The Chemistry of Cyclopentadienyl Nitrosyl Compounds of Molybdenum. Part 13.[1] Hydrazine, Hydrazido(1−)-, and Hydrazido(2−)-complexes †

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Reaction of $[\{Mo(\eta\text{-}C_5H_5)(NO)X_2\}_2]$ (X = Cl, Br, or I), $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$, or $[Mo(C_5H_5)_2I(NO)]$ with alkyl- or aryl-hydrazines, NHRNR′R″ (R = R′ = H, R″ = Me, Ph, $C_6H_4NO_2$-*p*, C_6H_4Me-*p*, or C_6F_5; R = H, R′ = R″ = Me or Et or R′ = Me, R″ = Ph; R = R′ = R″ = Me), affords (*i*) simple hydrazine adducts, $[Mo(\eta\text{-}C_5H_5)(NHRNR'R'')(NO)X_2]$ (1), (*ii*) hydrazido(1−)-complexes, $[Mo(\eta\text{-}C_5H_5)(NRNR'R'')I(NO)]$ (2), and (*iii*) hydrazido(2−) complexes, $[\{Mo(\eta\text{-}C_5H_5)(NO)X\}_2NNR'R'']$ (4). Protonation of (2) or (4) with HBF_4 gives the hydrazine adducts $[Mo(\eta\text{-}C_5H_5)I(NHRNR'R'')(NO)][BF_4]$ (3). The species (1), on the basis of spectral data, may contain either a unidentate or a chelating hydrazine, the latter forming a three-membered ring with the metal. Species (2) may also contain a three-membered MoNN chelate ring which on protonation affords (3), whose structure is known to involve a bidentate hydrazine bound to only one metal atom. The binuclear species (4) contain the hydrazido(2−)-ligand asymmetrically bridging the two Mo atoms, one N atom being bound to one Mo atom by a σ- and a $(p_\pi \rightarrow d_\pi)$-donor bond, and the other Mo atom being attached to both N atoms *via* σ bonds in a three-membered ring. The chemical and structural relationships between (1), (2), (3), and (4) are discussed.

HYDRAZIDO-(1−) and -(2−) complexes of transition metals are relatively rare and those examples which are known are largely confined to species containing tertiary phosphines or dithiocarbamates as ancillary ligands.[2-4] Hydrazido-compounds of molybdenum are of particular interest since it has been elegantly demonstrated by Chatt, Pearman, and Richards [3,5] that dinitrogen, bound to monomeric molybdenum (and tungsten) complexes, may be sequentially protonated giving hydrazido(2−) then hydrazido(1−) species and, ultimately, ammonia and some hydrazine. These results may have considerable relevance to the postulated modes of reduction of N_2 to NH_3 by the enzyme nitrogenase.[6]

The syntheses and modes of bonding of hydrazido-ligands have been relatively little explored. Our somewhat adventitious discovery that $[Mo(C_5H_5)_2I(NO)]$ reacted with $PhNHNH_2$ and Me_2NNH_2 giving a variety of hydrazido-complexes [7] led us to examine systematically the reactions of the η-cyclopentadienyl nitrosyl halides of molybdenum with a series of alkyl- and aryl-hydrazines. Preliminary accounts of some of our work have been given,[8,9] and this paper contains a full report of the synthesis of, and the structural relationships between, simple hydrazine adducts, hydrazido(1−) and binuclear hydrazido(2−) complexes.

The only other reported η-cyclopentadienyl hydrazido-(1−) complexes of molybdenum appear to be those obtained [10] by treatment of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ with RN=NR (R = Ph or CO_2Me), of which only $[Mo(\eta\text{-}C_5H_5)_2H(RNNHR)]$ (R = CO_2Me) was actually isolated. A possibly related series of complexes has been derived [11] by protonation of $[Mo(\eta\text{-}C_5H_5)(CO)_2\{NNHC(CO_2Et)C(OH)\}]$, itself produced by reaction of $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$ with $N_2CH_2CO_2Et$.

EXPERIMENTAL

The compounds $[\{Mo(\eta\text{-}C_5H_5)(NO)X_2\}_2]$ (X = Cl, Br, or I),[12] $[Mo(C_5H_5)_2I(NO)]$,[13] and $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$ [14] were prepared as described elsewhere. Trimethylhydrazine was prepared [15] by $Li[AlH_4]$ reduction of $Me_2NN{=}CH_2$, obtained by treatment of Me_2NNH_2 with formaldehyde. All yields are quoted relative to molybdenum-containing starting material, and all reactions were carried out under dinitrogen. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

Infrared spectra were obtained using Perkin-Elmer 457 and 180 spectrophotometers, and ^1H and ^{13}C n.m.r. spectra using Varian HA100, Perkin-Elmer R34, and JEOL PFT90 instruments. Mass spectra were recorded under ambient conditions and using a 'cold' probe, with A.E.I. MS9 and MS12 spectrometers. Molecular weights were determined osmometrically, and conductivity data were obtained using a Philips conductivity meter.

η-Cyclopentadienyldi-iodo(methylhydrazine)nitrosylmolybdenum, $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NHMe)(NO)]$ (1; X = I, R = R′ = H, R″ = Me).—A suspension of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) and methylhydrazine (0.10 g) was stirred at room temperature (r.t.) for 24 h in dichloromethane (40 cm^3). The dull yellow precipitate which formed was filtered off, washed three times in dichloromethane to remove iodine, and dried *in vacuo* (0.8 g, 72%).

η-Cyclopentadienyl(1,1-dimethylhydrazine)di-iodonitrosylmolybdenum, $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NMe_2)(NO)]$ (1; X = I, R = H, R′ = R″ = Me).—To a suspension of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g, 1.12 mmol) in dichloromethane (20 cm^3) was added a solution (20 cm^3) of 1,1-dimethylhydrazine (0.7 g, 1.167 mmol) in dichloromethane (100 cm^3). The mixture was stirred for 24 h, after which time the yellow suspension which had formed was filtered off. The compound $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NMe_2)(NO)]$ was washed with dichloromethane and dried *in vacuo* (0.8 g, 75%).

η-Cyclopentadienyldi-iodonitrosyl(trimethylhydrazine)-molybdenum, $[Mo(\eta\text{-}C_5H_5)I_2(NHMeNMe_2)(NO)]$ (1; X = I, R = R′ = R″ = Me).—A mixture of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) and trimethylhydrazine (0.17 g) in dichloromethane (50 cm^3) was stirred at room temperature for 24 h. The resulting orange solution was filtered and the solvent removed *in vacuo* affording the crude product. The *complex* was obtained from ethanol–di-isopropyl ether as an orange-brown powder (0.8 g, 69%).

η-Cyclopentadienyldi-iodonitrosyl(phenylhydrazine)molybdenum, $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NHPh)(NO)]$ (1; X = I, R =

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† No reprints available.

R′ = H, R″ = Ph).—To a suspension of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) in dichloromethane (30 cm^3) was added a solution (10 cm^3) of phenylhydrazine (2.4 g) in dichloromethane (100 cm^3). The mixture was stirred for 24 h, after which time the yellow suspension which had formed was filtered off. The *complex* was washed with dichloromethane and dried *in vacuo* (1.0 g, 80%). This compound is insoluble in all common organic solvents except SMe_2O in which it decomposes; it reacts with $(CD_3)_2CO$ giving $(CD_3)_2C{=}NNHPh$ and $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$.

η-Cyclopentadienyldi-iodonitrosyl(pentafluorophenylhydrazine)molybdenum, $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NHC_6F_5)(NO)]$ (1; X = I, R = R′ = H, R″ = C_6F_5).—*Method* (1). The compound $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) in dichloromethane (50 cm^3) was stirred overnight with $C_6F_5NHNH_2$ (0.49 g). The solution was then filtered and concentrated *in vacuo* producing a dark red-brown crystalline *compound*. This was filtered off, washed with diethyl ether, and dried *in vacuo* (1.33 g, 92%).

Method (2). A mixture of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) in $C_6F_5NHNH_2$ (an excess) was refluxed in benzene (100 cm^3) for 1 h. The mixture was then cooled, unchanged $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ filtered off, and the filtrate evaporated *in vacuo*. Iodine was removed from the residue by repeated washing with n-pentane, and the *complex* was recrystallised from dichloromethane–n-pentane affording a red-brown crystalline powder (45%).

The corresponding *bromide*, $[Mo(\eta\text{-}C_5H_5)Br_2(NH_2NHC_6F_5)(NO)]$ (1; X = Br, R = R′ = H, R″ = C_6F_5), was obtained similarly by method (2) and was recrystallised from dichloromethane–isopropyl alcohol giving yellow-brown crystals. The *p-nitrophenylhydrazine complex*, $[Mo(\eta\text{-}C_5H_5)I_2\{NH_2NH(C_6H_4NO_2\text{-}p)\}(NO)]$ (1; X = I, R = R′ = H, R″ = $C_6H_4NO_2$-*p*), was prepared according to method (1) and was obtained as a red-brown solid (78%).

*η-Cyclopentadienyldi-iodonitrosyl(*p*-tolylhydrazine)molybdenum*, $[Mo(\eta\text{-}C_5H_5)I_2\{NH_2NH(C_6H_4Me\text{-}p)\}(NO)]$ (1; X = I, R = R′ = H, R″ = C_6H_4Me-*p*).—To $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) in dichloromethane (50 cm^3) was added *p*-$MeC_6H_4NHNH_2$ (0.27 g). After 30 min a green-yellow precipitate had formed and was filtered off and dried *in vacuo* (0.22 g, 17%). The dark red filtrate, on evaporation *in vacuo*, afforded a dark yellow-brown solid which was collected, washed with n-hexane, and dried *in vacuo* (0.36 g, 28%).

