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ALKOXY, AMIDO AND THIOLATO COMPLEXES OF TRIS (3, 5-DIMETHYLPYRAZOLYL)BORATO(NITROSYL) MOLYBDENUM FLUORIDE, CHLORIDE AND BROMIDE

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Abstract—The complexes $Mo\{HB(Me_2pyz)_3\}(NO)XY$ $\{HB(Me_2pyz)_3 \equiv HB(3, 5\text{-}Me_2C_3HN_2)_3$; X=Y=F, Cl or Br; X=F, Y=OEt, NHMe or SBu^n; X=Cl, Y=NHR (R=Me Et, Bu^n, Ph, p-MeC_6H_4), NMe_2 and SR (R=Bu^n, C_6H_{11}, CH_2Ph, Ph); X=Br, Y=NHMe, NMe_2 and $SBu^n\}$ have been prepared and characterised spectroscopically. Their properties are generally similar to those of their iodo-analogues.

In a series of papers we have described the reactions of $Mo\{HB(Me_2pyz)_3\}(NO)I_2$, (1; X=Y=I) $[HB(Me_2pyz)_3 = HB(3, 5\text{-}Me_2C_3HN_2)_3 \equiv$ tris(3, 5-dimethylpyrazolyl)borate] with alcohols,[1,2] amines[3,4] and thiols,[5] affording alkoxy, amido and thiolato complexes of the type (1; X = I, Y=OR, NHR or SR). Our use of the diiodide precursor (1, X=Y=I) was dictated partly by its ease of preparation from (1, X=Y=CO),[1,6] and partly because the iodide ligand is bulky and therefore likely to be a good leaving group in potential substitution reactions. However, we felt that the preparation of the other halide derivatives should be attempted in order to explore the effects of the changes in electronegativity and ligand size in the properties of this unusual series of complexes.

SYNTHETIC STUDIES

In earlier attempts to prepare chloro- and bromo-complexes of the type (1; X=Y=CO) with chlorine and bromine we noted that partial halogenation of the pyrazolyl rings, especially at C-4, occurred very readily.[1] This caused great difficulties, and we were frequently unable to reproduce our results. Thus alternative routes to (1; X=Y=Cl and Br) were sought.

We have employed two methods for making the chloride and bromide precursors. Trofimenko had shown[7] that (1; X=Y=CO) reacted with NOCl to give (1; X=Y=Cl), and we found this the easiest and quickest way to prepare the chloride. The product so obtained was not usually very pure, but was entirely satisfactory for further reactions. The bromide was obtained similarly, using NOBr, and was isolated as a pure orange powder. The other method of synthesis involved reaction of (1; X=Y=OR; R usually Et) with HCl or HBr. The chloride was obtained as a yellow solid and this method is the best way of isolating the pure material. While the conversion of bis-alkoxide to dichloride is 70%, however, the overall yield from (1; X=Y=CO) is only 30%, requiring conversion of the dicarbonyl to (1; X=I; Y=OEt) and of this to (1, X=Y=OEt). The bromide obtained from HBr addition to (1; X=Y=OR) was not obtained sufficiently pure to justify exploration of this route, traces of water frequently interfering with the purification of the compound.

The difluoride, (1; X=Y=F) has not been previously described but was made by reaction of (1; X=Y=OEt) with aqueous HF. It was isolated as a virtually insoluble pale green solid (it is very slightly soluble in $CHCl_3$) which was substantially less stable towards air and moisture than its chloro-, bromo- and iodo-analogues.

The alkoxides (1; X=Cl, Br or I, Y=OR) have been previously described,[1] and are prepared by refluxing the appropriate dihalide in an alcohol. However, the fluoro ethoxide, (1, X=F, Y=OEt), despite the insolubility of the parent difluoride, is formed rapidly in ethanol without heating. The mono-amido species (1, X=F, Y=NHMe), (1; X=Cl, Y=NHMe, NHPh and NHC_6H_4Me-p) and (1; X=Br, Y=NHMe) were prepared in the same way as their iodo analogues,[3] namely by reaction of the dihalide with two mole equivalents of the amine in solution at room temperature. Similarly, the thiolato species (1, X=F, Y=SBu^n), 1, X=Cl, Y=SBu^n, SC_6H_{11}, SCH_2Ph and SPh) and (1, X=Br, Y=SBu^n) were obtained by refluxing the dihalide in hydrocarbon solvents containing the appropriate thiol.[5]

Of some interest was our ability to synthesise relatively stable dimethylamido complexes, (1; X=Cl or Br, Y=NMe_2). These compounds were obtained in the same way as their mono-alkylamido analogues, and are significantly more stable towards air, moisture and other hydroxylic solvents than the corresponding iodo complex (1; X=I, Y=NMe_2).[3] Indeed, the iodo species has been used as a convenient precursor for making alkoxides and monoalkylamides under mild conditions. We presume the lower chemical reactivity of the related chloro- and bromo-complexes is related to the relief of steric strain following the replacement of the iodide group by the less bulky Cl and Br.

