Nitrosyl Complexes of Molybdenum and Tungsten. Part 15.[1] Iodo(monoalkylamido)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum Complexes, some Related Tungsten Compounds, and the Crystal and Molecular Structure of Ethylamido(iodo)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum

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The complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(Y)]$ (Y = NMe_2 or NHR, where R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^t, C_6H_{11}, C_3H_5, or CH_2Ph) and $[W\{HB(3,5\text{-}Me_2C_3HN_2)_2(4\text{-}Br\text{-}3,5\text{-}Me_2C_3N_2)\}(NO)Br(Y)]$ (Y = H, Pr^i, or CH_2Ph) have been prepared by treatment of the species where Y = I (Mo) or Br (W) with ammonia, primary amines, and $NHMe_2$ respectively. Reaction of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NH_2)]$ with HCl, and with acetone in the presence of NEt_3 respectively, gives $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl_2]$ and $[NH_4]Cl$, and $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(N{=}CMe_2)]\cdot Me_2CO$. The crystal and molecular structure of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHEt)]$, as a di-isopropyl ether solvate, has been determined by *X*-ray diffraction methods using counter data and refined by block-diagonal least-squares procedures, to R = 0.0534 for 3 150 reflections. The molecule is six-co-ordinate, with a linear Mo–N–O group, and a short Mo–NHEt bond. Crystals are monoclinic with a = 40.00(3), b = 12.751(10), c = 10.60(3) Å, β = 97.23(2)°, space group $P2_1/a$, and Z = 8.

In a previous paper,[2] we described how $[Mo\{HB(Me_2pz)_3\}(NO)X(Y)]$, (1; X = Y = Cl, Br, or I) $[HB(Me_2pz)_3{=}HB(3,5\text{-}Me_2C_3HN_2)_3]$, reacted readily with alcohol forming air- and moisture-stable alkoxides, (1; X = halide, Y = OR, R = alkyl). An *X*-ray structure determination of a representative member of this group of complexes, $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OPr^i)]$ revealed the overall pseudo-octahedral geometry of this class of molecule and a very short Mo–O bond (1.86 Å). The shortness of the metal–alkoxide distance was attributed to p_π–d_π bonding between the O donor atom and the metal, caused by co-ordinative unsaturation of the metal [a seventh ligand cannot be accommodated at Mo because of the bulk of the $HB(Me_2pz)_3$ group] and the presence of the strongly electron-withdrawing Cl and NO groups.

Monoalkylamines are isoelectronic with alcohols, and it seemed quite probable that such species would react with (1; X = Y = halide) and related tungsten species affording rare examples of stable monoalkylamido-complexes, *e.g.* (1; X = halide, Y = NHR). Monoalkylamido-complexes are very uncommon, and attempts to prepare them usually lead either to proton loss and formation of imido-species,[3] or to oligo- or polymerisation.[4] However, the hydrolytically unstable complexes $[TiCl_2(NHR)_2]$ (R = Me, Et, or Pr^n) [5] and $[W({=}NR)_2(NHR)_2]$ (R = Me, Et, or Bu^t) have been described,[6] and the structure of *trans*-$[Mo(NHR)_2(OSiMe_3)_4]$ (R = 1-adamantyl) has been reported.[7]

In this paper we describe the formation of stable monomeric monoalkylamido-complexes of the type (1; X = I, Y = NHR), of related tungsten complexes, and of the simple amido-species, (1; X = I, Y = NH_2). The full characterisation of (1; X = I, Y = NHEt) by *X*-ray methods is reported. A preliminary account of some of this, and related work, has been given elsewhere.[8]

EXPERIMENTAL

All reagents were used as purchased without further purification except $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$, and $[W\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_2(NO)]$ which were prepared as described in the literature.[2, 9] Solvents were specially purified, dried, and degassed (N_2) by standard methods.

Molecular weights were determined osmometrically. Infrared spectra were obtained using PE 297 and 180 spectrophotometers, and n.m.r. spectra were measured using PE R12, R23, and JEOL PFT90 instruments. Microanalyses were performed by the Microanalytical Laboratory of this Department. All yields are quoted relative to metal-containing starting materials, and all reactions were carried out under N_2.

$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NH_2)]$, (1; X = I, Y = NH_2).—A solution of (1; X = Y = I) (1.0 g) and an excess of ammonia solution (*d* 0.88; 0.1 cm^3, 6 drops) in dichloromethane (150 cm^3) was stirred for 15 min, during which time the solution turned dark red in colour. The solution was filtered, the solvent removed *in vacuo*, and the residue recrystallised from dichloromethane–methanol affording the desired product as salmon pink crystals which were washed in spectroscopic grade methanol and dried *in vacuo* (yield: 0.6 g, 72%).

$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(N{=}CMe_2)]\cdot Me_2CO$, (1; X = I, Y = $NCMe_2$).—To (1; X = I, Y = NH_2) (0.3 g) in acetone (30 cm^3) was added triethylamine (0.1 cm^3, an excess) and the mixture was stirred and refluxed for 4 d. The resulting deep red solution was slowly evaporated affording an orange microcrystalline product, which was dried *in vacuo* (0.42 g, 72%).

$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHMe)]$, (1; X = I, Y = NHMe).—A solution of (1; X = Y = I) (0.5 g) and methylamine (33% aqueous solution, 0.1 cm^3) in dichloromethane (40 cm^3) was stirred at room temperature for 30 min, during which time the colour changed to deep red. The solvent was partially removed *in vacuo* and di-isopropyl ether was added, the precipitate of white methylamine iodide being then filtered off. The mixture was slowly evaporated, and on addition of methanol an orange-red microcrystalline product precipitated (0.39 g, 91%).

[Mo{HB(3,5-$Me_2C_3HN_2$)$_3$}(NO)I(NHEt)], (1; X = I, Y = NHEt).—This complex was prepared by treating (1; X = Y = I) (0.5 g) with an excess of ethylamine (0.1 cm^3) in a manner similar to that described for the preceding complex. The product was obtained as dark red crystals by recrystallisation from dichloromethane–di-isopropyl ether (0.44 g, 90%).

The analogous complexes [Mo{HB(3,5-$Me_2C_3HN_2$)$_3$}-(NO)I(NHR)] were prepared in a manner also similar to that described above, by addition of an excess of the appropriate amine to (1; X = Y = I). Yields and colours are as follows: R = Pr^n, 86%, bright red microcrystals; Bu^n, 82%, red crystals; Pr^i, 67%, dark red crystals; Bu^i, 74%, dark red microcrystals; $CH_2CH=CH_2$, 69%, dark red microcrystals.

[Mo{HB(3,5-$Me_2C_3HN_2$}(NO)I(NHCH$_2$Ph)], (1; X = I, Y = NHCH$_2$Ph).—A solution of (1; X = Y = I) (0.5 g) and an excess of benzylamine (0.1 cm^3) in dichloromethane (40 cm^3) was stirred at room temperature for *ca.* 1.5 h resulting in a dark red solution. The mixture was filtered under nitrogen and the solvent removed *in vacuo*. The product was recrystallised from methylcyclohexane–methanol affording a red microcrystalline compound (0.29 g, 60%).