η-Cyclopentadienyliodo{methylhydrazido(1−)}nitrosylmolybdenum, $[Mo(\eta\text{-}C_5H_5)I(NHNHMe)(NO)]$ (2; R = R′ = H, R″ = Me).—Methylhydrazine (0.12 g) in dichloromethane (5 cm^3) was added to a solution of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) in dichloromethane (40 cm^3) and the mixture was stirred for *ca.* 24 h at r.t. A bright yellow-green precipitate which had formed was filtered off and washed with di-isopropyl ether. More of the product was obtained by concentration *in vacuo* of the yellow filtrate followed by addition of an excess of di-isopropyl ether. The bright yellow powder which precipitated was combined with the earlier precipitate to give the complex (0.61 g, 75%).

η-Cyclopentadienyl{2,2-dimethylhydrazido(1−)}iodonitrosylmolybdenum, $[Mo(\eta\text{-}C_5H_5)I(NHNMe_2)(NO)]$ (2; R = H, R′ = R″ = Me).—To a suspension of $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NMe_2)(NO)]$ (1; X = I, R = H, R′ = R″ = Me) (1.0 g, 1.98 mmol) in dichloromethane (30 cm^3) was added a solution (10 cm^3) of 1,1-dimethylhydrazine (1.19 g, 19.83 mmol) in dichloromethane (100 cm^3). The mixture was stirred for 24 h and the white crystalline $[Me_2NNH_3]I$ (identified by its i.r. spectrum and mixed m.p.) was filtered off and washed with dichloromethane. The orange filtrate was evaporated *in vacuo* and the residue dissolved in dichloromethane (10 cm^3). After filtration to remove residual $[Me_2NNH_3]I$, the filtrate was partially evaporated *in vacuo* and treated with diethyl ether. The orange crystals of the *complex* which formed were filtered off and dried *in vacuo* (0.6 g, 80%).

This compound is unstable in solution except over very short periods, readily forming $[\{Mo(\eta\text{-}C_5H_5)I(NO)\}_2NNMe_2]$ (4; X = I, R′ = R″ = Me). Thermal decomposition *in vacuo* afforded gases which were collected and identified, by mass spectrometry and ^1H n.m.r. spectroscopy, as a mixture of, among other compounds, Me_2NNH_2 ($m/e = 60$) and C_5H_6 ($m/e = 66$), and some $[\{Mo(\eta\text{-}C_5H_5)I(NO)\}_2NNMe_2]$.

η-Cyclopentadienyliodonitrosyl{1,2,2-trimethylhydrazido(1−)}molybdenum, $[Mo(\eta\text{-}C_5H_5)I(NMeNMe_2)(NO)]$ (2; R = R′ = R″ = Me).—*Method* (1). A mixture of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g) and an excess of trimethylhydrazine (0.15 cm^3) was stirred in dichloromethane (40 cm^3) at r.t. for 24 h, during which time a bright orange solution formed. This solution was filtered and more trimethylhydrazine (0.15 cm^3) was added. After another 24 h, the resulting solution was filtered again and the solvent removed *in vacuo*. The residue was dissolved in ethanol and upon concentration of this the *product* was formed as a bright orange microcrystalline solid (0.6 g, 68%).

Method (2). The complex can also be prepared by treating $[Mo(\eta\text{-}C_5H_5)I_2(NHMeNMe_2)(NO)]$ (1; X = I, R = R′ = R″ = Me) (0.5 g) with an excess of trimethylhydrazine (0.15 cm^3) for 24 h, using the method described above. The *product* was obtained in comparable yield.

η-Cyclopentadienyliodonitrosyl{phenylhydrazido(1−)}molybdenum, $[Mo(\eta\text{-}C_5H_5)I(NHNHPh)(NO)]$ (2; R = R′ = H, R″ = Ph).—*Method* (1). To a stirred solution of $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$ (2.3 g) in dichloromethane (25 cm^3) was added phenylhydrazine (1.0 g). The yellow precipitate which formed immediately was filtered off after 3 h. The *complex* was washed with diethyl ether and dried *in vacuo* (2.1 g, 81%).

Method (2). A mixture of $[Mo(C_5H_5)_2I(NO)]$ (1.0 g, 2.6 mmol) and phenylhydrazine (0.3 g, 2.77 mmol) was stirred in dichloromethane (50 cm^3) for 24 h. The yellow precipitate of the *complex* was filtered off, washed with dichloromethane, and dried *in vacuo* (0.8 g, 90%).

Method (3). To a suspension of $[Mo(\eta\text{-}C_5H_5)I_2(NH_2NHPh)(NO)]$ (1; X = I, R = R′ = H, R″ = Ph) (0.8 g, 1.45 mmol) in dichloromethane (40 cm^3) was added a solution (10 cm^3) of triethylamine (1.5 g, 14.85 mmol) in dichloromethane (100 cm^3). The mixture was stirred for 24 h, after which time the yellow precipitate of the *complex* was filtered off, washed with dichloromethane, and dried *in vacuo* (0.5 g, 80%). A similar reaction using (1; X = I, R = R′ = H, R″ = Ph) (0.5 g) and phenylhydrazine [10 cm^3 of a solution of the hydrazine (1.0 g) in dichloromethane (100 cm^3)] as deprotonating agent similarly afforded the *complex* after 24 h (0.3 g, 80%).

η-Cyclopentadienyliodonitrosyl{pentafluorophenylhydrazido(1−)}molybdenum, $[Mo(\eta\text{-}C_5H_5)I(NHNHC_6F_5)(NO)]$ (2; X = I, R = R′ = H, R″ = C_6F_5).—To $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$ (1.0 g) dissolved in dichloromethane (30 cm^3) was added $C_6F_5NHNH_2$ (0.53 g). This mixture was stirred for 1 h, filtered, and the filtrate evaporated *in vacuo*, affording a dark brown residue. The *complex* was extracted with diethyl ether–n-pentane mixtures, and the extract filtered

giving a yellow-brown powder which was washed with n-pentane and dried *in vacuo* (0.83 g, 61%).

η-Cyclopentadienyliodo{p-*nitrophenylhydrazido*(1−)}*nitrosylmolybdenum*, $[Mo(\eta-C_5H_5)I\{NHNH(C_6H_4NO-p)\}(NO)]$ (2; R = R′ = H, R″ = $C_6H_4NO_2$-*p*).—A mixture of $[Mo(\eta-C_5H_5)I(NO)(O_2CMe)]$ (1.0 g) and *p*-$O_2NC_6H_4NHNH_2$ (0.41 g) was stirred in dichloromethane (50 cm^3) for 2 min. The dark yellow precipitate which formed was filtered off, washed with hexane, and dried *in vacuo* (0.97 g, 78%).

The p-*tolylhydrazido*(1−)-*complex* (2; R = R′ = H, R″ = C_6H_4Me-*p*), was prepared in the same way as (2; R = R′ = H, R″ = $C_6H_4NO_2$-*p*), using $[Mo(\eta-C_5H_5)I(NO)(O_2CMe)]$ (1.0 g) and *p*-$MeC_6H_4NHNH_2$ (0.32 g). The *complex* was isolated as a yellow solid (1.0 g, 86%). The compound could also be obtained by stirring a mixture of $[Mo(C_5H_5)_2I(NO)]$ (0.5 g) and the hydrazine (0.16 g) in dichloromethane (30 cm^3). After 2 h, the light yellow solid which had formed was filtered off, washed with n-pentane, and dried *in vacuo* (0.21 g, 36%).

η-Cyclopentadienyl(1,1-*dimethylhydrazine*-NN′)*iodonitrosylmolybdenum Tetrafluoroborate*, $[Mo(\eta-C_5H_5)I(NH_2NMe_2)(NO)][BF_4]$ (3; R = H, R′ = R″ = Me).—A mixture of $[\{Mo(\eta-C_5H_5)I(NO)\}_2NNMe_2]$ (4; X = I, R′ = R″ = Me) (1.0 g) (see below) and HBF_4 (0.7 g, 40% aqueous solution) in dichloromethane (50 cm^3) was stirred overnight. The resulting red-brown solution was passed through phase-separating paper and evaporated *in vacuo* to *ca.* 10 cm^3. n-Hexane was then added dropwise until the solution became slightly cloudy and the mixture was then stored at r.t. for *ca.* 24 h, during which time hexane was added to maintain cloudiness. The red-brown plate-like crystals which formed were filtered off and dried *in vacuo* (0.12 g). This was a very difficult preparation to repeat, and must be regarded as unreliable.

η-Cyclopentadienyliodonitrosyl(1,1,2-*trimethylhydrazine*-NN′)*molybdenum Tetrafluoroborate*, $[Mo(\eta-C_5H_5)I(NHMeNMe_2)(NO)][BF_4]$ (3; R = R′ = R″ = Me).—A mixture of $[Mo(\eta-C_5H_5)I(NMeNMe_2)(NO)]$ (2; R = R′ = R″ = Me) (0.5 g) and HBF_4 (0.3 g, 40% aqueous solution) in dichloromethane (40 cm^3) was stirred at r.t. overnight. The solution became dark red in colour and was filtered, the filtrate being concentrated *in vacuo* to 10 cm^3. To this was added n-pentane until the mixture became cloudy, and on standing for *ca.* 8 h the *complex* precipitated as an orange-brown powder (0.38 g, 36%).

