Arylamido and Aryloxy Complexes of Nitrosyl[tris(3,5-dimethylpyrazolyl)-borato]molybdenum, Some Mixed Alkoxy/Aryloxy and Aryloxy/Mono-alkylamido Species, and the Structures of $[Mo\{HB(3,5-Me_2C_3N_2H)_3\}(NO)I(NHC_6H_4R$-*p*$)]$ (R = Me and OMe) †

Jon A. McCleverty,* Gianfranco Denti, and Sarah J. Reynolds
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT
A. Stephen Drane, Nabil El Murr, A. Elizabeth Rae, Neil A. Bailey,* Harry Adams, and John M. A. Smith
Department of Chemistry, The University, Sheffield S3 7HF

The complexes $[Mo\{HB(Me_2pz)_3\}(NO)I(NHR)]$ [Me_2pz = 3,5-dimethylpyrazolyl; R = Ph, $C_{10}H_7$(2-naphthyl), C_6H_4X-*p* where X = Me, Et, OMe, OEt, F, Cl, Br, I, CO_2Me, NO_2, or CN], $[Mo\{HB(Me_2pz)_3\}(NO)I(OR)]$ (R = Ph, C_6H_4Me-*p*, and C_6H_4CN-*p*) and $[Mo\{HB(Me_2pz)_3\}XY]$ (X = Y = OPh; X = OPh, Y = OMe, OEt, or NHMe) have been prepared and characterised spectroscopically. The crystal and molecular structures of $[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4R$-*p*$)]$ (R = Me and OMe) have been determined crystallographically.

In previous papers we have described [1-4] the formation of mono- and di-alkoxy complexes, and mono-alkylamido-species of the type $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (1) (Me_2pz = 3,5-dimethylpyrazolyl; X = I, Y = OR or NHR, R = alkyl; X = Y = OR). In a continuation of this work, we now report the preparation and full characterisation of a series of mono-arylamido-complexes (1; X = I, Y = NHR″) (R″ = aryl) and the structures of (1; X = I, Y = NHC_6H_4R-*p*, R = Me and OMe). We also describe a series of isoelectronic aryloxy species, (1; X = I, Y = OR″). We have earlier described the mixed alkoxy-amido-complexes (1; X = OR, Y = NHR″) and unsymmetrical bis-alkoxides (1; X = OR, Y = OR′) have also been synthesised [5] and in order to complete this series of compounds, we have attempted to make mixed alkoxy-aryloxy, alkoxy-arylamido, and aryloxy-alkylamido-complexes.

There are relatively few examples of mono-arylamido-complexes of transition metals, the best characterised being $[Pt(NHR'')(PR_3)_2X]$ (R″ = Ph, $C_6H_4NO_2$-*p*, or $C_6H_4CO_2Me$-*p*; R = Et or Ph; X = Cl, NCO, N_3, or CN),[6] and $[Re(NHPh)(N_2)(PMe_3)_4]$.[7] Other species include $[Cu(NHPh)(PPh_3)_2]$,[8] $[Fe_2(CO)_6(\mu\text{-}NHPh)_2]$,[9] and a series of molybdenum complexes $[MoCl_{4-n}(dmf)(NPh)(NHPh)_n]^-$ (n = 0—3; dmf = dimethylformamide) and $[Mo(NPh)(NHPh)_5]^{2-}$.[10] Phenolato-complexes are much more common than their anilido-analogues, although there are relatively few simple aryloxy complexes of molybdenum. Most complexes of this type are derived from catecholato- or salicylaldehydato-ligands.

Experimental

All reactions were carried out under dry nitrogen, and all solvents were degassed immediately prior to use. Aniline, and *p*-ethyl-, *p*-ethoxy-, and *p*-fluoro-aniline were redistilled prior to use, and $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ was prepared as described previously.[1] Otherwise, all reagents were commercial grades and were used without further purification.

Table 1. Yields and colours for the complexes $[Mo\{HB(Me_2pz)_3\}(NO)I(NHR'')]$

R″	Yield (%)	Colour
C_6H_4Me-*p*	85	Black
C_6H_4Et-*p*	77	Black
C_6H_4OMe-*p*	79	Black
C_6H_4OEt-*p*	80	Black
$C_6H_4NO_2$-*p*	66	Brown
C_6H_4F-*p*	84	Brown
C_6H_4Cl-*p*	84	Brown
C_6H_4I-*p*	82	Brown
$C_6H_4CO_2Me$-*p*	69	Brown
$C_{10}H_7$ *	57	Red-brown

* 2-Naphthylamine was stirred in the reaction mixture overnight for complete reaction.

Molecular weights were determined osmometrically and i.r. spectra were measured using PE 457, 297, and 180 spectrophotometers. Hydrogen-1 and ^{13}C n.m.r. spectra were obtained using PE R34, JEOL PFT 90, and Bruker WH400 instruments. Microanalyses were performed by the Microanalytical Laboratory of the two Departments, and all yields are quoted relative to the metal-containing starting material. Data are in Tables 1—3.

Arylamido-complexes.—$[Mo\{HB(Me_2pz)_3\}(NO)I(NHPh)]$. $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (0.5 g) was dissolved in dichloromethane and aniline (0.2 cm^3) added. The solution was stirred at room temperature for 3 h, after which time it had changed to a red-brown colour. The solvent volume was reduced to *ca.* 5 cm^3 and diethyl ether added to precipitate $[NH_3Ph]I$ formed during the reaction. This white powder was filtered off and the filtrate volume again reduced to incipient crystallisation. This was completed at −10 °C, giving a brown powder which was recrystallised from dichloromethane–pentane or ethanol, giving black crystals (yield 0.36 g, 76%).

The analogous compounds $[Mo\{HB(Me_2pz)_3\}(NO)I(NHR'')]$ were prepared by a procedure similar to the above by addition of a two-fold excess of the appropriate arylamine to $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$. Yields and colours are given in Table 1.

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† *p*-Tolylamido- and *p*-methoxyphenylamido-iodo(nitrosyl)[tris-(3,5-dimethylpyrazolyl)borato]molybdenum.