[Mo{HB(3,5-$Me_2C_3HN_2$)$_3$}(NO)I(NHC$_6$H$_{11}$)], (1; X = I, Y = NHC$_6$H$_{11}$).—It was imperative that the dichloromethane used in this reaction was free of any methanol impurities. The methylene chloride was shaken with NaOH pellets, washed with water, dried over anhydrous $CaCl_2$, and fractionated, the fraction boiling at 40—41 °C being collected. The purity of the solvent was monitored by ^{1}H n.m.r. spectroscopy and dry alcohol-free batches were used for preparations involving bulky amines. An excess of cyclohexylamine (0.15 cm^3) was added to a dichloromethane solution (50 cm^3) of (1; X = Y = I) (0.5 g) and the mixture was stirred for *ca.* 16 h. The solvent was removed *in vacuo* until only 5 cm^3 remained, and on addition of di-isopropyl ether a white precipitate formed. This was identified as a mixture of cyclohexylammonium iodide and decomposed starting material, and was removed by filtration. The crude product was isolated as an orange-brown powder on the addition of n-pentane (30 cm^3). The compound was recrystallised from dichloromethane–di-isopropyl ether being obtained as dark red crystals after drying *in vacuo* (0.1 g, 21%).

[Mo{HB(3,5-$Me_2C_3HN_2$)$_3$}(NO)I(NMe$_2$)], (1; X = I, Y = NMe$_2$).—A solution of (1; X = Y = I) (0.4 g) and dimethylamine (0.2 cm^3, 33% aqueous solution) in dichloromethane (40 cm^3) was stirred at room temperature for 0.75 h until an orange-red solution had formed. The solvent was evaporated to a few cm^3 *in vacuo*, and di-isopropyl ether (30 cm^3) was added causing the precipitation of a white solid (dimethylammonium iodide). This was filtered off and the filtrate was slowly evaporated until the product started to precipitate as an orange-brown powder (0.16 g, 46%).

[W{HB(3,5-$Me_2C_3HN_2$)$_3$(4-Br-3,5-$Me_2C_3N_2$)}(NO)Br$_2$], (2; X = Y = Br).—To a carbon tetrachloride solution (100 cm^3) of [W{HB(3,5-$Me_2C_3HN_2$)$_3$}(CO)$_2$(NO)] (3.6 g) was added a solution of bromine (1.0 g) in carbon tetrachloride (50 cm^3). The colour of the mixture changed rapidly from orange through deep red to brown-green, then dark green, and finally became bright (yellow) green. During this time a fine yellow-green precipitate formed. After stirring for 1 h, light petroleum (10 cm^3, b.p. 40—60 °C) was added and the mixture was stirred for another hour. The precipitate was then filtered off, washed with carbon tetrachloride and n-pentane, and dried *in vacuo*. The product was a bright green, almost fluorescent, powder.

Large amounts of air- and moisture-sensitive uncharacterisable olive green materials were occasionally isolated from this reaction. Despite considerable effort, no absolutely reliable synthetic route to (2; X = Y = Br) could be devised.

[W{HB(3,5-$Me_2C_3HN_2$)$_2$(4-Br-3,5-$Me_2C_3N_2$)}(NO)Br-(NH$_2$)], (2; X = Br, Y = NH$_2$).—To a dichloromethane solution (30 cm^3) of (2; X = Y = Br) (2.0 g) was added ammonia (2.0 cm^3, *d* 0.88). The mixture rapidly became orange-red and was stirred for 40 min. The grey-green precipitate which had formed was filtered off, and the red filtrate was evaporated *in vacuo*. The dark orange residue was then treated with diethyl ether giving an orange solid which was filtered off, washed with diethyl ether, and dried *in vacuo*. The *complex* was obtained as a pale orange powder after recrystallisation of the residue from dichloromethane–diethyl ether (yield 73%).

[W{HB(3,5-$Me_2C_3HN_2$)$_2$(4-Br-3,5-$Me_2C_3N_2$)}(NO)Br-(NHPr^i)], (2; X = Br, Y = NHPr^i).—To a solution of (2; X = Y = Br) (0.15 g) in dichloromethane (20 cm^3) was added isopropylamine (0.03 g), and the mixture was stirred for 1 h. The resulting orange solution was evaporated *in vacuo* and the residue treated with methanol. The resulting orange solid was filtered off, washed with methanol, and dried *in vacuo*. The orange *complex* could then be recrystallised from diethyl ether (yield 0.12 g, 76%).

[W{HB(3,5-$Me_2C_3HN_2$)$_2$(4-Br-3,5-$Me_2C_3N_2$)}(NO)Br(NH-CH$_2$Ph)], (2; X = Br, Y = NHCH$_2$Ph).—This complex was prepared in the same way as (2; X = Pr, Y = NHPr^i), using (2; X = Y = Br) (0.3 g) and PhCH$_2$NH$_2$ (0.01 g) in dichloromethane (20 cm^3). The orange *complex* was recrystallised from diethyl ether–n-pentane mixtures (yield 70%).

Crystal Data.—$C_{17}H_{28}BIMoN_8O\cdot\frac{1}{2}(C_6H_{14}O)$, $M = 645.2$ (excluding solvent, 594.1), crystallises from dichloromethane–di-isopropyl ether as dark red plates, crystal dimensions 0.08 × 0.27 × 0.38 mm, Monoclinic, $a = 40.00(3)$, $b = 12.751(10)$, $c = 10.60(3)$ Å, $\beta = 97.23(2)°$, $U = 5\,365(13)$ Å^3, $D_m = 1.67$, $Z = 8$, $D_c = 1.60$ g cm^{-3}, space group $P2_1/a$ (non-standard setting of $P2_1/c$ from systematic absences), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 16.4 cm^{-1}, $F(000) = 2\,584$.

Three dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stöe Stadi-2 *X*-ray diffractometer by the ω scan method. 3 150 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation, and absorption effects. The structure was solved by Patterson, superposition, and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions (C–H 0.95, B–H 1.10, N–H 0.92 Å, C–C–H 110°); their contributions were included in structure-factor calculations ($B = 10.0$ Å^2) but no refinement of positional parameters was permitted. The geometry of the ethylamido-fragment of one molecule was constrained (N–C 1.40, C–C 1.50 Å, N–C–C 110.1°) as were the geometries of the two isopropyl groups (C–C 1.54 Å, C–C–C 110°) of a di-isopropyl ether solvent molecule of crystallisation. Refinement converged at *R* 0.0534 with allowance for anisotropic thermal motion of all non-hydrogen atoms (with the exceptions of those of the constrained

TABLE 1

Fractional co-ordinates of all non-hydrogen atoms with estimated standard deviations in parentheses *