Reaction of $[Mo(\eta-C_5H_5)I(NMeNMe_2)(NO)]$ *with Triethyloxonium Tetrafluoroborate;* $[Mo(\eta-C_5H_5)I(NMeEtNMe_2)(NO)][BF_4]$.—A solution of $[Mo(\eta-C_5H_5)I(NMeNMe_2)(NO)]$ (0.1 g) in dichloromethane was added to a suspension of an excess of $[OEt_3][BF_4]$ (0.1 g) in di-isopropyl ether (20 cm^3) and the mixture stirred for 48 h at r.t. until an oily red air-stable product had precipitated. The compound was washed with dichloromethane and dried *in vacuo*. This *product*, which was partially characterised by elemental analyses and i.r. spectroscopy, is thought to be $[Mo(\eta-C_5H_5)I(NMeEtNMe_2)(NO)][BF_4]$.

η-Cyclopentadienyliodonitrosyl(1-*phenylhydrazine*-NN′)*molybdenum Tetrafluoroborate*, $[Mo(\eta-C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ (3; R = R′ = H, R″ = Ph).—A stirred suspension of $[Mo(\eta-C_5H_5)I(NHNHPh)(NO)]$ (2; R = R′ = H, R″ = Ph) (0.9 g) in dichloromethane (25 cm^3) was treated with HBF_4 (5 cm^3, 40% aqueous solution). After 5 min the reaction mixture had become clear red and a yellow solid began to precipitate. The mixture was stirred for another 12 h giving a yellow suspension. This was collected by filtration and recrystallised from absolute ethanol giving the *complex* as orange crystals (0.27 g, 25%).

Deprotonation of $[Mo(\eta-C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ *with Triethylamine.*—To a solution of $[Mo(\eta-C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ (3; R = R′ = H, R″ = Ph) (0.5 g) in dichloromethane (20 cm^3) was added triethylamine (0.2 cm^3) After 5 h a pale yellow powder had precipitated and was filtered off, washed with diethyl ether, and dried *in vacuo*. The compound was characterised spectroscopically as (2; R = R′ = H, R″ = Ph) (0.3 g, 73%).

μ-[2,2-Dimethylhydrazido(2−)-NN′]-*bis[η-cyclopentadienyliodo(nitrosyl)molybdenum]*, $[\{Mo(\eta-C_5H_5)I(NO)\}_2NNMe_2]$ (4; X = I, R′ = R″ = Me).—*Method* (1). To a solution of $[Mo(\eta-C_5H_5)I(NO)(O_2CMe)]$ (0.5 g) in dichloromethane (30 cm^3) was added a solution of 1,1-dimethylhydrazine (2.0 cm^3) in dichloromethane (30 cm^3). The solution clarified and became dark red, and the mixture was partially evaporated *in vacuo*. On addition of isopropyl alcohol and cooling to 0 °C, dark red crystals of the *complex* formed and were filtered off, washed with diethyl ether, and dried *in vacuo* (0.4 g, 86%).

Method (2). To a suspension of $[Mo(\eta-C_5H_5)I_2(NH_2NMe_2)(NO)]$ (1; X = I, R = H, R′ = R″ = Me) (0.5 g, 0.99 mmol) in diethyl ether (20 cm^3) was added a solution (10 cm^3) of triethylamine (0.59 g, 9.8 mmol) in ether (100 cm^3). After stirring for 24 h the orange-red solution was filtered and the filtrate partially reduced *in vacuo*. The red crystals of the *complex* were filtered off, washed with ether, and dried *in vacuo* (0.3 g, 90%).

Method (3). Treatment of $[Mo(C_5H_5)_2I(NO)]$ (1.0 g) with 1,1-dimethylhydrazine (0.35 g) in dichloromethane (30 cm^3) for 2 h afforded the *complex* which was purified as described above (0.7 g, 76%).

μ-[2,2-Diethylhydrazido(2−)-NN′]-*bis[bromo(η-cyclopentadienyl)(nitrosyl)molybdenum]*, $[\{Mo(\eta-C_5H_5)Br(NO)\}_2NNEt_2]$ (4; X = Br, R′ = R″ = Et).—A solution of $[\{Mo(\eta-C_5H_5)Br_2(NO)\}_2]$ (1.0 g) in the minimum volume of absolute ethanol was stirred with 1,1-diethylhydrazine (an excess) for 1 h. The mixture was then cooled to −20 °C overnight and the red microcrystalline *complex* was collected by filtration (0.6 g, 66%).

μ-[2-Phenylhydrazido(2−)-NN′]-*bis[bromo(η-cyclopentadienyl)(nitrosyl)molybdenum]*, $[\{Mo(\eta-C_5H_5)Br(NO)\}_2NNHPh]$ (4; X = Br; R′ = H, R″ = Ph).—A mixture of $[\{Mo(\eta-C_5H_5)Br_2(NO)\}_2]$ (2.0 g) and phenylhydrazine (0.6 g) in absolute ethanol (100 cm^3) was refluxed for 10 min. The mixture was then cooled and after 3 h the *complex* was filtered off, washed with ethanol and n-pentane, and dried *in vacuo* (1.5 g, 90%).

The related complexes (4; X = Cl, R′ = H or Me, R″ = Ph) and (4; X = Br, R′ = Me or Ph, R″ = Me) were prepared similarly.

μ-[2-Phenylhydrazido(2−)-NN′]-*bis[η-cyclopentadienyliodo(nitrosyl)molybdenum]*, $[\{Mo(\eta-C_5H_5)I(NO)\}_2NNHPh]$ (4; X = I, R′ = H, R″ = Ph).—*Method* (1). A mixture of $[\{Mo(\eta-C_5H_5)I_2(NO)\}_2]$ (0.5 g, 0.56 mmol) and $[Mo(\eta-C_5H_5)I(NHNHPh)(NO)]$ (2; R = R′ = H, R″ = Ph) (0.48 g, 1.12 mmol) was stirred in dichloromethane (50 cm^3) for 24 h. After filtration of the orange solution, the filtrate was treated with diethyl ether and the mixture slowly and partially evaporated *in vacuo* until crystallisation began. The orange crystals of the *complex* were filtered off, washed with ether, and dried *in vacuo* (0.4 g, 95%).

Method (2). A suspension of $[Mo(\eta-C_5H_5)I(NHNHPh)(NO)]$ (2; R = R′ = H, R″ = Ph) (0.9 g) in absolute ethanol (50 $\mathrm{cm^3}$) was refluxed for 2 h, until a deep red solution had been formed. On cooling the solution was filtered and the filtrate evaporated *in vacuo* to give a brown powder. Recrystallisation of this powder from dichloromethane–n-pentane afforded the *complex* as orange crystals (0.25 g, 33%).

μ-[2-Methyl-2-phenylhydrazido(2−)-NN′]-bis[η-cyclopentadienyliodo(nitrosyl)molybdenum], $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)}\}_2\mathrm{NNMePh}]$ (4; X = I, R′ = Me, R″ = Ph).—To a solution of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)(O_2CMe)}]$ (1.1 g) in dichloromethane (20 $\mathrm{cm^3}$) was added 1-methyl-1-phenylhydrazine (0.35 g). After stirring for 5 h, the mixture was treated with n-pentane (5 $\mathrm{cm^3}$), and on partial evaporation *in vacuo* a dark red solid precipitated. This was filtered off and recrystallised from ethanol–n-pentane mixtures affording the *complex* as red crystals (1.0 g, 94%).

Mass Spectral Data obtained from selected Hydrazido-complexes.—$[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Br(NO)}\}_2\mathrm{NNHPh}]$ (4; X = Br, R′ = H, R″ = Ph): *m/e* = 638 (M^+); 608 ($[M - \mathrm{NO}]^+$), 578 ($[M - 2\mathrm{NO}]^+$), 558 ($[M - \mathrm{C_6H_6}]^+$), 532 ($[M - \mathrm{C_6H_6} - \mathrm{N_2}]^+$), 5.2 ($[M - \mathrm{C_6H_6} - \mathrm{N_2} - \mathrm{NO}]^+$), 371 $\{[M - \mathrm{Mo(C_5H_6)Br(NO)}]^+\}$, 344 (unidentified), 313 $\{[\mathrm{Mo(C_5H_5)Br_2}]^+\}$, 266 $\{[\mathrm{Mo(C_5H_5)Br_2(NO)}]^+\}$, 236 $\{[\mathrm{Mo(C_5H_5)Br}]^+\}$.

$[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Br(NO)}\}_2\mathrm{NNMe_2}]$ (4; X = Br, R′ = R″ = Me): *m/e* = 590 ($[M]^+$), 560 ($[M - \mathrm{NO}]^+$), 460—320 (continuum of unidentified peaks), 295 ($\frac{1}{2}[M]^+$), 280 $\{[\mathrm{Mo(C_5H_5)BrN_2O}]^+$ or $[\mathrm{Mo(C_5H_5)Br(NC_2H_6)}]^+\}$, 265 $\{[\mathrm{Mo(C_5H_5)Br(NH_3)}]^+\}$, 245 $\{[M - \mathrm{C_5H_5MoBr_2(NO)}]^+\}$, 236 ($[\mathrm{MoC_{10}H_{10}N}]^+$), 222 ($[\mathrm{MoC_{10}H_{10}}]^+$).