Supplementary data available (No. SUP 23421, 57 pp.): observed structure amplitudes, calculated structure factors, anisotropic thermal parameters, predicted hydrogen atom positional parameters, full bond length and angle data, full i.r. and ^1H n.m.r. data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Elemental analyses and molecular weight data for [$Mo\{HB(Me_2pz)_3\}(NO)XY$]

Complex		Analysis [a] (%)				
X	Y	C	H	N	I	*M* [a,b]
I	NHPh	39.15 (39.3)	4.2 (4.4)	17.3 (17.45)	20.1 (19.75)	640 (642)
I	NHC_6H_4Me-*p*	40.3 (40.25)	4.4 (4.6)	17.3 (17.1)	19.0 (19.35)	661 (656)
I	NHC_6H_4Et-*p*	41.3 (41.2)	4.75 (4.8)	16.6 (16.7)	19.3 (18.95)	662 (670)
I	NHC_6H_4OMe-*p*	39.25 (39.3)	4.55 (4.5)	16.95 (16.65)	19.05 (18.9)	670 (672)
I	NHC_6H_4OEt-*p*	40.1 (40.25)	4.7 (4.7)	16.35 (16.35)	18.5 (18.5)	675 (686)
I	$NHC_{10}H_7$	43.15 (43.4)	4.35 (4.4)	16.4 (16.2)	18.55 (18.35)	674 (692)
I	NHC_6H_4F-*p*	38.4 (38.2)	4.25 (4.1)	17.0 (16.95)	19.2 (19.25)	680 (660)
I	NHC_6H_4Cl-*p*	37.4 (37.3)	4.2 (4.0)	16.7 (16.55)	18.6 (18.75)	695 (676)
I	NHC_6H_4Br-*p*	35.3 (34.95)	3.4 (3.75)	15.85 (15.55)	17.2 (17.6)	700 (721)
I	NHC_6H_4I-*p*	32.9 (32.8)	3.65 (3.5)	14.6 (14.6)	32.55 (33.05)	751 (768)
I	$NHC_6H_4CO_2Me$-*p*	39.1 (39.45)	4.1 (4.3)	15.9 (16.0)	18.4 (18.1)	718 (700)
I	$NHC_6H_4NO_2$-*p*	36.5 (36.7)	4.1 (3.95)	18.4 (18.35)	18.35 (18.45)	690 (687)
I	NHC_6H_4CN-*p*	39.95 (39.6)	4.45 (4.1)	19.2 (18.9)	19.3 (19.0)	683 (667)
I	NHC_6H_4CN-*p*	37.05 (37.75) [c]	3.85 (3.9)	16.8 (16.75)		
I	OPh	39.4 (39.2)	4.05 (4.25)	15.4 (15.25)	19.6 (19.75)	666 (643)
I	OC_6H_4Me-*p*	40.35 (40.2)	4.45 (4.4)	14.75 (14.9)	19.55 (19.3)	673 (657)
I	OC_6H_4CN-*p*	39.6 (39.55)	4.1 (3.9)	16.55 (16.75)		
OPh	OPh	52.95 (53.2)	5.6 (5.3)	15.85 (16.1)		629 (609)
OPh	OMe	48.65 (48.3)	5.7 (5.55)	18.4 (17.9)		
OPh	OEt	48.9 (49.2)	5.65 (5.75)	17.8 (17.45)		
OPh	NHMe	48.05 (48.4)	5.4 (5.7)	20.15 (20.5)		

[a] Calculated values in parentheses. [b] Carried out using a Mechrolab 310A vapour pressure osmometer, in $CHCl_3$. [c] Containing one molecule of CH_2Cl_2 of crystallisation.

[$Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4Br)$]. [$Mo\{HB(Me_2pz)_3\}(NO)I_2$] (0.5 g) was mixed in toluene with *p*-bromoaniline and stirred at room temperature for 3 h. The arylammonium salt produced was filtered off and, upon addition of hexane to the filtrate, a brown powder precipitated. This was recrystallised from CH_2Cl_2–hexane, giving dark brown microcrystals (yield 0.32 g, 61%).

[$Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4CN)$]. [$Mo\{HB(Me_2pz)_3\}(NO)I_2$] (0.3 g) was dissolved in dichloromethane and *p*-aminobenzonitrile (0.15 g) was added. The mixture was stirred at room temperature overnight, after which time it had turned a brown colour. The solvent was reduced to *ca.* 5 cm^3 and diethyl ether added. The white precipitate was filtered off and the filtrate again reduced in volume to *ca.* 5 cm^3. Hexane was slowly added giving a thick black oil. This was left to stand under hexane for 3 days, then filtered giving a black solid (yield 0.13 g, 45%). Alternatively, after filtration, the solution was evaporated to dryness and the brown powder so obtained redissolved in dichloromethane and chromatographed (alumina, CH_2Cl_2 as eluant). The first dark fraction was discarded and the second brown-red fraction collected, treated with n-hexane, and partially evaporated *in vacuo*. The complex was obtained, as a mono-dichloromethane solvate, as black crystals.

Aryloxy Compounds.—[$Mo\{HB(Me_2pz)_3\}(NO)I(OPh)$]. [$Mo\{HB(Me_2pz)_3\}(NO)I_2$] (0.5 g) was mixed in toluene with phenol (0.07 g) and refluxed for 3 h, forming a red-brown solution. This was reduced to *ca.* 10 cm^3 in volume and hexane (*ca.* 20 cm^3) added. The mixture was then left at −10 °C until a brown powder was precipitated, which was recrystallised from ethanol to give dark brown microcrystals (yield 0.31 g, 65%).

[$Mo\{HB(Me_2pz)_3\}(NO)I(OC_6H_4Me)$] was prepared similarly using *p*-cresol in place of phenol. Dark brown microcrystals were obtained (yield 0.33 g, 67%).

[$Mo\{HB(Me_2pz)_3\}(NO)I(OC_6H_4CN)$]. To a solution of [$Mo\{HB(Me_2pz)_3\}(NO)I_2$] (0.27 g) in tetrahydrofuran (thf) (20 cm^3), *p*-hydroxybenzonitrile (0.48 g) dissolved in thf (25 cm^3) was added. The mixture was stirred at room temperature for 20 h, when the dark solution was evaporated *in vacuo*. The residue was dissolved in dichloromethane, filtered, and treated with n-hexane. After partial evaporation of the solvent mixture, the crude product was collected by filtration, purified by chromatography (alumina, CH_2Cl_2 eluant), the first brown-red fraction being collected and evaporated slowly to give black crystals of the complex (yield 0.17 g, 64%).

[$Mo\{HB(Me_2pz)_3\}(NO)(OPh)_2$]. Silver acetate (0.15 g) was added to [$Mo\{HB(Me_2pz)_3\}(NO)I_2$] (0.5 g) in dichloromethane (30 cm^3) and the mixture stirred for 2 h. Phenol (0.2 g) was added and the mixture refluxed overnight. The solvent was removed giving a brown powder which was recrystallised from hexane, producing brown microcrystals (yield 0.25 g, 55%).