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Molecule 1			
Mo(1)	0.387 68(3)	0.381 56(14)	−0.125 20(13)
I(1)	0.386 47(3)	0.425 11(13)	0.130 17(11)
O(1)	0.366 3(4)	0.168 9(13)	−0.077 6(13)
N(1)	0.442 2(3)	0.345 0(10)	−0.082 4(11)
N(2)	0.464 5(3)	0.403 7(9)	−0.143 5(10)
N(3)	0.400 1(3)	0.354 6(10)	−0.314 1(10)
N(4)	0.428 9(3)	0.400 2(10)	−0.350 8(10)
N(5)	0.404 6(3)	0.548 0(11)	−0.155 7(11)
N(6)	0.430 7(3)	0.564 4(10)	−0.222 9(11)
N(7)	0.374 9(4)	0.253 6(15)	−0.097 9(12)
N(8)	0.342 9(4)	0.434 8(19)	−0.189(2)
B(1)	0.452 4(4)	0.470 9(14)	−0.259 1(15)
C(1)	0.461 6(5)	0.281 9(14)	−0.002 1(14)
C(2)	0.496 1(4)	0.301 3(13)	−0.007 7(16)
C(3)	0.496 6(3)	0.378 9(13)	−0.099 1(14)
C(4)	0.447 0(5)	0.206 9(16)	0.081 1(20)
C(5)	0.526 5(4)	0.425 6(16)	−0.142 0(16)
C(6)	0.385 5(4)	0.298 2(13)	−0.410 6(13)
C(7)	0.404 3(4)	0.308 0(14)	−0.512 4(13)
C(8)	0.431 2(4)	0.371 8(13)	−0.471 3(13)
C(9)	0.353 2(4)	0.240 3(17)	−0.403 8(15)
C(10)	0.459 2(4)	0.405 4(16)	−0.543 7(15)
C(11)	0.392 9(4)	0.646 9(13)	−0.131 8(14)
C(12)	0.412 3(4)	0.717 2(14)	−0.185 2(16)
C(13)	0.435 9(4)	0.667 0(13)	−0.243 3(14)
C(14)	0.363 8(5)	0.665 7(17)	−0.059 6(19)
C(15)	0.462 0(5)	0.707 8(12)	−0.317 2(17)
C(16)	0.308 4(5)	0.412 8(20)	−0.216(2)
C(17)	0.288 4(4)	0.486 5(20)	−0.145(3)
(*b*) Molecule 2			
Mo(2)	0.199 12(3)	0.237 49(12)	−0.304 11(13)
I(2)	0.184 26(4)	0.224 35(12)	−0.566 67(11)
O(2)	0.269 2(3)	0.201 3(11)	−0.342 1(12)
N(9)	0.143 9(3)	0.258 7(10)	−0.285 1(11)
N(10)	0.135 5(3)	0.338 5(10)	−0.209 4(11)
N(11)	0.208 5(3)	0.283 6(10)	−0.107 9(10)
N(12)	0.189 3(3)	0.357 3(9)	−0.059 2(10)
N(13)	0.199 9(3)	0.412 9(10)	−0.321 3(10)
N(14)	0.179 2(3)	0.469 9(9)	−0.251 7(11)
N(15)	0.241 6(3)	0.216 9(11)	−0.324 2(12)
N(16)	0.190 6(3)	0.090 7(11)	−0.262 0(12)
B(2)	0.161 9(5)	0.415 9(15)	−0.145 2(17)
C(18)	0.114 6(4)	0.212 4(13)	−0.332 5(15)
C(19)	0.088 4(4)	0.261 9(17)	−0.279 1(17)
C(20)	0.101 9(4)	0.338 3(15)	−0.206 2(17)
C(21)	0.112 9(5)	0.121 7(16)	−0.419 4(19)
C(22)	0.084 9(4)	0.414 3(18)	−0.127 2(20)
C(23)	0.231 5(4)	0.250 7(14)	−0.008 7(14)
C(24)	0.226 0(4)	0.303 9(13)	0.098 6(14)
C(25)	0.199 7(3)	0.369 5(12)	0.064 4(12)
C(26)	0.257 3(4)	0.168 1(16)	−0.025 2(16)
C(27)	0.183 0(5)	0.443 9(16)	0.144 4(15)
C(28)	0.214 7(4)	0.482 8(14)	−0.389 8(13)
C(29)	0.204 8(4)	0.582 2(13)	−0.366 0(14)
C(30)	0.182 4(4)	0.571 5(13)	−0.277 8(13)
C(31)	0.239 6(4)	0.453 0(14)	−0.480 7(16)
C(32)	0.162 6(4)	0.655 6(13)	−0.218 2(17)
C(33)	0.208 3(5)	−0.005 0(16)	−0.263 0(18)
C(34)	0.190 6(5)	−0.078 1(16)	−0.360 8(21)
(*c*) Solvent molecule			
O(3)	0.444 9(7)	−0.004 2(17)	0.656(3)
C(35)	0.415 1(12)	0.020(4)	0.581(4)
C(36)	0.421 7(12)	0.005(6)	0.442(4)
C(37)	0.383 4(12)	−0.042(6)	0.605(4)
C(38)	0.459 8(7)	0.082(4)	0.730(5)
C(39)	0.486 0(17)	0.139(4)	0.660(4)
C(40)	0.477 5(17)	0.011(4)	0.835(4)

* The estimated standard deviations for atoms whose geometry was constrained during the refinement are derived from group parameters.

groups which were each assigned a common, isotropic thermal parameter); corrections were made for the anomalous scattering of molybdenum and iodine. Table 1 lists the atomic positional parameters with estimated standard deviations. Tables of anisotropic and isotropic thermal vibrational parameters with estimated standard deviations, calculated hydrogen-atom positional parameters, observed structure amplitudes and calculated structure factors, and least-squares planes are deposited in Supplementary Publication No. SUP 23170 (36 pp.).† Scattering factors were taken from ref. 10; unit weights were used throughout the refinement. Computer programs used formed part of the Sheffield *X*-ray system.

RESULTS AND DISCUSSION

Synthetic Studies.—The synthesis of (1; X = Y = I) has been described previously,[2] but the corresponding tungsten complexes $[W\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(Y)]$ (X = Y = Cl, Br, or I) have not been reported. However, direct addition of halogen to $[W\{HB(C_3H_3N_2)_3\}(CO)_2(NO)]$ in dichloromethane at low temperature apparently afforded[11] $[W\{HB(C_3H_3N_2)_3\}(NO)X(Y)]$ (X = Y = Cl, Br, or I). Our attempts to emulate this last reaction with $[W\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_2(NO)]$ were singularly unsuccessful, even under a wide variety of conditions. On attempting to prepare dichloro-derivatives using Cl_2, we observed not only displacement of CO, but also, on the basis of ^1H n.m.r. spectral results, substitution of H at C(4) on the pyrazolyl rings and also apparent chlorination of the methyl groups. Attack by Cl_2 at C(4) has been observed previously,[2] and is a common reaction of pyrazoles. Under no circumstances were we able to control these reactions or to isolate products with consistent elemental analyses or spectra. Upon bromination, similar but less severe difficulties were encountered, although we were able to reproduce, albeit unreliably, the synthesis of a 'tribromo'-derivative, subsequently identified as $[W\{HB(3,5\text{-}Me_2C_3HN_2)_2(4\text{-}Br\text{-}3,5\text{-}Me_2C_3N_2)\}(NO)Br_2]$, (2; X = Y = Br). Partial bromination of the $HB(C_3HMe_2N_2)_3$ ligand is somewhat unusual, since we have previously observed full bromination in the synthesis of $[Mo\{HB(4\text{-}Br\text{-}3,5\text{-}Me_2C_3N_2)_3\}(NO)Br_2]$[2] and $[Re\{HB(4\text{-}Br\text{-}3,5\text{-}Me_2C_3N_2)_3\}(CO)_3]$.[12] Attempts to make di- or even poly-iodo-tungsten complexes by treatment of $[W\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_2(NO)]$ with iodine afforded only brown amorphous materials which contained some NO, but could not otherwise be characterised.