$[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Cl(NO)}\}_2\mathrm{NNMePh}]$ (4; X = Cl, R′ = Me, R″ = Ph): *m/e* = 564 ($[M]^+$), 534 ($[M - \mathrm{NO}]^+$), 420, 390, 375, 342 (unidentified), 328 $\{[\mathrm{Mo(C_5H_5)(C_7H_8)Cl(NO)}]^+\}$, 307 (unidentified), 298 $\{[\mathrm{Mo(C_5H_5)(C_7H_8)Cl}]^+\}$, 282 $\{[\mathrm{Mo(C_5H_5)(C_6H_5)Cl}]^+\}$, 262 $\{[\mathrm{Mo(C_5H_5)(C_6H_5)N}]^+\}$, 222 ($[\mathrm{MoC_{10}H_{10}}]^+$), 192 $\{[\mathrm{Mo(C_5H_5)Cl}]^+\}$.

RESULTS AND DISCUSSION

Treatment of the complexes $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{(NO)X_2}\}_2]$ (X = halide), $[\mathrm{Mo(C_5H_5)_2I(NO)}]$, and $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)(O_2CMe)}]$ with hydrazines readily afforded hydrazine and/or hydrazido-complexes. Use of the dihalide dimers is preferable largely because of their ease of preparation, but unless reaction stoicheiometries are very carefully adhered to mixtures of products are obtained. However, in reactions specifically designed to effect ready deprotonation of relatively unreactive hydrazines (*i.e.* those containing electron-withdrawing substituents) it proved convenient to use the acetatoiodide precursor. The relevant analytical, ^{1}H n.m.r. and i.r., and ^{13}C n.m.r. spectral data are summarised in Tables 1, 2, and 3, respectively.

Synthetic Studies.—*Hydrazine adducts*, $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{(NHRNR'R'')(NO)X_2}]$ (1). Treatment of $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I_2(NO)}\}_2]$ with $\mathrm{RNHNH_2}$ (R = Ph, $\mathrm{C_6F_5}$, $\mathrm{C_6H_4NO_2}$-*p*, or $\mathrm{C_6H_4Me}$-*p*), $\mathrm{MeNHNH_2}$, $\mathrm{Me_2NNH_2}$, or $\mathrm{Me_2NNHMe}$ afforded the adducts $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I_2(NHRNR'R'')(NO)}]$ (1; X = I; R = R′ = H, R″ = Ph, $\mathrm{C_6F_5}$, $\mathrm{C_6H_4\text{-}NO_2}$-*p* and -Me-*p*, or Me; R = H, R′ = R″ = Me; and R = R′ = R″ = Me) as microcrystalline powders. Complex (1; X = Br, R = R′ = H, R″ = $\mathrm{C_6F_5}$) was obtained similarly from $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Br_2(NO)}\}_2]$.

With the exception of (1; X = I, R = R′ = R″ = Me), these species are generally insoluble in common organic solvents except $\mathrm{SMe_2O}$ and $\mathrm{(CD_3)_2CO}$. They decompose in the former and form $\mathrm{R''R'NN{=}C(CD_3)_2}$, regenerating $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{(NO)X_2}\}_2]$, in the latter. The species (1: X = I; R = R′ = H, R″ = Ph or $\mathrm{C_6H_4}$-Me-*p*; and R = H, R′ = R″ = Me) are particularly sensitive to deprotonation by slight excesses of hydrazines, thereby affording hydrazido(1−)- and sometimes hydrazido(2−)-complexes.

Hydrazido(1−)-complexes, $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NRNR'R'')(NO)}]$ (2).—When the hydrazine adducts (1: X = I; R = R′ = H, R″ = Ph, $\mathrm{C_6H_4Me}$-*p*, or Me; R = H, R′ = R″ = Me; or R = R′ = R″ = Me) were treated with stoicheiometric amounts of base, *e.g.* $\mathrm{NEt_3}$ or $\mathrm{R''R'NNHR}$, deprotonation occurred, as mentioned above, with the formation of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NRNR'R'')(NO)}]$ (2: R = R′ = H, R″ = Ph, $\mathrm{C_6H_4Me}$-*p*, or Me; R = H, R′ = R″ = Me; or R = R′ = R″ = Me), and, concomitantly, either $[\mathrm{NEt_3H}]\mathrm{I}$ or $[\mathrm{R''R'NNH_2R}]\mathrm{I}$. This type of reaction does not occur with (1: X = I, R = R′ = H, R″ = $\mathrm{C_6F_5}$ or $\mathrm{C_6H_4NO_2}$-*p*; or X = Br, R = R′ = H, R″ = $\mathrm{C_6H_5}$). However, hydrazido(1−)-complexes containing the $\mathrm{C_6F_5}$ and $\mathrm{C_6H_4NO_2}$-*p* groups could be prepared by treating $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)(O_2CMe)}]$ with 1 mol of the appropriate hydrazine. The phenylhydrazido(1−)-complex could also be obtained *via* the acetatoiodide or even from $[\mathrm{Mo(C_5H_5)_2I(NO)}]$, but with $\mathrm{Me_2NNH_2}$ these two precursors invariably afforded the hydrazido(2−)-compound $[\{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)}\}_2\mathrm{NNMe_2}]$ (4; X = I, R′ = R″ = Me).

The arylhydrazido(1−)-complexes and (1; X = I, R = R′ = R″ = Me) are insufficiently soluble for molecular-weight determinations, and the mass spectra of the former group fail to show parent molecular ions. Indeed, the mass spectra of the arylhydrazido(1−)-complexes reveal binuclear ion fragments which are identical to those found in the spectra of the corresponding binuclear hydrazido(2−)-species, (4). In fact, a suspension of (2; X = I, R = R′ = H, R″ = Ph) which had been heated in refluxing ethanol afforded a modest yield of (4; X = I, R′ = H, R″ = Ph), and presumably this dimerisation with loss of a hydrazido-fragment also occurs in the probe of the mass spectrometer. The dimethylhydrazido(1−)-complex (2; R = H, R′ = R″ = Me) is very unstable, readily dimerising with loss of dimethylhydrazine giving (4; X = I, R′ = R″ = Me). Hence molecular-weight and mass-spectral measurements of this species could not be made. However, when thermal decomposition of solid (2; R = H, R′ = R″ = Me) was carried out *in vacuo* the volatile products were trapped, analysed by g.c.–m.s. techniques, and identified as, among other compounds, $\mathrm{Me_2NNH_2}$ and $\mathrm{C_5H_6}$; the solid residue consisted mainly of (4; X = I, R′ = R″ = Me).

However, (2; R = R′ = R″ = Me) is both soluble and stable in organic solvents, and osmometric molecular-weight measurements established that this complex is monomeric in solution.

TABLE 1

Elemental analytical and molecular-weight data obtained from molybdenum hydrazine derivatives