[$Mo\{HB(Me_2pz)_3\}(NO)(OMe)(OPh)$]. [$Mo\{HB(Me_2pz)_3\}(NO)I(OMe)$] (0.3 g), dissolved in dichloromethane (20 cm^3), was treated with phenol (0.1 g) and silver acetate (0.1 g). The mixture was stirred overnight at room temperature, and a brown solution with a white suspension was produced. The mixture was filtered through Kieselguhr and the filtrate reduced in volume to *ca.* 5 cm^3, then the product was allowed to crystallise over several days, giving brown microcrystals (yield 0.19 g, 67%). The complex [$Mo\{HB(Me_2pz)_3\}(NO)(OEt)(OPh)$] was prepared similarly from [$Mo\{HB(Me_2pz)_3\}(NO)I(OEt)$] (yield 0.18 g, 65%).

[$Mo\{HB(Me_2pz)_3\}(NO)(OPh)(NHMe)$]. To [$Mo\{HB(Me_2pz)_3\}(NO)I(NHMe)$] (0.3 g) in dichloromethane (20 cm^3) was added phenol (0.1 g) and silver acetate (0.1 g). The mixture was stirred overnight at room temperature and developed a brown colour. After filtration through Kieselguhr, the filtrate was reduced in volume to *ca.* 5 cm^3, and the red product allowed to crystallise slowly over several days (yield 0.15 g, 53%).

Crystallographic Studies.—[$Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4Me)$]·$Et_2O$. This complex crystallises from diethyl ether as black needles; a crystal of dimensions 0.33 × 0.04 × 0.07 mm was used.

Table 3. Selected i.r. and ^{1}H n.m.r. spectral data for [Mo{HB(Me$_2$pz)$_3$}(NO)XY] [a]

Complex			I.r. data ν(NO)/cm^{-1}		^{1}H n.m.r. data		
	X	Y	KBr	CHCl$_3$	δ [b]/p.p.m.	*A* [c]	Assignment
(1)	I	NHPh	1 659	1 665	13.08	1	(s) N*H*Ph
					7.63	2	(d) *o*-H, NHC$_6$*H*$_5$, *J*(HH) 9.0 Hz
					7.33	1	(t) *p*-H, NHC$_6$*H*$_5$, *J*(HH) 9.0 Hz
					7.30	2	(t) *m*-H, NHC$_6$*H*$_5$, *J*(HH) 9.0 Hz
					5.91	1	(s) C$_3$N$_2$*H*Me$_2$
					5.82	1	(s)
					5.76	1	(s)
					2.67	3	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.43	6	(s)
					2.35	6	(s)
					1.94	3	(s)
(1)	I	NHC$_6$H$_4$Me-*p*	1 668	1 672	13.15	1	(s) N*H*C$_6$H$_4$Me
					7.37	4	(m) A$_2$B$_2$, NHC$_6$*H*$_4$Me, δ(A) 7.55, δ(B) 7.18, *J*(AB) 11.0 Hz
					5.92	1	(s) C$_3$N$_2$*H*Me$_2$
					5.86	1	(s)
					5.78	1	(s)
					2.69	3	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.44	6	(s)
					2.35	6	(s)
					1.98	3	(s)
					2.28	3	(s) NHC$_6$H$_4$C*H*$_3$
(1)	I	NHC$_6$H$_4$Et-*p*	1 656	1 662			
(1)	I	NHC$_6$H$_4$OMe-*p*	1 647	1 659			
(1)	I	NHC$_6$H$_4$OEt-*p*	1 654	1 657			
(1)	I	NHC$_{10}$H$_7$	1 654	1 666			
(1)	I	NHC$_6$H$_4$F-*p*	1 659	1 665	13.08	1	(s) N*H*C$_6$H$_4$F
					7.60	2	(quartet) NHC$_6$*H*$_4$F, protons *ortho* to F; *J*(HH) 9.5 Hz, *J*(HF) 5.5 Hz
					7.06	2	(t) NHC$_6$*H*$_4$F, protons *meta* to F; *J*(HH) 9.5 Hz, *J*(HF) 9.5 Hz
					5.92	1	(s) C$_3$N$_2$*H*Me$_2$
					5.86	1	(s)
					5.78	1	(s)
					2.68	3	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.45	6	(s)
					2.37	6	(s)
					1.97	3	(s)
(1)	I	NHC$_6$H$_4$Cl-*p*	1 661	1 668			
(1)	I	NHC$_6$H$_4$Cl-*p* [d]			11.14	1	(s) N*H*C$_6$H$_4$Cl
					7.44	4	(m) A$_2$B$_2$, NHC$_6$*H*$_4$Cl, δ(A) 7.56, δ(B) 7.33, *J*(AB) 8.8 Hz
					2.68	18	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.46		(s)
					2.45		(s)
					2.38		(s)
					2.36		(s)
					1.97		(s)
(1)	I	NHC$_6$H$_4$Br-*p*	1 660	1 666	12.94	1	(s) N*H*C$_6$H$_4$Br
					7.47	4	(s) NHC$_6$*H*$_4$Br
					5.93	1	(s) C$_3$N$_2$*H*Me$_2$
					5.85	1	(s)
					5.79	1	(s)
					2.67	3	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.44	6	(s)
					2.36	6	(s)
					1.96	3	(s)
(1)	I	NHC$_6$H$_4$Br-*p* [d]			11.21	1 [d]	(s) N*H*C$_6$H$_4$Br
					7.49	4	(s) NHC$_6$*H*$_4$Br
					5.93	1	(s) C$_3$N$_2$*H*Me$_2$
					5.86	1	(s)
					5.78	1	(s)
					2.68	18	(s) C$_3$N$_2$H(C*H*$_3$)$_2$
					2.46		(s)
					2.45		(s)
					2.38		(s)
					2.37		(s)
					2.36		(s)

Table 3 (*continued*)