The complex (2; X = Y = Br) was isolated as a yellow-green, almost fluorescent powder (elemental analyses, Table 2) which was readily soluble in chlorinated hydrocarbons (except CCl_4) giving yellow-green solutions. The i.r. spectrum (Table 3) of the compound exhibited one NO stretching frequency, at 1 665 cm^{-1}, at least 35 cm^{-1} lower than that of comparable molybdenum complexes. From the ^1H n.m.r. spectrum of (2; X = Y = Br) (Table 3) it was quite clear that one of

† For details see Notices to Authors No. 7, *J. Chem. Soc. Dalton Trans.*, **1981**, Index issue.

the C(4) atoms in the pyrazolyl rings was brominated since the signals associated with protons at this position occurred as two singlets of equal intensity instead of the characteristic two singlets of relative intensity 1 : 2. Furthermore, integration of the spectra revealed the ratio of C(4) protons to methyl protons was 1 : 9. The compound was insufficiently soluble for molecular-weight determinations, but in view of its similarity to related molybdenum complexes, we presume it to be monomeric and therefore that the W atom is co-ordinatively unsaturated (16-electron system).

Table 2

Analytical data

		Analysis (%)								
		Found				Calc.				
Compound	Y	C	H	N	X [b]	C	H	N	X [b]	*M* [a]
[Mo{HB($Me_2C_3HN_2)_3$}(NO)I(Y)]										
	NH_2	31.9	4.3	19.8	22.2	31.8	4.2	19.8	22.5	555 (565)
	NHMe	33.3	4.5	19.2	22.2	33.1	4.5	19.3	21.9	655 (686)
	NHEt	34.6	4.7	18.6	21.1	34.4	4.7	18.9	21.4	
	$NHPr^n$	35.5	5.1	18.2	20.7	35.5	4.9	18.4	20.9	610 (608)
	$NHPr^i$	35.7	4.9	18.3	20.2	35.5	4.9	18.4	20.9	
	$NHBu^n$	36.7	5.3	17.8	20.5	36.7	5.2	18.0	20.4	619 (623)
	$NHBu^i$	36.8	5.1	17.7	20.7	36.7	5.2	18.0	20.4	
	$NHCH_2Ph$	40.3	4.4	16.7	19.5	40.3	4.6	17.1	19.4	670 (656)
	NHC_6H_{11}	38.6	5.0	16.9	20.4	39.0	4.9	17.3	19.6	
	NHC_3H_5	35.5	4.6	18.1	20.9	35.7	4.6	18.5	21.0	
	$N{=}CMe_2$ [c]	38.1	5.0	17.1	18.5	38.0	5.1	16.9	19.1	
[W{HB($Me_2C_3HN_2)_2(BrMe_2C_3N_2)$}(NO)Br(Y)]										
	NH_2	26.9	3.3	16.1	25.8	26.3	3.4	16.3	23.3	
	$NHBu^i$	29.1	3.9	14.7	24.1	29.7	3.9	15.4	22.0	
	$NHCH_2Ph$	34.2	3.9	14.2	20.6	34.0	3.7	14.4	20.6	
	Br	23.7	2.6	12.6	31.9	24.0	2.8	13.1	32.0	

[a] Determined osmometrically in $CHCl_3$, calculated values are given in parentheses. [b] X = I or Br as appropriate. [c] Compound isolated with 1 mole of acetone.

Reaction of (1; X = Y = I) and (2; X = Y = Br) with an excess of NH_3 (*d* 0.88) or NH_2R afforded (1; X = I, Y = NHR, R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, CH_2Ph, C_6H_{11}, or $CH_2CH{=}CH_2$) and (2; X = Br, Y = NHR, R = H, Pr^i, or CH_2Ph). These complexes were isolated as orange or orange-red solids which formed deep red solutions in dichloromethane, acetone, and benzene. All of these compounds were air- and moisture-stable and can be kept as solids in open containers for several weeks without noticeable decomposition.

For the synthesis of (1; X = I, Y = NHR) and (2; X = Br, Y = NHR), from the corresponding dihalides, the slight excess of NH_2R is necessary in order to facilitate removal of HX generated in the reaction, *viz.* equations (i) and (ii). On some occasions, the mono-

$$(1;\ X = Y = I) + 2\,NH_2R \longrightarrow (2;\ X = I,\ Y = NHR) + [NH_3R]I \quad (i)$$

$$(2;\ X = Y = Pr) + 2\,NH_2R \longrightarrow (2;\ X = Pr,\ Y = NHR) + [NH_3R]Br \quad (ii)$$

alkylammonium salts could be recovered after the reaction was finished.

From our knowledge of the structure of [Mo{HB(4-Cl-3,5-$Me_2C_3HN_2)_3$}(NO)Cl(OPr^i)] [2] and from the study of molecular models of (1; X = I, Y = NHR), it seemed unlikely that we would be able to prepare *dialkylamido*-complexes, *e.g.* (1; X = I, Y = NR_2). Indeed, we were confirmed in this view when we were unable to make complexes containing NPr^i_2 or $N(C_6H_{11})_2$. However, when (1; X = Y = I) was treated with $NHMe_2$, red solutions were formed from which we were able to isolate the unstable dimethylamide, (1; X = I, Y = NMe_2). This compound could only be characterised satisfactorily by spectroscopic methods. A similar diethylamide was apparently formed in solution but could not be isolated.

Spectral Studies of (1; X = I, Y = NHR) *and* (2; X = Br, Y = NHR).—The i.r. spectra of the new complexes exhibit ν(BH) at 2 500 cm^{-1} and a further group of absorptions around 1 400 cm^{-1} which are characteristic of the tris(3,5-dimethylpyrazolyl)borato-ligand.

The NO stretching frequencies of (1; X = I, Y = NHR) fall in the range 1 640—1 672, the highest absorption being associated with Y = NH_2 and the lowest with Y = NHMe. Clearly, the basicity of NHR (R = alkyl) is greater than that of NH_2, and this must account for the relative position of ν(NO) when Y = NH_2. In general, however, ν(NO) does not appear to be greatly influenced by the electronic nature of the alkyl group. The spectra of the tungsten complexes show that ν(NO) is significantly lower than those in the comparable molybdenum analogues. Given the relative sizes of Mo and W, assuming comparable oxidation states, it is tempting to rationalise the positions of ν(NO) in (1) and (2) in terms of steric interactions between NHR and the pyrazolyl-borato- and halide ligands. If it is assumed that the only significant difference between (1) and (2) is the size of the metal atom, then taking into account the relative size of HB(3,5-$Me_2C_3HN_2)_3$ and the fact that the molybdenum complexes contain iodine whereas the tungsten species

TABLE 3

Infrared and n.m.r. spectral data obtained from (1; X = I, Y = NHR), (1; X = I, Y = NMe$_2$ or N=CMe$_2$), and (2; X = Br, Y = NHR)