	Analysis (%)								
	Calc.				Found				
Complex	C	H	N	X[b]	C	H	N	X[b]	M[a]
$[Mo(C_5H_5)I_2(NH_2NHMe)(NO)]$ (1; $X = I, R = R' = H, R'' = Me$)	14.7	2.2	8.6	51.7	14.6	2.0	8.6	51.0	
$[Mo(C_5H_5)I_2(NH_2NMe_2)(NO)]$ (1; $X = I, R = H, R' = R'' = Me$)	16.6	2.6	8.3	50.2	17.1	2.7	8.0	49.0	
$[Mo(C_5H_5)I_2(NHMeNMe_2)(NO)]$ (1; $X = I, R = R' = R'' = Me$)	18.5	2.9	8.1	48.9	18.4	2.9	8.0	48.9	507 (519)
$[Mo(C_5H_5)I_2(NH_2NHPh)(NO)]$ (1; $X = I, R = R' = H, R'' = Ph$)	23.9	2.4	7.6	45.9	23.2	2.5	7.9	45.9	
$[Mo(C_5H_5)I_2(NH_2NHC_6F_5)(NO)]$ (1; $X = I, R = R' = H, R'' = C_6F_5$)	20.5	1.3	6.5	39.5	20.6	1.4	6.6	39.7	
$[Mo(C_5H_5)Br_2(NH_2NHC_6F_5)(NO)]$ (1; $X = Br, R = R' = H, R'' = C_6F_5$)	24.0	1.5	7.7	29.1[c]	24.1	1.7	7.5	29.1[c]	
$[Mo(C_5H_5)I_2(NH_2NHC_6H_4NO_2\text{-}p)(NO)]$ (1; $X = I, R = R' = H, R'' = C_6H_4NO_2\text{-}p$)	22.1	2.0	9.4	42.5	22.8	2.2	9.6	43.9	
$[Mo(C_5H_5)I_2(NH_2NHC_6H_4Me\text{-}p)(NO)]$ (1; $X = I, R = R' = H, R'' = C_6H_4Me\text{-}p$)	25.4	2.6	7.4	44.8	25.7	2.9	7.5	44.0	
$[Mo(C_5H_5)I(NHNHMe)(NO)]$ (2; $R = R' = H, R'' = Me$)	19.8	2.8	7.7	35.0	19.7	2.5	7.6	34.8	
$[Mo(C_5H_5)I(NHMe_2)(NO)]$ (2; $R = H, R' = R'' = Me$)	22.3	3.2	11.2	33.7	22.6	3.5	11.3	34.5	
$[Mo(C_5H_5)I(NMeNMe_2)(NO)]$ (2; $R = R' = R'' = Me$)	34.6	3.6	10.7	32.5	34.9	3.7	10.9	32.4	409 (391)
$[Mo(C_5H_5)I(NHNHPh)(NO)]$ (2; $R = R' = H, R'' = Ph$)	31.1	2.6	9.9	30.0	31.4	2.9	9.8	29.7	
$[Mo(C_5H_5)I(NHNHC_6F_5)(NO)]$ (2; $R = R' = H, R'' = C_6F_5$)	25.6	1.6	8.1	24.6	25.5	1.6	7.5	24.3	
$[Mo(C_5H_5)I(NHNHC_6H_4NO_2\text{-}p)(NO)]$ (2; $R = R' = H, R'' = C_6H_4NO_2\text{-}p$)	28.0	2.5	11.9	26.9	28.1	2.5	11.1	27.2	
$[Mo(C_5H_5)I(NHNHC_6H_4Me\text{-}p)(NO)]$ (2; $R = R' = H, R'' = C_6H_4Me\text{-}p$)	32.8	3.4	9.6	28.9	32.4	3.2	9.5	28.7	
$[Mo(C_5H_5)I(NH_2NMe_2)(NO)][BF_4]$ (3; $R = H, R' = R'' = Me$)	18.1	2.6	9.1	27.4	18.4	2.8	9.3	28.3	
$[Mo(C_5H_5)I(NHMeNMe_2)(NO)][BF_4]$ (3; $R = R' = R'' = Me$)	22.6	2.9	8.8	26.5	22.8	3.3	8.8	26.7	
$[Mo(C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ (3; $R = R' = H, R'' = Ph$)	25.7	2.5	8.2	24.8	26.2	2.6	7.8	24.6	
$[Mo(C_5H_5)I(NMeEtNMe_2)(NO)][BF_4]$	23.7	3.8	8.3		20.2	3.0	8.7		
$[\{Mo(C_5H_5)I(NO)\}_2N_2Me_2]$ (4; $X = I, R' = R'' = Me$)	20.8	2.3	8.1	36.6	20.3	2.8	8.6	37.0	695 (684)
$[\{Mo(C_5H_5)Br(NO)\}_2N_2Me_2]$ (4; $X = Br, R' = R'' = Me$)	24.0	2.7	9.3	26.7[c]	24.1	3.3	9.8	26.1[c]	580 (590)
$[\{Mo(C_5H_5)Br(NO)\}_2N_2Et_2]$ (4; $X = Br, R' = R'' = Et$)	26.8	3.2	8.9	25.5[c]	27.1	3.4	9.2	25.5[c]	
$[\{Mo(C_5H_5)I(NO)\}_2N_2MePh]$ (4; $X = I, R' = Me, R'' = Ph$)	27.0	2.4	7.4	33.6	27.3	2.4	7.6	33.3	730 (747)
$[\{Mo(C_5H_5)Br(NO)\}_2N_2MePh)]$ (4; $X = Br, R' = Me, R'' = Ph$)	30.8	2.7	8.5	24.2[c]	30.8	3.1	8.3	24.2[c]	
$[\{Mo(C_5H_5)Cl(NO)\}_2N_2MePh]$ (4; $X = Cl, R' = Me, R'' = Ph$)	35.6	3.1	9.8	12.4[d]	35.8	3.4	9.8	12.2[d]	
$[\{Mo(C_5H_5)I(NO)\}_2N_2HPh]$ (4; $X = I, R' = H, R'' = Ph$)	25.9	2.2	7.6	34.2	25.6	2.9	7.8	34.5	
$[\{Mo(C_5H_5)Br(NO)\}_2N_2HPh]$ (4; $X = Br, R' = H, R'' = Ph$)	29.6	2.5	8.6	24.7[c]	29.9	2.9	8.9	24.7[c]	
$[\{Mo(C_5H_5)Cl(NO)\}_2N_2HPh]$ (4; $X = Cl, R' = H, R'' = Ph$)	34.3	2.9	10.0	12.7[d]	34.2	3.3	10.3	12.9[d]	

[a] Determined osmometrically in $CHCl_3$; calculated values are given in parentheses. [b] $X = I$ unless otherwise stated. [c] Br. [d] Cl.

Treatment of (2; $R = R' = H$, $R'' = Ph$) with $Na[S_2CNMe_2]$ and with Na[SPh] gave the known $[Mo(\eta\text{-}C_5H_5)I(NO)(S_2CNMe_2)]$ [16] and $[\{Mo(\eta\text{-}C_5H_5)I(NO)(SPh)\}_2]$; [17] $[Mo(\eta\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ [15] did not react with $PhNHNH_2$. With $P(OMe)_3$, the phenylhydrazido(1—)-complex afforded good yields (*ca.* 80%) of $[Mo(\eta\text{-}C_5H_5)I(NO)\{P(OMe)_3\}_2]I$, a type of compound already described elsewhere.[18]

Cationic hydrazine complexes, $[Mo(\eta\text{-}C_5H_5)I(NHRNR'R'')(NO)]^+$ (3). When a suspension of (2; $R = R' = H$, $R'' = Ph$) was treated with a mixture of aqueous HBF_4 in dichloromethane a red solution was formed from which the salt $[Mo(\eta\text{-}C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ (3; $R = R' = H$, $R'' = Ph$) was isolated. Species (3; $R = R' = R'' = Me$), also as a $[BF_4]^-$ salt, was obtained similarly, but attempts to produce the analogous (3; $R = H$, $R' = R'' = Me$) by this route were unsuccessful. However, this last complex was obtained, unreliably and in very low yields, by protonation of (4; $X = I$, $R' = R'' = Me$) with HBF_4 in aqueous dichloromethane. Attempts to produce these monoiodo(hydrazine) adducts by treatment of (1) with

TABLE 2

Infrared and ^{1}H n.m.r. spectral data obtained from molybdenum hydrazine derivatives

	Complex				I.r. data (cm^{-1})[a]		^{1}H N.m.r. data	
Type	X	R	R′	R″	ν(NO)	ν(NH)	δ(RA)[b]	Assignment
(1)	I	H	H	Me	1 660s	2 850m	*c*	
	I	H	Me	Me	1 655s	2 800m	*c*	
	I	Me	Me	Me	1 650s	2 670m	6.53(5)[d]	s, C_5H_5
							6.17(1)	br s, N*H*MeNMe$_2$
							3.56(6)	s, NHC*H*$_3$N(C*H*$_3$)Me
							3.36(3)	s, NHMeNMe(C*H*$_3$)
	I	H	H	Ph	1 655s	2 930m,br	*c*	
						2 820m,br		
	I	H	H	C_6H_4Me-*p*	1 660m	3 200m	*c*	
					(1 620s)[e]	2 900br		
	I	H	H	C_6F_5	1 675s	3 280m	6.62(1)[f,g]	s, NH
						3 245m	6.21(5)	s, C_6H_5
							5.40(2)[g]	m, NH_2
	Br	H	H	C_6F_5	1 678s	3 245m	*c*	
	I	H	H	$C_6H_4NO_2$-*p*	1 662s	3 300m	8.10(2)[g]	C_6H_4
							7.15(2)	
							8.00(1)	NH
							6.40(2)	NH_2
							6.22(5)	C_5H_5
(2)		H	H	Me	1 640s	3 140m	*c*	
					1 620s	3 100m		
		H	Me	Me	1 595s	3 230m	6.15(1)[d]	br s, N*H*NMe$_2$
					1 580s		6.00(5)	s, C_5H_5
							3.30(3)	s, NHN(C*H*$_3$)Me
							3.00(3)	s, NHMe(C*H*$_3$)
		Me	Me	Me	1 615 (sh)		5.95(5)[d,h]	s, C_5H_5
					1 600		3.28(3)	s, NC*H*$_3$NMe$_2$
							3.08(6)	br.s, NMeN(C*H*$_3$)$_2$
							5.95(5)[d,i]	s, C_5H_5
							3.28(3)	s, NC*H*$_3$NMe$_2$
							3.21(3)	s, NMeN(C*H*$_3$)Me
							2.97(3)	s, NMeNMe(C*H*$_3$)
		H	H	Ph	1 625s	3 200m	7.90(1)[g,j]	s, NH
							7.20(5)	m, C_6H_5
							6.80(1)[g]	s, NH
							6.19(5)	s, C_5H_5
		H	H	C_6H_4Me-*p*	1 620s	3 200m	7.79(1)[g,j]	s, NH
							6.99(4)	m, C_6H_4
							6.29(1)[g]	s, NH
							6.13(5)	s, C_5H_5
							2.22(3)	s, C_6H_4C*H*$_3$
		H	H	C_6F_5	1 660br,s	3 200m	6.17(5)[f]	s, C_5H_5
					1 645br,s		6.39 6.21 (2) 5.99	m, N*H*N*H*C$_6$F$_5$
		H	H	$C_6H_4NO_2$-*p*	1 632m	3 290m	8.00[j] 7.18 (6)	m, NH and C_6H_4
							6.21(5)	s, C_5H_5
(3)		Me	Me	Me	1 650s	3 100m	7.70(1)[d]	br s, NH
						(1 100s)[k]	6.39(5)	s, C_5H_5
							3.53(3)	s, NHMeN(C*H*$_3$)Me
							3.36(3)	s, NH(C*H*$_3$)NMe$_2$
							3.30(3)	s, NHMeNMe(C*H*$_3$)
[Mo(η-C_5H_5)I(NMeEtNMe$_2$)(NO)][BF$_4$]					1 645s		*c*	
						(1 100s)[k]		
(3)		H	Me	Me	1 645s	3 100m	*c*	
						(1 100s)[k]		
		H	H	Ph	1 660s	3 190m	*c*	
(4)	Cl		Me	Ph	1 630br,s		7.65(5)[j]	m, C$_6$*H*$_5$
							6.44(5)	s, C_5H_5
							6.05(5)	s, C_5H_5
							3.87(3)	s, NCH_3
	Cl		H	Ph	1 630br,s	3 240m	7.91(1)[g,j]	s, NH
							7.00(5)	m, C_6H_5
							6.12(10)	s, C_5H_5
	Br		Me	Me	1 632br,s[f]		6.14(5)[f]	s, C_5H_5
							6.10(5)	s, C_5H_5
							3.51(3)	s, NCH_3
							3.30(3)	s, NCH_3
	Br		H	Ph	1 660 (sh)	3 180m	10.80(1)[g,i]	s, NH
					1 645s		7.25(5)	m, C_6H_5
							6.25(5)	s, C_5H_5
							6.20(5)	s, C_5H_5

