6)-Mo-N(8)	89.5(11)	91.7(7)
C(19)-C(20)	1.32(7)		Mo-N(1)-O	174(3)	174.8(19)
C(20)-C(21)	1.39(7)		Mo-N(8)-N(9)	144(2)	140.3(15)
C(21)-C(22)	1.40(6)		N(8)-N(9)-C(16)	115(3)	116(2)
C(22)-C(17)	1.34(6)		N(8)-N(9)-C(17)	123(3)	118(2)
Mo-N(2)-N(3)	116(2)	117.4(13)	C(16)-N(9)-C(17)	121(3)	121(2)
Mo-N(4)-N(5)	120(2)	120.0(13)	N(9)-C(17)-C(18)	120(3)	
Mo-N(6)-N(7)	116(2)	121.3(13)	N(9)-C(17)-C(22)	119(4)	
Mo-N(2)-C(2)	137(2)	136.0(15)	C(18)-C(17)-C(22)	121(4)	
Mo-N(4)-C(7)	133(2)	132.8(14)	C(17)-C(18)-C(19)	121(4)	
Mo-N(6)-C(12)	133(2)	131.8(16)	C(18)-C(19)-C(20)	118(4)	
I-Mo-N(1)	90.3(10)	88.5(7)	C(19)-C(20)-C(21)	119(5)	
I-Mo-N(2)	90.4(6)	89.2(5)	C(20)-C(21)-C(22)	125(4)	
I-Mo-N(4)	89.0(7)	90.2(5)	C(21)-C(22)-C(17)	116(4)	

* The geometry of pyrazolyl ring N(2), N(3), C(1)—C(5) of the methylphenylhydrazido-complex was constrained during refinement. The C-Cl bond length for the solvent dichloromethane in the structure of the methylphenylhydrazido-complex was constrained at 1.768 Å and the Cl-C-Cl angle at 111.9°.

The hydrazido(1-) ligands * are too bulky to adopt their more familiar dihapto-mode of attachment at this sterically crowded co-ordination site and the monohapto-bonding mode is imposed, with a very large Mo-N-N angle. As in related structures in this series,^{1,7} the Mo-N(pyrazolyl) bond lengths reflect the competitive nature of the π bonding by the *trans* ligand. The N(1)-Mo(1)-N(8)-N(9) torsion angles are moderately small (+18.7° for the methylphenylhydrazido-complex, +14.3° for the dimethylhydrazido-complex) and are comparable to those found in related amido-complexes;^{1,7} however, they are much larger than those observed in complexes with alkoxy ligands^{1,5} where in-plane π bonding is facilitated by an approximate eclipsing of the alkoxy residue by the electron-withdrawing nitrosyl ligand.

Conclusion

From the spectral and crystallographic data described above, it is quite clear that the hydrazido(1-) species reported here contain unidentate -NHNRR' groups. While the spectroscopic evidence for the existence of the -NHNH₂ species is circumstantial (*i.e.* we were unable unambiguously to assign the -NH₂ groups by ¹H n.m.r. spectroscopy), from the combination of this with the chemical findings (formation of -NHN=CMe₂ species) it seems that the species (1; X = I, Y = NHNH₂) and (2; X = Br, Y = NHNH₂) represent one of the very few, if not the only, characterised hydrazido(1-), -NHNH₂, complexes.

Unlike the behaviour of [Mo(η^5 -C₅H₅)(NO)I(NHNRR')], where protonation afforded [Mo(η^5 -C₅H₅)(NO)I(NH₂-NRR')]⁺,² addition of acid to the tris(dimethylpyrazolyl)-

borato-complexes caused scission of the M-N bond with loss of the hydrazine function apparently without N-N bond rupture. That this happens is consistent with the structure of the pyrazolylborate complexes in relation to their cyclopentadienyl analogues, and with the chemistry of the related amido-complexes (1; X = I, Y = NHR) which lose amine on treatment with acid.⁷

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* The n.m.r. and i.r. evidence for the hydrazido-proton shows that the ligand is clearly hydrazido(1-) and not hydrazido(2-), which, in any case, would lead to a paramagnetic complex.

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