Complex			I.r. data ν(NO)/cm^{-1}		^{1}H n.m.r. data		
	X	Y	KBr	CHCl$_3$	δ [b]/p.p.m.	*A* [c]	Assignment
(1)	I	NHC_6H_4I-*p*	1 657	1 668	12.89	1	(s) $N\mathit{H}C_6H_4I$
					7.52	4	(m) A_2B_2, δ(A) 7.67, δ(B) 7.37, *J*(AB) 9.0 Hz
					5.92	1	(s) $C_3N_2\mathit{H}Me_2$
					5.84	1	(s)
					5.78	1	(s)
					2.65	3	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.42	6	(s)
					2.35	6	(s)
					1.96	3	(s)
(1)	I	$NHC_6H_4CO_2Me$-*p*	1 646	1 672			
			1 698 [ν(CO)]				
(1)	I	$NHC_6H_4NO_2$-*p*	1 666	1 675			
			1 520 1 335 ν(NO$_2$)				
(1)	I	NHC_6H_4CN-*p*	1 666	1 668			
			2 224 [ν(CN)]				
(1)	I	OPh	1 673	1 682	7.3	5	(m) $OC_6\mathit{H}_5$
					5.90	1	(s) $C_3N_2\mathit{H}Me_2$
					5.93	2	(s)
					2.55	3	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.43	3	(s)
					2.38	3	(s)
					2.37	3	(s)
					2.29	3	(s)
					1.97	3	(s)
(1)	I	OC_6H_4Me-*p*	1 672	1 681	7.27	4	(m) A_2B_2, δ(A) 7.37, δ(B) 7.16, *J*(AB) 9.0 Hz, $OC_6\mathit{H}_4Me$
					5.89	1	(s) $C_3N_2\mathit{H}Me_2$
					5.82	2	(s)
					2.56	3	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.42	6	(s)
					2.32	6	(s)
					1.97	3	(s)
					2.29	3	(s) $OC_6H_4C\mathit{H}_3$
(1)	I	OC_6H_4CN-*p*	1 686,				
			2 220 [ν(CN)]				
(1)	OPh	OPh	1 656	1 662	7.30	4	(t) $OC_6\mathit{H}_5$, *meta* protons, *J*(HH) 7.0 Hz
					7.17	4	(d) $OC_6\mathit{H}_5$, *ortho* protons, *J*(HH) 7.0 Hz
					6.95	2	(t) $OC_6\mathit{H}_5$, *para* protons, *J*(HH) 7.0 Hz
					5.82	2	(s) $C_3N_2\mathit{H}Me_2$
					5.73	1	(s)
					2.38	3	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.35	6	(s)
					2.20	6	(s)
					2.10	3	(s)
(1)	OPh	OMe	1 656	1 652	7.48	2	(d) $OC_6\mathit{H}_5$, *ortho* protons, *J*(HH) 8.0 Hz
					7.32	2	(t) $OC_6\mathit{H}_5$, *meta* protons, *J*(HH) 8.0 Hz
					7.16	1	(t) $OC_6\mathit{H}_5$, *para* protons, *J*(HH) 8.0 Hz
					5.88	1	(s) $C_3N_2\mathit{H}Me_2$
					5.86	1	(s)
					5.82	1	(s)
					5.47	3	(s) $OC\mathit{H}_3$
					2.60	18	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.37		(s)
					2.35		(s)
					2.18		(s)
					2.15		(s)
(1)	OPh	OEt	1 655	1 661			
(1)	OPh	NHMe	1 650	1 657	12.12	1	(s) $N\mathit{H}Me$
					7.03	5	(m) $OC_6\mathit{H}_5$
					5.84	1	(s) $C_3N_2\mathit{H}Me_2$
					5.81	2	(s)
					4.68	3	(d) $NHC\mathit{H}_3$, *J*(HH) 7.0 Hz
					2.45	18	(s) $C_3N_2H(C\mathit{H}_3)_2$
					2.42		(s)
					2.33		(s)
					2.31		(s)
					2.18		(s)
					2.07		(s)

[a] Full data are in the Supplementary Publication. [b] Spectra determined using PE R34 spectrometer, 37 °C, in CDCl$_3$ unless otherwise stated. [c] Relative area (multiplicities in parentheses). [d] Spectra determined using Bruker WH400 spectrometer, in CDCl$_3$.

Table 4. Atomic positional parameters for $[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4Me)]\cdot Et_2O$ * with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	0.361 4(2)	0.169 54(8)	0.202 3(2)
Mo	0.267 9(2)	0.116 49(8)	−0.025 5(2)
O(1)	0.176 7(17)	0.049 4(6)	0.148 2(19)
N(1)	0.212 0(17)	0.074 6(7)	0.076 1(20)
N(2)	0.112 1(19)	0.151 6(7)	−0.084 7(20)
N(3)	0.451 2(17)	0.081 6(6)	−0.005 3(18)
N(4)	0.504 3(16)	0.085 9(6)	−0.114 1(17)
N(5)	0.340 1(18)	0.172 1(8)	−0.145 2(21)
N(6)	0.410 5(17)	0.158 0(7)	−0.232 4(20)
N(7)	0.237 5(18)	0.073 8(7)	−0.201 3(19)
N(8)	0.311 8(19)	0.077 3(7)	−0.287 1(18)
C(1)	0.002(2)	0.159 5(8)	−0.052(2)
C(2)	−0.027(2)	0.137 7(9)	0.058(3)
C(3)	−0.139(3)	0.145 7(10)	0.090(3)
C(4)	−0.225(2)	0.176 3(10)	0.015(2)
C(5)	−0.195(2)	0.197 5(11)	−0.094(3)
C(6)	−0.084(3)	0.190 6(10)	−0.125(3)
C(7)	−0.345(3)	0.185 3(11)	0.057(3)
C(8)	0.495(2)	0.047 9(11)	0.220(2)
C(9)	0.526(2)	0.057 2(9)	0.091(2)
C(10)	0.634(2)	0.048 1(8)	0.046(2)
C(11)	0.619(2)	0.064 7(7)	−0.078(2)
C(12)	0.706(3)	0.064 0(9)	−0.169(3)
C(13)	0.264(3)	0.250 3(10)	−0.082(3)
C(14)	0.328(2)	0.218 9(8)	−0.161(3)
C(15)	0.395(2)	0.233 9(8)	−0.253(3)
C(16)	0.452(2)	0.194 0(9)	−0.291(3)
C(17)	0.521(3)	0.191 0(11)	−0.394(3)
C(18)	0.047(2)	0.031 4(11)	−0.188(3)
C(19)	0.147(2)	0.042 3(9)	−0.256(3)
C(20)	0.166(3)	0.026 7(9)	−0.379(3)
C(21)	0.273(2)	0.050 1(10)	−0.395(2)
C(22)	0.334(3)	0.043 6(11)	−0.510(3)
B	0.434(3)	0.104 0(11)	−0.247(3)
O(3)	0.436(2)	0.361(1)	−0.042(2)
C(23)	0.357(3)	0.375(2)	0.040(4)
C(24)	0.236(3)	0.394(1)	−0.046(8)
C(25)	0.547(3)	0.344(2)	0.041(4)
C(26)	0.636(3)	0.328(1)	−0.044(8)

* Atoms O(3),C(23)—C(26) comprise the diethyl ether solvent molecule, the geometry of which was constrained during refinement; the estimated standard deviations for the positional parameters of these atoms were derived from the e.s.d.s of the group parameters which were used to refine the position of this solvent molecule.