TABLE 2 (*Continued*)

	Complex				I.r. data (cm^{-1})		^1H N.m.r. data	
Type	X	R	R′	R″	ν(NO)	ν(NH)	δ(RA) [b]	Assignment
(4)	Br		Me	Ph	1 650 (sh)		7.40(5) [j]	n, C_6H_5
					1 625s		6.47(5)	s, C_5H_5
							6.11(5)	s, C_5H_5
							3.90(3)	s, NCH_3
	Br		Et	Et	1 628br,s [f]		6.09 [f] (10)	s, C_5H_5
							4.30—2.90 (4)	m, NCH_2Me
							1.60(3)	t, NCH_2CH_3 [J(HH) 7.0 Hz]
							1.00(3)	t, NCH_2CH_3 [J(HH) 7.0 Hz]
	I		Me	Me	1 652s		6.20(5) [f]	s, C_5H_5
					1 618s		6.19(5)	s, C_5H_5
							3.60(3)	s, NCH_3
							3.35(3)	s, NCH_3
	I		H	Ph	1 645br,s	3 230	9.88(1) [g,j]	br s, NH
							7.70(5)	m, NC_6H_5
							6.36(5)	s, C_5H_5
							6.28(5)	s, C_5H_5
	I		Me	Ph	1 650 (sh)		7.50(5) [f]	m, NC_6H_5
					1 624s		6.25(5)	s, C_5H_5
							5.95(5)	s, C_5H_5
							4.00(3)	s, NCH_3

[a] In KBr discs unless otherwise stated. [b] Relative to $SiMe_4$, solvent as stated. [c] Either too insoluble or unstable for measurement. [d] In CD_2Cl_2 solution. [e] Due to impurities of (2; R = R′ = H, R″ = C_6H_4Me-*p*). [f] $CDCl_3$ solution. [g] Signal disappears on shaking with D_2O. [h] 37 °C. [i] −70 °C. [j] In $S(CD_3)_2O$ solution. [k] ν(BF) of $[BF_4]^-$.

TABLE 3

Carbon-13 n.m.r. spectra of hydrazine and hydrazido-complexes

	Chemical shifts (δ/p.p.m.) [a]							
		N_2Me_x [b]		N_2H_x (aryl)				
Compound	C_5H_5	NMe	NMe_2	N–C	*o*-C	*m*-C	*p*-C	Other
PhNHNH$_2$				151.3 [c]	112.0	129.0	118.9	
PhMeNNH$_2$		44.3 [c]		153.0	113.6	128.9	118.3	
Me$_2$NNH$_2$			51.4 [c]					
Me$_2$NNHMe		35.6 [c]	47.1 [c]					
(1; X = I, R = R′ = R″ = Me)	107.0 [d]	41.5	57.3					
			49.9					
(3; R = R′ = R″ = Me)	107.6 [d]	41.5	57.0					
			49.1					
(2; R = R′ = R″ = Me)	105.3 [d]	46.0	59.3					
(2; R = H, R′ = R″ = Me)	105.0 [c]		57.6					
			57.1					
(4; X = I, R′ = R″ = Me)	107.2 [d]		59.3					
	106.0		57.5					
(4; X = I, R′ = R″ = Et)	107.4 [e]							66.3 [f]
	105.6							55.5 [f]
								13.2 [g]
(2; R = R′ = H, R″ = Ph)	105.0 [e]			158.2	118.6	129.1	121.8	
(4; X = I, R′ = H, R″ = Ph)	107.2 [h]			155.8	119.5	129.2	126.7	
	106.6							
(4; X = Br, R′ = H, R″ = Ph)	107.7 [e]			154.8	118.8	128.4	125.9	
	106.7							
(4; X = Cl, R′ = H, R″ = Ph)	108.4 [e]			155.0	119.0	128.6	126.2	
	107.4							
(4; X = I, R′ = Me, R″ = Ph)	108.1 [h]			150.4	121.4	129.4	127.5	54.5
	107.0							
(4; X = Br, R′ = Me, R″ = Ph)	108.4 [e]			150.5	119.9	128.8	125.9	58.4
	107.1							
(4; X = Cl, R′ = Me, R″ = Ph)	108.9 [e]			150.9	119.7	129.0	126.7	57.9
	107.4							

[a] Relative to $SiMe_4$, solvent as indicated. [b] Methyl group on N atoms of hydrazido-group. [c] In $CDCl_3$. [d] In CD_2Cl_2. [e] In $S(CD_3)_2O$ to which has been added 10% $(CD_3)_2CO$ to provide internal H-lock signal. [f] CH_2 signals of NEt_2. [g] CH_2CH_3 signal of NEt_2. [h] In $(CD_3)_2CO$.

Ag[PF$_6$] or Tl[BF$_4$] were singularly unsuccessful. Treatment of (3) with NEt$_3$ caused the quantitative regeneration of (2).

Attempts to prepare other cationic species by treatment of (2; R = R′ = H, R″ = Ph) with MeI, MeOSO$_2$F, or [OEt$_3$][BF$_4$] resulted in the formation of intractable black tars. However, with [OEt$_3$][BF$_4$], (2; R = R′ = R″ = Me) afforded an oily red solid which we were unable to purify satisfactorily and hence could not obtain reliable elemental analytical data.

However, on the basis of i.r. spectroscopic data, we suggest that this red species may be $[Mo(\eta\text{-}C_5H_5)I(NMeEtNMe_2)(NO)][BF_4]$.

Binuclear hydrazido(2—)-*complexes*, $[\{Mo(\eta\text{-}C_5H_5)I(NO)\}_2NNR'R'']$ (4). With the exception of $[\{Mo(\eta\text{-}C_5H_5)I(NO)\}_2NNHPh]$, the complexes (4: X = Cl or Br, R′ = H or Me, R″ = Ph; X = Br, R′ = R″ = Me; and X = I, R′ = Me or Ph, R″ = Me) were easily obtained by reactions of $[\{Mo(\eta\text{-}C_5H_5)(NO)X_2\}_2]$ with the appropriate hydrazine in hot or refluxing ethanol. Species (4; X = I, R′ = Me, R = Ph) could also be prepared by reaction of $PhMeNNH_2$ with either $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$ or $[Mo(C_5H_5)_2I(NO)]$, and it is noticeable that complexes of the type (1) or (2) derived from this hydrazine could not be prepared despite many attempts.

The phenylhydrazido(2—)-complex (4; X = I, R′ = H, R″ = Ph) could be prepared most conveniently by the reaction of (2; R = R′ = H; R″ = Ph) with $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ (in the mol ratio 2 : 1) or $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$. An alternative but low-yield method is available, as described above, by heating (2; R = R′ = H, R″ = Ph) in ethanol.

Other Reactions.—Careful addition of anhydrous hydrazine to $[\{Mo(\eta\text{-}C_5H_5)Br_2(NO)\}_2]$ gave a yellow insoluble solid whose elemental analysis was consistent with an empirical formula closely approximating to $[Mo_2(C_5H_5)_2Br_3(NO)_2(N_2H_x)]$ (*x ca.* 4). We cannot tell from spectral measurements what is the precise nature of this solid, but it is probably a mixture comprised of varying amounts of (1), (2), (3), and/or (4) (X = Br, R = R′ = R″ = H). In the absence of definitive analytical data and reliable spectral information, further speculation seems fruitless. Treatment of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ with anhydrous hydrazine afforded intractable black tars.

When $[Mo(\eta\text{-}C_5H_5)I(NO)(O_2CMe)]$ was treated with secondary amines acetic acid was liberated and amorphous brown solids were formed. The latter species could not be satisfactorily characterised, but from i.r. and ^1H n.m.r. spectral studies it appears that they contain NO and NR_2 but no C_5H_5 groups; elemental analyses provided no further useful information other than indicating the presence of iodide.

Treatment of $[\{Mo(\eta\text{-}C_5H_5)Br_2(NO)\}_2]$ with ethanolic solutions of NEt_3 or $NPr^i{}_2H$ afforded $[\{Mo(\eta\text{-}C_5H_5)Br(NO)(OH)\}_n]$ and either $[NEt_3H]Br$ or $[NPr^i{}_2H_2]Br$. The hydroxyl group presumably arises, as reported earlier,[14] from traces of water in the ethanol and/or amines.