			I.r. data[a]		N.m.r. spectral data		
Complex	X	Y	ν(NH)	ν(NO)	δ[b]	A[c]	Assignments
(1)	I	$\mathrm{NH_2}$	3 252	1 672	11.68[d]	2	AB pair, δ(A) 11.78, δ(B) 11.48, J(AB) = 3.7 Hz, $\mathrm{N}\mathit{H}_2$
			3 364 3 315 3 410	1 671[f]	5.90[e] 5.84 5.78	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					2.64 2.61 2.42 2.35 2.31	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)_2N_2}$
(1)	I	NHMe	3 270	1 640	12.97[d, g]	1	quartet, ^3J 7.8 Hz, $\mathrm{N}\mathit{H}\mathrm{Me}$
					5.86[e] 5.81	3	s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					4.08	3	d, ^3J(N–H) 7.8 Hz, NHMe
					2.62 2.54 2.45 2.41 2.34	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)_2N_2}$
(1)	I	NHEt	3 250	1 655	12.80[d]	1	dd, separation 2.7 Hz, ^3J(NH) 7.1 and 9.8 Hz, NHEt
					5.90[e] 5.82 5.80	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					4.51	2	AB pair, δ(A) 4.88, δ(B) 4.13, J(AB) 14.5, ^3J(NH) 9.8 (A) and 7.1 (B), ^3J 7.0 Hz, $\mathrm{NHC}\mathit{H}_2\mathrm{Me}$
					2.60 2.58 2.43 2.36 2.33	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)N_2}$
					1.39	3	t, ^3J 7.1 Hz, $\mathrm{NHCH_2C}\mathit{H}_3$
(1)	I	NHPr^n	3 280	1 655	12.75	1	br, $\mathrm{N}\mathit{H}\mathrm{Pr^n}$
					5.90 5.80	3	s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					4.42	2	m, AB pair, δ(A) 4.77, δ(B) 4.07, J(AB) 15.1, ^3J(NH) 9.9 (A) and 7.0 (B), ^3J 7.0 Hz, $\mathrm{NHC}\mathit{H}_2\mathrm{Et}$
					2.60 2.56 2.40 2.33 2.31	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)_2N_2}$
					1.77	2	m (AB pair, not resolved), $\mathrm{NHCH_2C}\mathit{H}_2\mathrm{Me}$
					1.01	3	t, ^3J 7.3 Hz, $\mathrm{NH(CH_2)_2C}\mathit{H}_3$
(1)	I	NHPr^i	3 280	1 660	12.49	1	br, NHPr^i
					5.89 5.79 5.77	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					5.35	1	m, $\mathrm{NHC}\mathit{H}\mathrm{Me_2}$ (poorly resolved)
					2.58(3) 2.40(1) 2.35(1) 2.31(1)	18	s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)_2N_2}$
					1.40	6	dd, separation 66 Hz, ^3J 5.9 Hz, $\mathrm{NHCH(C}\mathit{H}_3\mathrm{)_2}$
(1)	I	NHBu^n	3 227 3 284[f]	1 646 1 666[f]	12.72	1	br, $\mathrm{N}\mathit{H}\mathrm{Bu^n}$
					5.90 5.80	3	s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					4.45	2	m, AB pair, δ(A) 4.82, δ(B) 4.08, J(AB) 16.0, ^3J(NH) 10.0 (A) and 7.0 (B), ^3J 7.0 Hz, $\mathrm{NHC}\mathit{H}_2\mathrm{Pr^n}$
					2.61 2.56 2.40 2.33 2.32	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3\mathrm{)_2N_2}$
					1.76	2	m (AB pair, poorly resolved), $\mathrm{NHCH_2C}\mathit{H}_2\mathrm{Et}$
					1.55	2	m, $\mathrm{NH(CH_2)_2C}\mathit{H}_2\mathrm{Me}$, ^3J 7.0 Hz
					0.96	3	t, ^3J 6.6 Hz, $\mathrm{NH(CH_2)_3C}\mathit{H}_3$

TABLE 3 (*continued*)

			I.r. data[a]		N.m.r. spectra data		
Complex	X	Y	ν(NH)	ν(NO)	δ[b]	*A*[c]	Assignments
(1)	I	$NHBu^i$	3 290	1 661	12.83	1	br, $N\mathit{H}Bu^i$
					5.90 5.80	3	s m } $C_3\mathit{H}Me_2N_2$
					4.29	2	m, AB pair, δ(A) 4.61, δ(B) 3.98, *J*(AB) 14.7, ^3J(NH) 10.0 (A) and 7.3 (B), ^3J 7.1 Hz, $NHC\mathit{H}_2Pr^i$
					2.61 2.58 2.40 2.35 2.34	18	s s s s s } $C_3H(C\mathit{H}_3)_2N_2$
					2.02	1	m, $NHCH_2C\mathit{H}Me_2$
					1.01	6	dd, separation 6.7 Hz, ^3J 6.7 Hz, $NHCH_2CH(C\mathit{H}_3)_2$
(1)	I	$NHCH_2Ph$	3 261	1 658	12.45	1	br, $N\mathit{H}CH_2Ph$
					7.37	5	m, $NHCH_2C_6\mathit{H}_5$
			3 288[f]	1 666[f]	5.95— 5.08	5	m, AB pair, δ(A) 5.88, δ(B) 5.16, *J*(AB) 15.0, ^3J(NH) 9.4 (A) and 7.1 (B) Hz, $NHCH_2Ph$, and δ 5.80 and 5.82, $C_3\mathit{H}Me_2N_2$
					2.65 2.42 2.38 2.34 2.21	18	s s s s s } $C_3H(C\mathit{H}_3)_2N_2$
(1)	I	NHC_6H_{11}	3 255	1 660	12.60	1	br, $N\mathit{H}C_6H_{11}$
					5.92 5.80	3	s m } $C_3\mathit{H}Me_2N_2$
					4.97	1	m, H(1) of C_6H_{11}
					2.60 2.59 2.40 2.35 2.33 2.31	18	s s s s s s } $C_3H(C\mathit{H}_3)_2N_2$
					2.05—1.30	10	m, CH_2 groups of C_6H_{11}
(1)	I	$NHCH_2CH{=}CH_2$	3 270	1 655	12.40	1	br, $N\mathit{H}C_3H_5$
					6.10 4.85	2	m, AB pair (poorly resolved), $NHC\mathit{H}_2CH{=}CH_2$
					5.89 5.82	3	s m } $C_3HMe_2N_2$
					5.30 5.03	3	m, $NHCH_2$ and $NHCH_2CH{=}CH_2$ (poorly resolved)
					2.60 2.53 2.40 2.33 2.32 2.31	18	s s s s s s } $C_3H(C\mathit{H}_3)_2N_2$
(1)	I	$N{=}CMe_2$[h]		1 665 1 710[i]	5.84 5.82 5.78	1	s s s } $C_3\mathit{H}Me_2N_2$
					2.63(1) 2.47(1) 2.40(1) 2.33(3) 2.30(1) 2.14(2) 1.90(1)	10	s s s s s s s } $C_3H(C\mathit{H}_3)_2N_2$, $N{=}CC\mathit{H}_3$, and $(CH_3)_2CO$
(1)	I	NMe_2		1 638[f]	5.86 5.84 5.80	1	s s s } $C_3\mathit{H}Me_2N_2$
					4.30	1	s $N(C\mathit{H}_3)Me$
					3.18	1	s $NMe(C\mathit{H}_3)$
					2.61 2.53 2.39 2.35 2.31	18	s s s s s } $C_3H(C\mathit{H}_3)_2N_2$
(2)	Br	NH_2	3 300 3 390	1 630	9.50	2	AB pair, δ(A) 9.68, δ(B) 9.32, *J*(AB) 3.8 Hz, NH_2
					5.89 5.87	2	s s } $(C_3\mathit{H}Me_2N_2)_2$
					2.67 2.59 2.44 2.33	18	s s s s } $\{C_3H(C\mathit{H}_3)_2N_2\}_2\{C_3Br(C\mathit{H}_3)_2N_2\}$