Table 5. Atomic positional parameters for $[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4OMe)]\cdot Et_2O$ * with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	0.161 67(5)	0.260 09(7)	0.123 91(9)
Mo	0.169 50(5)	0.374 88(7)	−0.093 78(10)
O(1)	0.160 4(4)	0.528 6(6)	0.093 9(9)
O(2)	0.464 0(4)	0.563 7(7)	−0.109 6(11)
N(1)	0.164 3(5)	0.466 0(8)	0.016 9(10)
N(2)	0.261 2(4)	0.378 9(7)	−0.179 3(9)
N(3)	0.065 4(4)	0.366 8(7)	−0.046 5(9)
N(4)	0.041 9(4)	0.334 2(6)	−0.147 0(9)
N(5)	0.176 9(4)	0.254 4(7)	−0.231 4(8)
N(6)	0.134 5(4)	0.247 2(7)	−0.304 5(8)
N(7)	0.157 3(4)	0.449 1(6)	−0.264 0(9)
N(8)	0.122 8(4)	0.414 7(6)	−0.338 2(9)
C(1)	0.312 5(5)	0.421 7(8)	−0.156 7(12)
C(2)	0.309 3(6)	0.454 6(9)	−0.026 4(13)
C(3)	0.359 4(6)	0.500 0(10)	−0.007 8(14)
C(4)	0.413 1(6)	0.515 0(9)	−0.119 6(14)
C(5)	0.418 5(6)	0.482 7(9)	−0.247 7(14)
C(6)	0.368 6(6)	0.436 3(10)	−0.265 1(13)
C(7)	0.458 6(7)	0.610 6(10)	0.014 6(17)
C(8)	0.021 1(6)	0.422 5(10)	0.191 3(13)
C(9)	0.015 8(5)	0.383 6(8)	0.063 3(11)
C(10)	−0.039 7(6)	0.360 4(9)	0.037 1(13)
C(11)	−0.022 1(5)	0.330 7(8)	−0.095 4(13)
C(12)	−0.062 8(6)	0.295 4(10)	−0.173 6(15)
C(13)	0.265 4(7)	0.162 1(10)	−0.214 3(14)
C(14)	0.212 2(5)	0.180 9(8)	−0.267 0(11)
C(15)	0.192 8(5)	0.127 5(8)	−0.350 9(12)
C(16)	0.143 4(5)	0.174 2(9)	−0.375 2(12)
C(17)	0.103 8(7)	0.144 7(11)	−0.461 9(15)
C(18)	0.220 2(6)	0.588 9(9)	−0.261 2(15)
C(19)	0.178 7(5)	0.530 8(8)	−0.315 7(12)
C(20)	0.157 1(6)	0.548 6(9)	−0.424 1(12)
C(21)	0.122 3(5)	0.474 7(9)	−0.437 7(12)
C(22)	0.089 5(7)	0.456 2(10)	−0.540 9(13)
B	0.087 1(7)	0.325 8(10)	−0.295 9(14)
O(3)	0.362 4(6)	0.316 6(10)	0.432 9(13)
C(23)	0.429 8(10)	0.305 6(18)	0.355(2)
C(24)	0.460 9(11)	0.271 9(22)	0.448(3)
C(25)	0.330 5(10)	0.346 2(16)	0.334(2)
C(26)	0.265 1(9)	0.349 8(14)	0.410(2)

* Atoms O(3),C(23)—C(26) comprise the diethyl ether solvent molecule.

Crystal data. $C_{26}H_{40}BIMoN_8O_2$, $M = 762.3$, Monoclinic, $a = 11.218(3)$, $b = 28.215(8)$, $c = 10.316(3)$ Å, $\beta = 102.66(2)°$, $U = 3\ 185.8(16)$ Å^3, $D_m = 1.58$, $Z = 4$, $D_c = 1.590$ g cm^{-3}, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14, C_{2h}^5), Mo-K_α radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 13.95 cm^{-1}, $F(000) = 1\ 472$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method, 1 783 independent reflections for which $I/\sigma(I) > 3.0$ being corrected for Lorentz, polarisation, and absorption effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. All hydrogen atoms, except for that of the amido-nitrogen atom, were detected on electron-density difference syntheses and were placed in calculated positions [C–H 0.96, B–H 1.12 Å, C–C–H(methyl) 111°]; their contributions were included in structure factor calculations ($B = 8.0$ Å^2) but no refinement of positional parameters was permitted. The geometry of the diethyl ether molecule of solvation was constrained during the final cycles of refinement which converged at *R* 0.0749 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of iodine and molybdenum. Table 4 lists the atomic positional parameters with estimated standard deviations.

$[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4OMe)]\cdot Et_2O$. This complex crystallises from diethyl ether as black elongated crystals; a crystal of dimensions 0.14 × 0.27 × 0.54 mm was used.

Crystal data. $C_{26}H_{40}BIMoN_8O_3$, $M = 746.3$, Monoclinic, $a = 22.33(6)$, $b = 14.90(4)$, $c = 10.33(7)$ Å, $\beta = 70.79(13)°$, $U = 3\ 245(23)$ Å^3, $D_m = 1.47$, $Z = 4$, $D_c = 1.53$ g cm^{-3}, space group $P2_1/a$ (non-standard setting of $P2_1/c$, no. 14, C_{2h}^5), Mo-K_α radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 13.7 cm^{-1}, $F(000) = 1\ 504$.

The data were collected ($6.5 < 2\theta < 50°$) and processed (3 081 independent reflections) and the structure solved and refined (*R* 0.0539) as for the *p*-toluidine complex above; no geometric constraints were applied to the diethyl ether solvent molecule. The hydrogen atom of the amido-group was detected and its contribution included in structure factor calculations in its calculated position (N–H 0.94 Å). Table 5 lists atomic positions and estimated standard deviations.

Scattering factors were taken from ref. 11; unit weights were used throughout the refinement. Computer programs formed part of the Sheffield *X*-ray system.

Results and Discussion

Synthetic Studies.—Arylamido-species. In general, the preparation of the mono-arylamido-species (1; X = I, Y = NHR″) (R″ = aryl) involved the addition of a two-fold excess of the appropriate amine to (1; X = Y = I) in dichloromethane at room temperature. The excess of amine is desirable since it facilitates removal of HI produced during the reaction (i).

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

This procedure is identical to that followed for the analogous mono-alkylamido-species,[4] and works well for all complexes except that containing NHC_6H_4Br. For the synthesis of the bromoanilide, dichloromethane was replaced by toluene since $[NH_3C_6H_4Br]I$ is insoluble in this solvent. Analytical and molecular weight data are summarised in Table 2.