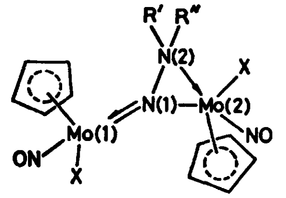


FIGURE 1 Structure of (4; X = I, R′ = R″ = Me)

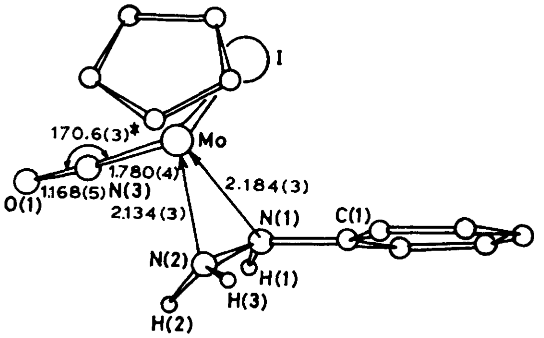


FIGURE 2 Structure of (3; R = R′ = H, R″ = Ph)

The Structures of $[\{Mo(\eta\text{-}C_5H_5)I(NO)\}_2NNMe_2]$ (4; X = I, R′ = R″ = Me) *and* $[Mo(\eta\text{-}C_5H_5)I(NH_2NHPh)(NO)][BF_4]$ (3; R = R′ = H, R″ = Ph).—The structures of the title compounds have been determined crystallographically,[8,9] and full details will be published elsewhere.

The molecule (4; X = I, R′ = R″ = Me) is unique in that it contains a hydrazido(2—)-ligand asymmetrically bridging two metal atoms and a three-membered MoNN chelate ring. The important bond lengths and angles are given in Figure 1. The Mo(1)N(1)N(2)Mo(2) group is essentially coplanar and of significance is the length of the Mo(1)–N(1) bond (1.92 Å), which is substantially shorter than either Mo(2)–N(1) or Mo(2)–N(2). We may compare it with the formal Mo=N distances in the related hydrazido(2—)-complexes $[Mo(=NNMe_2)(=O)(S_2CNEt_2)_2]$ (1.80 Å),[19] $[Mo(=NNEtPh)\{S_2CN(CH_2)_5\}_3]^+$ (1.72 Å),[20] and $[MoI(=NNHC_8H_{17})(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (1.80 Å) [21] and, taking into account the formal oxidation state of +III for Mo(1) in (4) (assuming that NO is a neutral ligand) in comparison to +VI and +IV in the other species, it seems clear that the Mo(1) bond order is close to 2. This is entirely consistent with the Mo(2)–N(2) distance (2.13 Å) since the NMe_2 group is donating its lone electron pair to Mo(2) *via* a conventional σ bond. The N(1)–N(2) bond length (1.40 Å) is quite close to that in free hydrazines and in (3; R = R′ = H, R″ = Ph), and is significantly longer than the equivalent distances in the other hydrazido(2—)-complexes, indicating that the form $Mo^- \leftleftharpoons N{=}\overset{+}{N}R_2$ is of no importance in the description of the bonding in the $Mo_2(NNR_2)$ group. Of further note is the Mo(1)–N(1)–N(2) bond angle (135°) which is considerably more bent than the corresponding angles in the other hydrazido(2—)-complexes discussed above. Thus, the bonding within the metal hydrazido-fragment may be described as follows: σ bonding between Mo(1) and N(1) with $p_\pi \rightarrow d_\pi$ donation of the 'lone pair' or 'p_z' electrons from N(1) to Mo(1), while Mo(2) is σ-bonded to N(1) and receives a σ-lone pair from N(2).

The phenylhydrazine adduct (3; R = R′ = H, R″ = Ph) has the conventional 3 : 4 co-ordination observed for many $Mo(\eta\text{-}C_5H_5)^{n+}$ complexes (*n* = 1 or 2) (Figure 2). The conformation about the N–N bond of the hydrazine ligand is eclipsed, the N–N distance (1.43 Å) being entirely consistent with a bond order of 1. This length is comparable with that in $[N_2H_5][N_3]$,[22] but is a little longer than the N(1)–N(2) distance found in (4; X = I, R′ = R″ = Me). It is significantly longer than the values found in the hydrazido(2−)-complexes discussed previously and in $[PtCl(NH{=}NPh)(PEt_3)_2][ClO_4]$ (1.24 Å) [23] and $[RuCl(CO)_2(HN{=}NPh)(PPh_3)_2][ClO_4]$ (1.22 Å).[24]

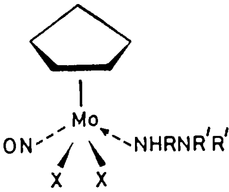
These two complexes appear to be the first fully characterised species containing a hydrazido- or hydrazine ligand which is bidentate with respect to one metal atom. It has been suggested [25] that $AlR_3(Me_2NNMe_2)$ also contains a bidentate hydrazine ligand, but this claim was made on the basis of relatively low-resolution ^1H n.m.r. spectral studies.

Spectral Studies.—The important features of the i.r. spectra of the new complexes are summarised in Table 2. The NO stretching frequencies of the compounds are diagnostic and depend on (*i*) the nature of the hydrazine or hydrazido-substituent, (*ii*) the charge on the complex, and (*iii*) the form and structure of the complex. Thus ν(NO) decreases as the electron-withdrawing properties of the hydrazine substituent increase. The values of ν(NO) in the hydrazido(1−)-complexes (2) are significantly lower than those of the related species (1). However, many of the values of ν(NO) for (1) are close to those observed in some of the species (3). Many of the compounds (4) exhibit two NO stretching frequencies which are consistent with the asymmetric structure revealed crystallographically for (4; X = I, R′ = R″ = Me) (some species have a broad NO absorption which is presumably insufficiently well resolved to appear as the expected doublet).

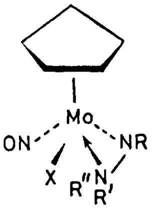
In all of those compounds containing the N–H group ν(NH) has been detected. Of significance in the spectra of a number of complexes of type (1) is the appearance of ν(NH) at $<3\,000$ cm^{-1}. Such anomalously low NH stretching frequencies have been observed in the i.r. spectra of the hydrazido(2−)-complexes $[M(NNH_2)L(PMe_2Ph)_3X]X$ (L = pyridine, PMe_2Ph, or quinolin-8-olate) and $[M(NNH_2)(dppe)_2X]X$ (M = Mo or W) [26] and these have been explained in terms of hydrogen bonding between the $M{=}NNH_2$ group and the ionic X^- in a strongly ion-paired species. Thus, a possible explanation for our observations may lie in the occurrence of a weak hydrogen bond between the N–H group and an ionic halide, as in an ion-paired species such as $[Mo(\eta\text{-}C_5H_5)I(NO)(NR''R'NRH^+\cdots I^-)]$. Complexes (1; R = R′ = H, R″ = C_6H_5 or $C_6H_4NO_2$-*p*) exhibit normal values of ν(NH), and so the proposed hydrogen bonding between the hydrazine and Br or I is presumed not to occur. It should be noted that those species with anomalously low NH stretching frequencies are very easily deprotonated giving (2), and it is possible that the structure of these particular adducts may be very similar to (3) (*i.e.* as indicated in Figure 3).

The ^1H and ^{13}C n.m.r. spectra (Tables 2 and 3, respectively) of those compounds which were sufficiently soluble and stable to be measured are consistent with their formulations. However, since the interpretation of these spectra are dependent on prior crystallographic knowledge of the molecular structures of (4; X = I, R′ = R″ = Me) and (3; R = R′ = H, R″ = Ph), it is necessary to discuss these species first.

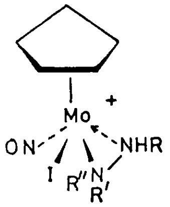
The ^1H n.m.r. spectrum of (4; X = I, R′ = R″ = Me) consisted of two C_5H_5 and two methyl-proton signals, which is entirely consistent with the solid-state structure. The ^{13}C n.m.r. spectrum is similar, and of importance are the separations between the respective signals of the methyl groups, 25 Hz (^1H) and 1.8 p.p.m. (^{13}C). The molecule is stereochemically rigid on the n.m.r. time scale over the temperature range 25—130 °C, above which decomposition occurred. Consequently, the hydrazido(2−)-ligand does not undergo a 'windscreen-wiper' motion in which the NMe_2 group jumps backwards and forwards between the two metals.



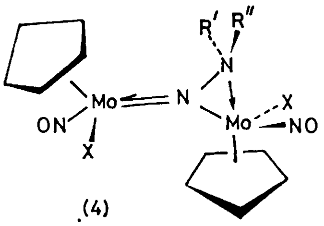
(1)
and isomers



(2)
and isomers



(3)



(4)
or isomers

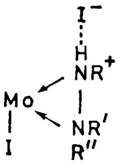


FIGURE 3

The spectra of the other molecules in this class are consistent with a rigid structure analogous to that of (4; X = I, R′ = R″ = Me). Of note is the observation that the species (4; X = Cl, Br, or I; R′ = Me, R″ = Ph) exhibit only one methyl signal. If it is assumed that these molecules too are not fluxional, then it appears that there is only one isomer present in solution. Isomerism in this group of compounds can occur by virtue of the relative positions of the Me and Ph groups and/or of the NO and X ligands with respect to the Mo_2N_2 plane.

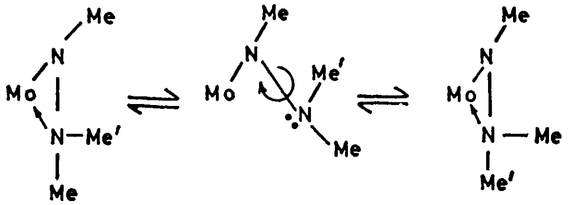
Because of its instability and insolubility in useful 'n.m.r. solvents,' we were unable to obtain spectra of (3; R = R′ = H, R″ = Ph). However, (3; R = R′ = R″ = Me) was sufficiently soluble and stable for such measurements. Both the ^1H and ^{13}C n.m.r. spectra revealed three methyl-group resonances which is entirely consistent with a structure analogous to that of (3; R = R′ = H, R″ = Ph). The proton signals at δ = 3.53 and 3.30 p.p.m. are tentatively assigned to the NMe_2 group (separation 23 Hz) and that at δ = 3.36 p.p.m. to the unique methyl group. We can less confidently assign the ^{13}C signals at δ = 57.0 and 49.1 p.p.m. to the NMe_2 group (separation 7.9 p.p.m.) and that at δ = 41.5 p.p.m. to the NHMe group.