TABLE 3 (*continued*)

			I.r. data[a]		N.m.r. spectral data		
Complex	X	Y	ν(NH)	ν(NO)	δ[b]	*A*[c]	Assignments
(2)	Br	NHPr^i	3 275	1 615	10.05	1	br s, N*H*Pr^i, ^3J *ca.* 9.0 Hz
					5.88 5.85	2	s s $(C_3\mathit{H}Me_2N_2)_2$
					2.65 2.61 2.51 2.45 2.36 2.32	18	s s s s s s $\{C_3H(C\mathit{H}_3)_2N_2\}_2\{C_3Br(C\mathit{H}_3)_2N_2\}$
					1.35	6	dd, separation 27 Hz, ^3J 7.0 Hz, NHCH$(C\mathit{H}_3)_2$
(2)	Br	NHCH$_2$Ph	3 275	1 625	10.10	1	br, m, N*H*CH$_2$Ph, poorly resolved
					7.35	5	m, NHCH$_2$C$_6$*H*$_5$
					5.87	2	AB pair, δ(A) 6.25, δ(B) 5.49, *J*(AB) 13.4, ^3J(NH) 9.8 (A) and 8.0 (B) Hz, NHC*H*$_2$Ph
					5.88 5.85	2	s s $(C_3\mathit{H}Me_2N_2)_2$
					2.68 2.57 2.40 2.34 2.32 2.14	18	s s s s s s $\{C_3HC\mathit{H}_3N_2\}_2\{C_3Br(C\mathit{H}_3)_2N_2\}$
(2)	Br	Br		1 665	5.96	2	s $(C_3\mathit{H}Me_2N_2)_2$
					2.59 2.46 2.36	18	s s s $\{C_3H(C\mathit{H}_3)_2N_2\}_2\{C_3Br(C\mathit{H}_3)_2N_2\}$

[a] In KBr discs unless otherwise stated. [b] At 220 MHz at 37 °C in CDCl$_3$ using SiMe$_4$ as internal reference unless otherwise stated. [c] Relative intensity. [d] H signals resolved by irradiation at ^{14}N resonance frequency. [e] At 100 MHz in CDCl$_3$ solution, unless otherwise stated. [f] In CHCl$_3$ solution. [g] Spectra recorded at −60 and 50 °C, without change. [h] Complex contains 1 mole of (CH$_3$)$_2$CO. [i] ν(CO) of (CH$_3$)$_2$CO.

carry bromine, then there will be more room around the tungsten. This will permit a closer approach of NHR to the metal than in the molybdenum analogue. Consequently, there will be more effective N→M donation in (2; X = Br, Y = NHR) therefore greater back donation from W to NO and hence a lower value of ν(NO).

In the complex (1; X = I, Y = NMe$_2$), ν(NO) is not substantially different from that of its NHMe analogue. This, too, may be rationalised on steric grounds. Thus the increased basicity of NMe$_2$ *versus* NHMe, with its expected effect on ν(NO), must be balanced by an increase in the Mo–N bond distance, and hence less effective N→Mo charge transfer. This increase in Mo–N bond length when Y = NMe$_2$ is occasioned by the repulsive interactions between the methyl groups of the amino-group and of the pyrazolyl ring. The complex (1; X = I, Y = NMe$_2$) does not, as expected, exhibit ν(NH) in the range 3 200—3 300 cm^{-1}. The monoalkylamides show only one such absorption.

In the ^{1}H n.m.r. spectra of the new complexes, the proton signals of the tris(pyrazolyl)borato-ligands occur in two regions: at δ 2.0—2.6 due to the methyl protons and around δ 5.85 due to the protons attached to C(4) of the pyrazolyl group. On the basis of our earlier studies of (1; X = I, Y = OR),[2] we expected that the H(4) signals in (1; X = I, Y = NHR) would appear as three singlets because of the asymmetry of these six-co-ordinate complexes. A number of the compounds do exhibit this spectral pattern in CDCl$_3$, but others do not, showing instead two resonances of relative intensity 1 : 2. This effect has been observed by us before,[2] and we attribute it to accidental degeneracy of two of the three H(4) resonances. The H(4) signals in the spectra of (2; X = Br, Y = NHR) appear as two singlets of equal intensity, which is consistent with the asymmetry of the complexes and with the fact that one pyrazolyl ring is brominated at C(4).

All of the complexes, except (1; X = I, Y = NMe$_2$) and (1; X = I, Y = N=CMe$_2$) (see later), exhibit signals due to the NH proton of the amido-group. In the spectra of the molybdenum complexes these appear in the range δ 11.96—12.80, while in those of their tungsten analogues they fall between δ 9.50 and 10.10. These signals appear as broad singlets (NHR, R = alkyl) or broad doublets (Y = NH$_2$) which sharpen on irradiation at the ^{14}N resonance frequency. Thus, on ^{14}N irradiation of (1; X = I, Y = NH$_2$) the NH$_2$ protons appear as an AB pair whereas in (1; X = I, Y = NHMe) the NH signal was a quartet. On ^{14}N irradiation at the appropriate frequency of (1; X = I, Y = NHEt) the NH proton appeared as a double doublet because of coupling with the inequivalent protons attached to the α-C atom. No H/D exchange was observed when solutions of (1; X = I, Y = NHR, R = alkyl) and its tungsten analogues were treated with D$_2$O, and only slow exchange occurred with (1; X = I, Y = NH$_2$) and (2; X = Br, Y = NH$_2$).

Because of the lack of a plane of symmetry in the alkylamido-halide complexes, the methylene proton resonances in those species containing Y = NHC*H*$_2$R appear as AB pairs. A number of these have been satisfactorily resolved, and couplings involving the NH and other CH protons detected. As in the case of the analogous alkoxides, (1; X = I, Y = OR),[2] a distinctive feature of the spectra of the alkylamido-complexes is the occurrence of resonances due to the α protons of the NHR group at relatively low fields (δ 4.08—5.50). This is almost certainly due to the very strongly electron-withdrawing nature of the $[M\{HB(Me_2pz)_3\}(NO)X]$ group which causes a net withdrawal of electron density from the amido-ligand, the effect manifesting itself in a substantial deshielding of the α-H atoms. Similar effects are observed in the ^1H n.m.r. spectra of $[WF_5(OMe)]$ and $[WF_4(OMe)_2]$.[13]

Reactions of Molybdenum Amido-complexes.—The Mo–N (amido) bond in (1; X = I, Y = NH_2 or NHMe) was cleaved by HCl in aqueous ethereal solution. The products were identified as (1; X = Y = Cl) * and either $[NH_4]Cl$, identified by colour test † and determined quantitatively by standard methods (yield of NH_4^+ essentially quantitative), or $[NH_3Me]Cl$, isolated as white crystals from the reaction mixture. There was no reaction between (1; X = I, Y = NH_2) and MeI, and extensive decomposition occurred when (1; X = I, Y = NH_2 or NHMe) was treated with $[OR_3][BF_4]$ (R = Me or Et).