We were unable to prepare derivatives containing NRR″ (R = alkyl, R″ = aryl) or NR''_2, presumably because of steric hindrance. It may be recalled that (1; X = I, Y = NMe_2)[4] is very unstable, and we were unable to isolate analogues containing more bulky dialkylamido-substituents. We attributed this to unfavourable steric interactions between NR_2 and the methyl groups of the $HB(Me_2pz)_3^-$ ligand, which was confirmed using molecular models based on a series of crystal structure determinations of related complexes. We were also unable to make bis-arylamido-complexes (1; X = Y = NHR″) under the conditions whereby the bis-alkoxide and mixed amido–alkoxide complexes described earlier can be made. In view of our ability to make bis-aryloxy complexes (1; X = Y = OR″), we find this failure surprising.

The Mo–N bond in (1; X = I, Y = NHR″) is readily cleaved by HCl, giving (1; Y = I, Y = Cl) and $[NH_3R'']Cl$. Treatment of (1; X = I, Y = NHR″) with refluxing alcohols afforded (1; X = Y = OR), and not (1; X = OR, Y = NHR″), but there was no reaction between the mono-arylamido-species and primary alkylamines.

Aryloxy species. The alkoxides (1; X = I, Y = OR; R = alkyl) were readily obtained [1,3,5] by refluxing (1; X = Y = I) in the appropriate alcohol. The corresponding aryloxides, (1; X = I, Y = OPh, OC_6H_4Me-*p*, or OC_6H_4CN-*p*) were similarly produced by refluxing (1; X = Y = I) with HY in toluene. If (1; X = Y = I) was treated by AgO_2CMe in dichloromethane and phenol was added, after a short time the bis-phenoxide (1; X = Y = OPh) could be obtained. The mono-aryloxides are red-brown in solution where (1; X = Y = OPh) is yellow-brown, these colours contrasting with the corresponding alkoxides which are green (mono) and pink (bis).

Treatment of (1; X = I, Y = OMe or OEt) with AgO_2CMe and phenol afforded the brown mixed alkoxy–aryloxy species (1; X = OPh, Y = OMe or OEt). Similarly, reaction of (1; X = I, Y = NHMe) with AgO_2CMe and phenol gave the red aryloxy–mono-alkylamido-complex (1; X = OPh, Y = NHMe). Attempts to prepare mixed-ligand species by reaction either of (1; X = I, Y = OR, R = alkyl) with aniline or of (1; X = I, Y = OPh) with alcohols were unsuccessful, the products being (1; X = I, Y = NHPh) and (1; X = I, Y = OR), respectively.

Spectral Studies.—The i.r. spectra of the arylamido-complexes showed, in addition to the bands associated with the $HB(Me_2pz)_3^-$ ligand, a nitrosyl group absorption at 1 666 ± 10 cm^{-1} (Table 3). There is apparently no significant dependence of ν(NO) on the aryl group substituent. It is difficult to make meaningful comparisons between ν(NO) in these new complexes and that in the corresponding mono-alkylamido-species (1; X = I, Y = NHR),[4] but the value of ν(NO) in the former would seem to be generally slightly higher than in the latter. This is consistent with the lower basicity of the aryl relative to the alkyl amines, and with the reduction in $p_\pi \longrightarrow d_\pi$ bonding between N and Mo in (1; X = I, Y = NHR″) when compared with (1; X = I, Y = NHR, R = alkyl). The new complexes also exhibit a single ν(NH) in the region between 3 200 and 3 300 cm^{-1}, as well as characteristic group frequencies associated with the aromatic ring substituents.

The aryloxy complexes showed ν(NO) at *ca.* 1 680 (1; X = I, Y = OR″) and 1 662 cm^{-1} (1; X = Y = OPh) in solution. These values are higher than those in the related alkoxides,[1,3,5] which is to be expected because of the reduced donor capacity of the aryloxides relative to the alkoxides. Furthermore, ν(NO) in these species is higher than that in the comparable arylamido-species, presumably because OR″ is a poorer donor than NHR″. The NO stretching frequency of the mixed species (1; X = OPh, Y = OMe, OEt, or NHMe) occurs between 1 652 and 1 661 cm^{-1}, close to that of (1; X = Y = OPh) but higher than those in (1; X = OR, Y = OR′) and (1; X = OR, Y = NHR′).[5]

The ^1H n.m.r. spectra of the new complexes are summarised in Table 3. All complexes exhibit resonances in the region around δ 2.5 p.p.m. due to the methyl groups of the $HB(Me_2pz)_3^-$ ligand. Signals due to the proton attached to C^4 of the pyrazolyl group occur between δ 5.0 and 6.0 p.p.m., and when X ≠ Y in $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ they usually occur as three singlets because of the absence of a plane of symmetry in these six-co-ordinate species. Occasionally, as in (1; X = I, Y = OPh or OC_6H_4Me-*p*) and (1; X = OPh, Y = NHMe), there are only two C^4 proton resonances, of relative intensity 1 : 2, and we presume that there is accidental overlap of two of the three expected signals, a phenomenon we have noted earlier. In (1; X = Y = OPh), only two C^4 proton signals were expected and were indeed observed.

The NH protons in (1; X = I, Y = NHR″) and (1; X = OPh, Y = NHMe) generally appeared as sharp singlet in the range δ 11.14—13.15 p.p.m. These signals do not disappear when solutions of the complexes are shaken with D_2O, as was similarly observed when the related mono-alkylamido-complexes were so treated.[4] The chemical shifts of the protons attached to the α-C atoms of the alkyl groups in (1; X = OPh, Y = OMe, OEt, and NHMe) resonate at fields significantly lower than normal. We have observed and commented on this effect before [1,4,5] and reiterate that it is due to the strongly electronegative $Mo\{HB(Me_2pz)_3\}(NO)I$ group.

The number and form of the signals due to the aromatic groups in the arylamido and aryloxy species is as expected, with the exception of those in (1; X = I, Y = NHC_6H_4Br-*p* and NHC_6H_4CN-*p*). In the spectra of these compounds the four protons appear as a singlet, and we presume that this is due to accidental degeneracy. Otherwise, the spectra are unexceptional and substantiate our formulation of these complexes.

Crystallographic Studies.—The structures of the two complexes are illustrated in Figures 1 and 2 showing the atom labelling used in the corresponding Tables. Bond lengths and angles (with e.s.d.s) and details of planar fragments are given in Tables 6 and 7.