The ^{13}C n.m.r. spectra of (3; R = R′ = R″ = Me) and (1; X = I, R = R′ = R″ = Me) are remarkably similar, which indicates that there is probably a structural similarity between them. Thus the separation between the tentatively assigned NMe_2 group signals is 7.9 p.p.m. in the former and 7.4 p.p.m. in the latter. However, the ^1H n.m.r. spectra of the two complexes are more difficult to reconcile. The former exhibited three Me proton resonances while the latter showed only two, of relative intensity 2 : 1. If the signal of relative intensity 2 is due to a coincidence of the signals of the NHMe and one of the methyl groups of $NHMe_2$, then the separation between this resonance and that at δ = 3.36 p.p.m., *viz.* 20 Hz, is comparable to that between the NMe_2 signals of (4; X = I, R′ = R″ = Me) and (3; R = R′ = R″ = Me). The alternative explanation that the signal of intensity 2 is due to both methyl groups of NMe_2 which is undergoing free rotation about the N–N bond of a unidentate hydrazine complex (*i.e.* containing $Mo\leftarrow NHMe{-}NMe_2$) must be discounted because of the ^{13}C n.m.r. spectral data. The ^1H n.m.r. spectra of (1; X = I, R = R′ = H, R″ = C_6F_5 or $C_6H_4NO_2$-*p*) are consistent with our formulation, and show that the unique NH proton resonates at chemical shifts of significantly lower fields than those of the NH_2 group which is presumed to be adjacent to the metal.

The ^1H and ^{13}C n.m.r. spectra of (2; R = H, R′ = R″ = Me) both revealed inequivalence of the methyl groups of the hydrazido(1–)-moiety. The separations between the signals are, respectively, 30 Hz (^1H) and 0.5 p.p.m. (^{13}C) which, although not identical to those in other complexes containing the NMe_2 group, do imply that there may be a structural relationship between (1), (2), (3), and (4). However, the ^1H and ^{13}C n.m.r. spectra of (2; R = R′ = R″ = Me) were more revealing, exhibiting, in the methyl regions at room temperature, one sharp and one broad signal of relative intensity 1 : 2. The former is clearly due to the unique Me group while the latter must be due to the two Me groups of NMe_2 which are undergoing rapid site exchange. At –70 °C the ^1H n.m.r. spectrum revealed that the broad line had been resolved into two singlets of separation 24 Hz [*cf.* (3) and (4) (R = R′ = R″ = Me)]. These observations are consistent with a molecule containing a chelating hydrazido(1–)-ligand, bound to one metal atom, which is undergoing ring opening and closure, as in Scheme 1.

The activation energy for the methyl site-averaging process, as calculated from the coalescence temperature, is *ca.* 59 kJ mol^{-1}, which is significantly higher than that in the complex $[Mo\{HB(C_3N_2HMe_2\text{-}3,5)_3\}I(NHNMe_2)(NO)]$ (*ca.* 40 kJ mol^{-1})[27] where it is known that the hydrazido(1–)-ligand is always unidentate.* That complex (2; R = H, R′ = R″ = Me) does not apparently undergo chelate ring opening at room temperature presumably reflects the electronic and steric differences between $[Me_2NNH]^-$ and $[Me_2NNMe]^-$; it is not possible to investigate the n.m.r. spectral properties of this molecule at higher temperatures because it is so readily converted into (4; X = I, R′ = R″ = Me). The ^1H and ^{13}C spectra of the arylhydrazido(1–)-complexes in this class are generally consistent with their formulations but provide no further structural information.

The Structural and Chemical Relationships of the Hydrazine and Hydrazido-complexes.—While the structures of the complexes (3) and (4) are known with certainty, those of (1) and (2) cannot be decided upon unequivocally. It seems quite possible that those species (1) having anomalously low values of ν(NH) may have a structure analogous to (3) while those species which have 'normal' spectral properties contain a unidentate hydrazine ligand. This last arrangement is that usually found in alkyl- and aryl-hydrazine complexes.[2] The occurrence in some complexes of unidentate as opposed to chelating hydrazine ligands could be rationalised in terms of the presence in the latter of electron-withdrawing substituents R and NH_2NHR. This would reduce the ligating power of the N atom to which R is attached. However, this does not explain the occurrence of chelating hydrazine ligands in these species, a point to which we return later.



Scheme 1

From the spectral data, and the facts that (2; R = R′ = R″ = Me) is monomeric and (3) may be readily deprotonated to give (2) quantitatively, it seems quite probable that the hydrazido(1–)-complexes[3] contain a three-membered MoNN chelate ring. The stability of such small chelate-ring systems has already been established crystallographically in $[Mo(\eta\text{-}C_5H_5)(CO)_2(MeSCH_2)]$,[28] $[Mo(\eta\text{-}C_5H_5)(CO)_2(Me_2CNO)]$,[29] and $[Mo(\eta\text{-}C_5H_5)(CO)_2(MeCNPh)]$.[30] An alternative possibility for (2), that some species may be binuclear and contain the group in Figure 4 cannot be dismissed entirely, but seems unlikely. The observation that (2; R = H, R′ = R″ = Me) is so readily converted into (4; X = I, R′ = R″ = Me) can be explained by the rapid deprotonation of $NHNMe_2$ attached to one metal atom by the ring-opened $Mo{-}NHNMe_2$ group of another complex (Scheme 2). Such proton loss is, of course, impossible

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* The structure of this complex, and of $[Mo\{HB(C_3HN_2Me_2\text{-}3,5)_3\}I(NHNMePh)(NO)]$, have been determined crystallographically (J. A. McCleverty, A. E. Rae, I. Wołochowicz, N. A. Bailey, and J. M. A. Smith, *J. Organometallic Chem.*, 1979, **168**, C1.

in (2; R = R' = R'' = Me) which explains why it is so stable and does not dimerise to give (4).

Acceptance of the foregoing structural arguments allows an explanation of the chemical relationships between (1), (2), (3), and (4), and this is set out in Scheme 3.

Finally, it is appropriate to comment on the structures of the new hydrazido(1—)- and hydrazido(2—)-complexes in relation to those of the species [M(NNH$_2$)(PMe$_2$Ph)$_3$X$_2$], [M(NHNH$_2$)(PMe$_2$Ph)$_2$X$_3$], and [M(NNRR')(dppe)$_2$X]$^+$. Of the phosphine complexes, those containing hydrazido(2—)-ligands have linear $\mathrm{M{=}N\overset{\cdots}{-}N\!<}$ groups, and [M(NHNH$_2$)(PMe$_2$Ph)$_2$X$_3$] presumably have a unidentate M–NH–NH$_2$ bond system. In contrast, the η-cyclopentadienyl nitrosyl species (2) and (4) contain chelating hydrazido-groups. A simple explanation for this difference in behaviour is difficult to advance. It could be said that the metal in the phosphine complexes is likely to be relatively more electron-rich (PMe$_2$Ph and dppe are good σ donors) than that in the η-cyclopentadienyl nitrosyl species [NO is a very powerful π acceptor and ν(NO) for (2) and (4) usually occurs at $<1\,650$ cm^{-1} indicating significant back donation to NO from Mo]. This could have the effect of encouraging NHNRR' and NNRR' to act as three-electron donors,* *via* the chelating mode, towards Mo in the nitrosyl species while acting only as one- or two-electron donors in the phosphine complexes. These arguments, however, are difficult to sustain since the relative donor–acceptor properties of PR$_2$R', η-C$_5$H$_5$, and NO in these complexes are not precisely known and may not be directly comparable. Steric factors may also play an important role in determining the bonding mode of the hydrazido-fragments, but there are insufficient examples of hydrazido(1—)- and hydrazido-(2—)-complexes of metals other than Mo or W to permit a meaningful discussion of this aspect.

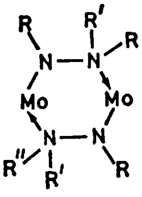
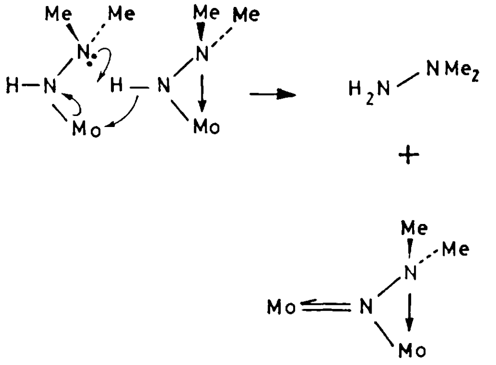
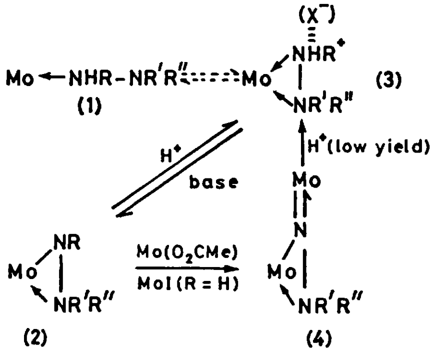


FIGURE 4



SCHEME 2



SCHEME 3

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* The ligands in these complexes are taken as neutral entities for the purposes of electronic book-keeping.

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