The complex (1; X = I, Y = NH_2) reacted slowly with acetone in the presence of triethylamine giving an orange ketimido-complex (1; X = I, Y = $N{=}CMe_2$) which was isolated as a monoacetone solvate. This reaction did not occur when NEt_3 was replaced by $Na_2[CO_3]$. In the absence of triethylamine, no reaction occurred, implying that the base may be required to deprotonate the amido-complex giving an anionic imido-intermediate, *viz.* equation (iii). Nucleophilic attack by

$$(1;\ X = I,\ Y = NH_2) + NEt_3 \longrightarrow [(1;\ X = I,\ Y = NH)]^- + NHEt_3^+ \quad \text{(iii)}$$

this intermediate on the keto-group, followed by dehydration, would give (1; X = Y, Y = $N{=}CMe_2$). From the spectral and analytical data, there is no doubt that the group $N{=}CMe_2$ has been formed, and that replacement of the NH_2 group by an enolate ion, *e.g.* $CH_2C(O)Me^-$, reduction of acetone to propan-2-ol, followed by formation of (1; X = I, Y = OPr^i), or addition of the amido- or imido-group to a methyl or methylene C atom, had not occurred. Metal complexes containing ketimido-groups are quite well known,[14] and it is possible for $N{=}CR_2$ to act as a unidentate or as a bridging ligand. Although (1; X = I, Y = $N{=}CMe_2$) was insufficiently stable for molecular-weight determination, by analogy with the other complexes described in this paper and elsewhere,[2] it seems likely that it is monomeric. In such a situation, the ketimido-ligand could function as a one-electron donor, apparently as in $[Rh(CNMeCH_2CH_2NMe)\{N{=}C(CF_3)_2\}(PPh_3)_2]$,[15] or as a three-electron donor, as in $[Mo(\eta\text{-}C_5H_5)(CO)_2(N{=}CBu^t{}_2)]$.[16] However, in the absence of accurate bond-length and -angle data for (1; X = I, Y = $N{=}CMe_2$), we can draw no definite conclusions as to the nature of the ketimido-ligand. Certainly, if $N{=}CMe_2$ acts as a three-electron donor, the the Mo–N=C bond angle should be 180° and the molecule would be isoelectronic with (1; X = NO, Y = Cl).[17]

Reactions occurred between (1; X = I, Y = NH_2) and MeCOPh and PhCOPh, but the products were too unstable to be satisfactorily characterised. The amido-compound also reacted with $(HCHO)_3$ (trioxan), but instead of obtaining the desired (1; X = I, Y = $N{=}CH_2$), we isolated instead small amounts of (1; X = Y = OMe).

In an attempt to identify imido-species, we treated (1; X = I, Y = NH_2) with NEt_3 alone but, while observing transient colour changes, we failed to detect $[(1;\ X = I,\ Y = NH)]^-$ spectroscopically. In an effort to obtain alkylimido-complexes, we treated (1; X = I, Y = NHR, R = Me or Et) with $Tl[PF_6]$ in acetonitrile to which NEt_3 was subsequently added, *viz.*, equation (iv).

$$(1;\ X = I,\ Y = NHR) \xrightarrow[\text{MeCN}]{Tl^+} [(1;\ X = NCMe,\ Y = NHR)]^+ \xrightarrow{NEt_3} (1;\ X = NR) \text{ or } (1;\ X = NCMe,\ Y = NR) \quad \text{(iv)}$$

However, although TlI precipitated from the reaction mixture, we were unable to isolate a characterisable Mo-containing product. When $Ag[PF_6]$ or $Ag[O_2CMe]$ was used instead of $Tl[PF_6]$, extensive decomposition occurred, possibly because of the oxidising property of Ag^I.

No reaction occurred when (1; X = I, Y = NHR, R = H or Me) was treated with CS_2 or CO_2, in contrast to the well known behaviour of simple molybdenum and tungsten dialkylamides.[18] This must reflect the steric restraints imposed by the bulky pyrazolylborate on the ' insertion ' reaction.

In attempts to prepare (1; X = Y = NHR), we treated (1; X = I, Y = NHR) with an excess of the appropriate monoamine, but no reaction occurred. Even when (1; X = I, Y = NHMe) was first treated with $Ag[O_2CMe]$, when AgI precipitated, and then an excess of NH_2Me was added, no bis(amido)-complex could be isolated. When $Ag[PF_6]$ was used instead of $Ag[O_2CMe]$, a complex containing $HB(Me_2C_3HN_2)_3$, NO [ν(NO) 1 600 cm^{-1}], NH_xMe ($x \geqslant 1$), and PF_6^- was isolated as indicated by i.r. spectral studies, but we were unable to characterise this species further.

In refluxing alcohols, (1; X = I, Y = NHR) was converted into (1; X = Y = OR, R = Me, Et, or Pr^i). These bis(alkoxides) will be described in a subsequent paper.

Treatment of (1; X = I, Y = NMe_2) with an excess of NH_2Me in dichloromethane afforded the monoalkylamido-complex (1; X = I, Y = NHMe). Indeed, in 1 : 1 mixtures of mono- and di-methylamine, (1; X = Y = I) formed the monomethylamide preferentially.

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* Identified spectroscopically.

† By indophenol method (M. W. Weatherburn, *Anal. Chem.*, 1967, **39**, 971).

Reactions of the tungsten monoalkylamido-complexes were not investigated.

Structure of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I(NHEt)], (1; X = I, Y = NHEt).—The asymmetric unit comprises two crystallographically independent but chemically identical molybdenum complexes and a solvent molecule of crystallisation (Figure). Each complex molecule comprises a tris(3,5-dimethylpyrazolyl)hydroborato-ligand of conventional geometry bonded to a molybdenum atom with iodo, nitrosyl, and ethylamido as the three *trans* ligands, producing a distorted octahedral stereochemistry (Table 4). The molybdenum–nitrosyl group is linear with normal bond lengths; the molybdenum–iodine bond length is markedly shorter than other such single bonds,[19-21] suggesting a small degree of π-donor bonding. The ethylamido-ligand is attached by a short molybdenum–nitrogen bond and exhibits a large Mo–N–C angle which is again evidence for significant $p_\pi \rightarrow d_\pi$ donation from the ligand. Such π donation is well characterised[2] for such sterically crowded, octahedral molybdenum(II), 16-electron systems in which the further donation of π electrons from