Both (1; X = I, Y = NHC_6H_4Me-*p*) and (1; X = I, Y = NHC_6H_4OMe-*p*) exhibit distorted octahedral co-ordination geometries around the molybdenum atom. As observed in related structures,[1,4,5] the three pyrazolyl rings in each molecule are essentially planar with generally small out-of-plane deviations of the substituent methyl groups and larger

Table 6. Bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses, for [Mo{HB($Me_2pz)_3$}(NO)I(NHC_6H_4Me)]·Et_2O [a] (A) and [Mo{HB($Me_2pz)_3$}(NO)I(NHC_6H_4OMe)]·Et_2O (B)

	A	B
Mo–N(3)	2.249(19)	2.215(9)
Mo–N(5)	2.255(22)	2.263(10)
Mo–N(7)	2.140(20)	2.169(9)
Mo–N(1)	1.78(2)	1.754(11)
N(1)–O(1)	1.16(3)	1.211(14)
Mo–I	2.790(3)	2.785(2)
Mo–N(2)	1.99(2)	1.945(10)
N(2)–C(1)	1.37(3)	1.396(15)
C(1)–C(2)	1.39(4)	1.413(18)
C(2)–C(3)	1.38(4)	1.373(19)
C(3)–C(4)	1.40(4)	1.382(19)
C(4)–C(5)	1.37(4)	1.376(19)
C(5)–C(6)	1.37(4)	1.372(20)
C(6)–C(1)	1.40(4)	1.395(18)
C(4)–C(7)	1.53(4)	
C(4)–O(2)		1.380(17)
O(2)–C(7)		1.431(19)
Solvent molecule		
O(3)–C(23)	1.42	1.46(3)
O(3)–C(25)	1.42	1.49(3)
C(23)–C(24)	1.54	1.44(4)
C(25)–C(26)	1.54	1.41(3)
Mo–N(3)–N(4)	115.7(13)	118.7(7)
Mo–N(5)–N(6)	118.8(15)	118.6(7)
Mo–N(7)–N(8)	120.7(15)	120.8(7)
Mo–N(3)–C(9)	135.0(16)	134.5(8)
Mo–N(5)–C(14)	135.8(18)	137.9(8)
Mo–N(7)–C(19)	132.6(17)	131.2(8)

	A	B
I–Mo–N(1)	88.7(7)	88.6(4)
I–Mo–N(2)	97.7(6)	99.4(3)
I–Mo–N(3)	89.4(5)	90.4(2)
I–Mo–N(5)	88.5(6)	89.6(3)
I–Mo–N(7)	167.4(6)	167.6(3)
N(1)–Mo–N(2)	96.5(9)	96.1(4)
N(1)–Mo–N(3)	95.0(8)	93.4(4)
N(1)–Mo–N(5)	177.1(9)	178.1(4)
N(1)–Mo–N(7)	96.5(9)	97.8(4)
N(2)–Mo–N(3)	166.6(8)	166.6(4)
N(2)–Mo–N(5)	83.2(8)	83.8(4)
N(2)–Mo–N(7)	93.1(8)	90.6(4)
N(3)–Mo–N(5)	85.6(7)	87.1(3)
N(3)–Mo–N(7)	78.8(7)	78.7(3)
N(5)–Mo–N(7)	86.4(8)	84.2(4)
Mo–N(1)–O(1)	175.8(19)	179.6(10)
Mo–N(2)–C(1)	141.7(17)	137.5(8)
N(2)–C(1)–C(2)	121(2)	122.1(11)
N(2)–C(1)–C(6)	121(2)	120.4(11)
C(2)–C(1)–C(6)	118(2)	117.5(11)
C(1)–C(2)–C(3)	120(3)	121.1(12)
C(2)–C(3)–C(4)	122(3)	119.0(13)
X–C(4)–C(3)	120(2)	122.2(12)
X–C(4)–C(5)	123(2)	116.2(12)
C(3)–C(4)–C(5)	117(3)	121.6(13)
C(4)–C(5)–C(6)	122(3)	119.0(13)
C(5)–C(6)–C(1)	121(3)	121.8(13)
C(4)–O(2)–C(7)		119.7(11)
Solvent molecule		
C(23)–O(3)–C(25)	108	107.2(16)
O(3)–C(23)–C(24)	110	107.9(20)
O(3)–C(25)–C(26)	110	106.0(18)

[a] In the structure of the *p*-toluidino-complex, the geometry of the diethyl ether solvent molecule was constrained during refinement, thus the bond lengths and angles are quoted without estimated standard deviations. [b] X represents atom C(7) in the *p*-toluidino-complex and atom O(2) in the *p*-anisidino-complex.

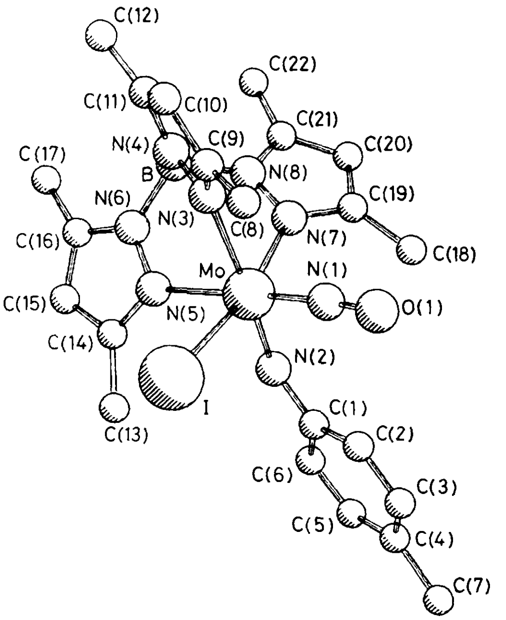


Figure 1. The molecular structure of [Mo{HB($Me_2pz)_3$}(NO)I(NHC_6H_4Me)] with full atom labelling

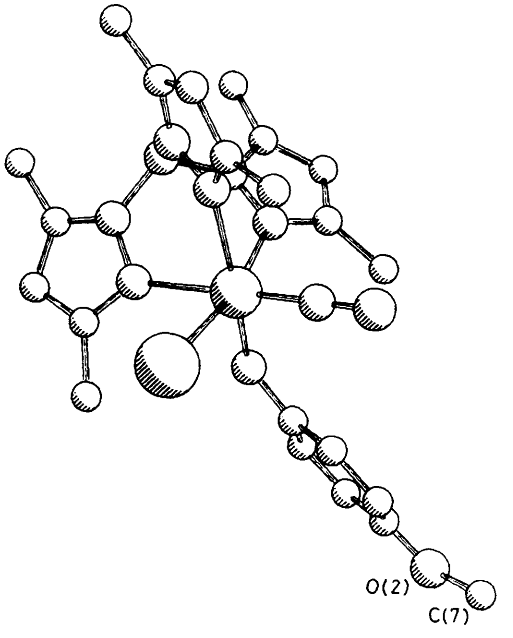


Figure 2. The molecular structure of [Mo{HB($Me_2pz)_3$}(NO)I(NHC_6H_4OMe)] showing only labelling different to that of Figure 1

Table 7. Details of planar fragments of the two arylamido-complexes. Equations of the planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to axes a, b, c^*; deviations (Å) of atoms from the mean planes are given in square brackets

(*a*) $[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4Me)]{\cdot}Et_2O$

Plane A: N(3), N(4), C(9)—C(11)
$-0.3248X - 0.8704Y - 0.3702Z = -3.6147$
[N(3) −0.018, N(4) 0.008, C(9) 0.020, C(10) −0.015, C(11) 0.004, Mo −0.146, B 0.219, C(8) −0.022, C(12) −0.025]

Plane B: N(5), N(6), C(14)—C(16)
$0.6535X + 0.1189Y + 0.7476Z = 2.1683$
[N(5) 0.024, N(6) −0.035, C(14) −0.005, C(15) −0.015, C(16) 0.031, Mo 0.032, B −0.132, C(13) 0.107, C(17) −0.091]

Plane C: N(7), N(8), C(19)—C(21)
$-0.4639X + 0.7579Y - 0.4588Z = 1.0580$
[N(7) 0.003, N(8) −0.004, C(19) −0.002, C(20) −0.000, C(21) 0.002, Mo 0.130, B −0.211, C(18) 0.041, C(22) −0.045]

Plane D: Mo, N(2), C(1)
$-0.2734X - 0.7816Y - 0.5607Z = -3.2621$
[C(2) 0.013, C(6) −0.053]

Plane E: C(1)—C(6)
$-0.2734X - 0.7672Y - 0.5802Z = -3.1985$
[C(1) 0.011, C(2) −0.006, C(3) 0.003, C(4) −0.005, C(5) 0.011, C(6) −0.014, Mo −0.012, N(2) 0.015, C(7) −0.054]

(*b*) $[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4OMe)]{\cdot}Et_2O$

Plane A: N(3), N(4), C(9)—C(11)
$0.1691X - 0.9322Y + 0.3201Z = -5.0261$
[N(3) 0.006, N(4) −0.002, C(9) −0.009, C(10) 0.008, C(11) −0.004, Mo 0.112, B −0.264, C(8) −0.055, C(12) 0.043]

Plane B: N(5), N(6), C(14)—C(16)
$0.4123X + 0.4719Y - 0.7794Z = 4.8633$
[N(5) −0.012, N(6) 0.001, C(14) 0.018, C(15) −0.016, C(16) 0.009, Mo −0.086, B 0.064, C(13) 0.048, C(17) −0.026]

Plane C: N(7), N(8), C(19)—C(21)
$-0.6556X + 0.4200Y + 0.6276Z = -0.5206$
[N(7) 0.001, N(8) 0.001, C(19) −0.002, C(20) 0.003, C(21) −0.002, Mo 0.021, B 0.132, C(18) −0.033, C(22) −0.040]

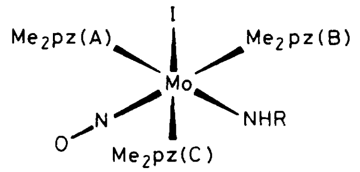
Plane D: Mo, N(2), C(1)
$0.2968X - 0.7664Y + 0.5697Z = -3.7735$
[C(2) 0.459, C(6) −0.507]

Plane E: C(1)—C(6)
$0.4717X - 0.8588Y + 0.2001Z = -2.6529$
[C(1) −0.009, C(2) −0.000, C(3) 0.011, C(4) −0.013, C(5) 0.002, C(6) 0.009, Mo −0.693, N(2) −0.083, O(2) −0.064, C(7) −0.279]

Selected angles (°) between planes

	(*a*)	(*b*)
A—B	126.3	128.3
A—C	109.8	107.5
B—C	123.8	124.1
A—D	12.4	18.7
D—E	1.4	24.2

deviations of the molybdenum and boron atoms. The considerable angular distortion (Table 7) from trigonal symmetry (about the Mo ··· B direction) can be correlated with the bulk of the adjacent unidentate ligands: the large angle between planes A and B results from the steric interaction between the 3-methyl substituents and the iodo-ligand, whereas planes A and C embrace the small nitrosyl ligand (see below).



The molybdenum–nitrosyl linkages are conventionally linear and the molybdenum–iodine bonds are slightly short, suggesting a small degree of π bonding. The molybdenum–nitrogen bonds to the arylamido-groups are much shorter than a single Mo–N bond but are significantly longer (even allowing for the difference is covalent radii) than the Mo–O bond in a comparable monoalkoxy complex,[1] somewhat longer than those in less comparable bis-alkoxy complexes,[5] and comparable to that in an alkylamido-complex.[4] There is clearly less potential for π donation by amido-ligands than by the isoelectronic alkoxy ligands, since there can be no in-plane (Mo–N–C) π-bond formation with amido-ligands as the site is occupied by a hydrogen atom,* whereas the alkoxy ligand carries an in-plane lone pair of electrons. Thus, π donation can only occur from the out-of-plane lone pair. The enlarged Mo–N–C bond angle in the amido-complexes must therefore result from steric rather than electronic factors. Additionally, arylamido-ligands have an alternative π-delocalisation option to the phenyl ring. This is particularly true for the *p*-toluidine complex where the phenyl ring is closely coplanar with the Mo–N–C plane, and the donor capacity of the nitrogen would be reduced and indeed the molybdenum–nitrogen bond is the longer. In the *p*-anisidine complex, where the aromatic ring is markedly twisted with respect to the Mo–N–C plane, the molybdenum–nitrogen bond length is comparable to those found in complexes of the ethylamido-ligand [4] where no such competitive delocalisation is possible.

As in previous structures of this type,[4,12] the N(1)–Mo(1)–N(2)–C(1) torsion angles are moderately small (*p*-toluidine complex +19.3°, *p*-anisidine complex +11.5°), thus avoiding steric overcrowding with adjacent bulky ligands and substituents. However, these angles are not as small as those found in comparable alkoxy complexes [5] where the eclipsing of alkyl and nitrosyl about the molybdenum–oxygen bond facilitates the in-plane π donation.

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* Although there is little conclusive crystallographic evidence for this hydrogen atom, n.m.r. and magnetic evidence for the formulation of this ligand as $NHC_6H_4R(1-)$ is overwhelming.

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