TABLE 4

Bond lengths and angles with estimated standard deviations in parentheses *

	Molecule 1			Molecule 2		
	Ring 1 [N(1),N(2), C(1)—C(5)]	Ring 2 [N(3),N(4) C(6)—C(10)]	Ring 3 [N(5),N(6) C(11)—C(15)]	Ring 3′ [N(9),N(10) C(18)—C(22)]	Ring 2′ [N(11),N(12) C(23)—C(27)]	Ring 1′ [N(13),N(14) C(28)—C(32)]
(*a*) Bond lengths (Å)						
Mo(1)–N(1)	2.220(12)	2.152(12)	2.263(12)	2.259(12)	2.150(11)	2.245(11)
N(2)–B(1)	1.52(2)	1.55(2)	1.55(2)	1.54(2)	1.53(2)	1.56(2)
N(1)–N(2)	1.387(16)	1.386(16)	1.351(16)	1.364(16)	1.356(16)	1.383(16)
N(2)–C(3)	1.346(18)	1.342(18)	1.346(19)	1.351(19)	1.334(18)	1.334(19)
C(3)–C(2)	1.39(2)	1.38(2)	1.35(2)	1.32(3)	1.36(2)	1.38(2)
C(3)–C(5)	1.46(2)	1.50(2)	1.48(2)	1.50(3)	1.48(2)	1.52(2)
C(2)–C(1)	1.41(2)	1.40(2)	1.35(2)	1.40(2)	1.37(2)	1.36(2)
C(1)–N(1)	1.35(2)	1.35(2)	1.38(2)	1.35(2)	1.37(2)	1.33(2)
C(1)–C(4)	1.47(3)	1.50(2)	1.49(3)	1.48(3)	1.50(2)	1.52(2)
Mo(1)–I(1)		2.771(2)			2.778(2)	
Mo(1)–N(7)		1.744(16)			1.760(13)	
N(7)–O(1)		1.16(2)			1.160(18)	
Mo(1)–N(8)		1.954(23)			1.964(13)	
N(8)–C(16)		1.40			1.41(2)	
C(16)–C(17)		1.50			1.50(3)	
(*b*) Bond angles (°)						
Mo(1)–N(1)–N(2)	117.7(8)	119.5(8)	119.0(9)	117.2(8)	121.3(8)	117.7(8)
Mo(1)–N(1)–C(1)	136.8(11)	132.4(10)	135.7(10)	136.6(10)	132.6(10)	136.1(10)
N(2)–N(1)–C(1)	105.3(12)	108.2(11)	105.0(11)	106.1(12)	106.1(11)	106.1(11)
N(1)–N(2)–C(3)	110.6(11)	108.3(11)	112.4(12)	109.5(12)	109.5(11)	108.7(11)
B(1)–N(2)–C(3)	127.3(12)	130.1(12)	127.2(12)	128.3(13)	129.8(12)	130.0(12)
N(1)–N(2)–B(1)	121.3(11)	121.7(11)	120.3(11)	122.2(12)	120.7(11)	120.4(11)
N(1)–C(1)–C(2)	111.0(14)	108.7(13)	107.6(14)	108.1(14)	108.9(13)	111.1(13)
N(1)–C(1)–C(4)	121.9(15)	122.0(14)	123.2(14)	122.9(15)	122.0(14)	123.3(14)
C(2)–C(1)–C(4)	127.1(16)	129.3(15)	129.2(15)	128.9(16)	129.1(15)	125.6(14)
C(1)–C(2)–C(3)	104.7(14)	106.5(14)	110.2(15)	107.4(16)	106.5(14)	105.3(14)
C(2)–C(3)–C(5)	126.3(15)	127.7(14)	131.0(15)	128.7(17)	129.0(14)	129.1(14)
N(2)–C(3)–C(5)	125.3(14)	123.8(13)	124.2(14)	122.5(16)	122.0(13)	122.1(14)
N(2)–C(3)–C(2)	108.4(13)	108.5(13)	104.8(14)	108.8(16)	109.0(13)	108.8(13)
Mo(1)–N(7)–O(1)		178.8(15)			177.2(12)	
Mo(1)–N(8)–C(16)		146.9(18)			136.2(12)	
N(8)–C(16)–C(17)		110.1			110.5(16)	

(*c*) Angles (°) around the boron

	Molecule 1	Molecule 2
N(2)–B(1)–N(4)	106.5(12)	107.4(13)
N(4)–B(1)–N(6)	106.7(12)	110.5(13)
N(6)–B(1)–N(2)	111.4(12)	107.7(13)

(*d*) Angles (°) around the molybdenum

N(1)–Mo(1)–N(8)	167.8(7)	N(9)–Mo(2)–N(15)	177.5(5)
N(3)–Mo(1)–I(1)	167.5(3)	N(11)–Mo(2)–I(2)	167.4(3)
N(5)–Mo(1)–N(7)	178.7(6)	N(13)–Mo(2)–N(16)	166.6(5)

(*e*) Solvent geometry

(i) Bond angles (°)

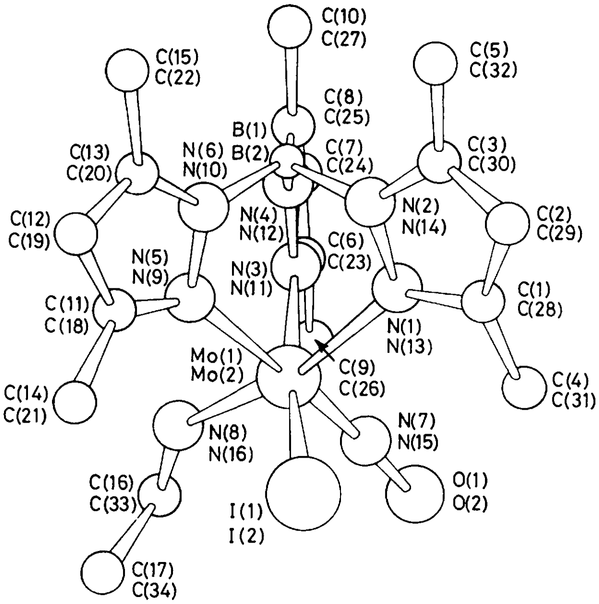
C(35)–O(3)–C(38)	115(3)
C(36)–C(35)–C(37)	110
C(39)–C(38)–C(40)	110

(ii) Bond lengths (Å)

O(3)–C(35)	1.38(6)	C(35)–C(37)	1.54
O(3)–C(38)	1.43(5)	C(38)–C(39)	1.54
C(35)–C(36)	1.54	C(38)–C(40)	1.54

* No estimated standard deviations are quoted for atoms whose geometry was constrained during the refinement.

the ligands increases the ' electron count ' at the metal towards the optimal 18. A preferable description would be to say that such ligand interaction raises the energy of the single empty metal-based non-bonding orbital by increasing its antibonding character, thus further favouring the formation of a diamagnetic complex. The presence of three mutually *cis* unidentate ligands, each of which is capable in some way and to some extent of π bonding to the metal, gives rise to a significant *trans* influence on the bonds between the molybdenum and the pyrazolyl rings which can themselves engage in limited π acceptance. It is, therefore, not surprising that such molybdenum–nitrogen bonds exhibit a pattern of bond lengths reflecting the competition between π acceptance by the pyrazolyl ring and the π-bonding nature of the *trans* ligand. Thus the molybdenum–nitrogen(pyrazolyl) bond which is *trans* to the strongly π-accepting nitrosyl group shows the least π character and is generally the longest such bond, whereas those bonds *trans* to π-donating iodo- and ethylamido-ligands show more π character and are shorter. The molybdenum atom lies, to varying extents, out of the planes defined by the pyrazolyl rings, suggesting that there is some strain involved in the bonding of the tris(3,5-dimethylpyrazolyl)hydroborato-ligand, resulting in a distortion from the local C_{3v} symmetry. In addition, a trigonal expansion of one side of the octahedral co-ordination polyhedron [mean B · · · Mo–N(pyrazolyl) 50.2°] and a small trigonal compression of the three unidentate ligands results in a π-bonding energy-level diagram in which one formally non-bonding molybdenum orbital is higher in energy than the other two,[22] leading to spin pairing. This effect is enhanced by the π bonding mentioned above, since the N–C(ethyl) bonds approximately eclipse the nitrosyl groups when viewed down the molybdenum–nitrogen(amido) bonds.



Molecular structure of $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I(NHEt)]$. The atom labelling is for molecule 1 (upper labels) and for molecule 2 (lower labels)

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