Spectral studies

The IR spectra of the new complexes (Table 2) exhibit bands typical of the $HB(Me_2pyz)_3$ ligand, and a strong absorption due to ν(NO). The dichloride and dibromide exhibit ν(NO) at values very similar to those of the diiodide, whereas the frequency in the difluoride was lower. On electronegativity grounds alone, we would have expected an *increase* in ν(NO) in the difluoride if any change occurred. It is possible, however, that (1; X=Y=F) is di- or poly-meric, with Mo–F–Mo bridges, which would be consistent with its insolubility. The coordination sphere of the metal would then increase from 6 to 7 by virtue of F atom bridging, leading to more electron donation to Mo, and hence a lowering of ν(NO) relative to the other dihalides. There is very little evidence for a

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Table 1. Analytical and molecular weight data obtained from $[Mo\{HB(Me_2pyz)_3\}(NO)XY]$

Complex X	Complex Y	Elemental Analyses Found (Calcd)% C	H	N	Hal[b]	Mol wt.[a] Found(Calcd)
F	F	39.3(39.1)	4.9(4.8)	20.8(21.3)	8.2(8.3)	
Cl	Cl	36.6(36.5)	4.5(4.5)	19.4(19.9)	14.0(14.4)	524(494)
Br	Br	30.7(30.9)	3.9(3.8)	16.5(16.8)	27.0(27.4)	620(583)
F	OEt	42.4(41.9)	5.97(5.61)	19.8(20.1)	3.6(3.9)	
F	NHMe	40.4(40.7)	5.81(5.51)	23.9(23.7)	4.2(4.0)	
Cl	NHMe	39.5(39.3)	5.5(5.4)	23.3(22.9)	7.6(7.3)	
Cl	NHEt	40.3(40.6)	5.9(5.6)	22.0(22.3)	7.3(7.1)	521(503)
Cl	$NHBu^n$	43.4(43.0)	6.0(6.1)	21.3(21.1)	6.4(6.7)	
Cl	NHPh	46.0(45.8)	5.2(5.1)	20.4(20.4)	6.3(6.4)	
Cl	NHC_6H_4Me	46.4(46.8)	5.2(5.4)	19.7(19.8)	6.5(6.3)	540(565)
Cl	NMe_2	40.2(40.5)	5.6(5.8)	22.5(22.3)	7.1(7.0)	
Br	NHMe	36.4(36.1)	4.7(4.9)	21.2(21.0)	15.2(15.0)	562(533)
Br	NMe_2	37.0(37.3)	4.9(5.2)	20.2(20.5)	14.3(14.6)	
F	SBu^n [c]	42.7(43.0)	5.7(5.8)	18.1(18.5)	3.9(3.6)	
Cl	SBu^n [d]	41.4(41.7)	5.7(5.7)	17.6(17.9)	6.4(6.5)	575(548)
Cl	SPh [e]	44.7(44.4)	4.6(4.8)	17.5(17.3)	6.1(6.2)	591(568)
Cl	SC_6H_{11} [f]	43.6(44.0)	5.5(5.8)	16.8(17.1)	5.8(6.2)	
Cl	SCH_2Ph [g]	45.3(45.4)	5.3(5.0)	16.7(16.9)	5.8(6.1)	
Br	SBu^n [h]	38.8(38.5)	5.0(5.3)	16.8(16.6)	13.3(13.5)	

[a] Determined osmometrically in $CHCl_3$; [b] F, Cl or Br; [c] S: 5.8(6.1)%; [d] S: 6.0(5.9)%; [e] S: 5.84(5.7)%; [f] S: 5.2(5.6)%; [g] S: 5.6(5.5)%; [h] S: 5.0(5.4)%.

Table 2. IR and NMR spectral data from $Mo\{HB(Me_2pyz)_3\}(NO)XY$

X	Y	ν(NO)(cm^{-1}) KBr	$CHCl_3$	δ(RA)[a]		Assignments
F	F	1688	b	6.03(2)[c]	s	$C_3\underline{H}Me_2N_2$
				5.31(1)	s	
				2.56	s	
				2.41 (18)	s	$C_3H(C\underline{H}_3)_2N_2$
				2.30	s	
				2.28	s	
Cl	Cl	1702	1720	5.98(2)	s	$C_3\underline{H}Me_2N_2$
				5.80(1)	s	
				2.40(18)	s;	$C_3H(C\underline{H}_3)_2N_2$
Br	Br	1702	1720	6.00(2)	s	$C_3\underline{H}Me_2N_2$
				5.95(1)	s	
				2.60	s	
				2.51 (18)	s	$C_3H(C\underline{H}_3)_2N_2$
				2.46	s	
				2.41	s	
F	OEt	1666	b	b		
F	NHMe	1640	b	b		
F	SBu^n	1655	b	b		
Cl	NHMe	1643	1664	12.32(1)	s;	$N\underline{H}Me$
				5.83(1)	s	
				5.82(1)	s	$C_3\underline{H}Me_2N_2$
				5.80(1)	s	
				4.45(3)	d;	$NHC\underline{H}_3$, $^3J(HH)8.0Hz$
				2.58	s	
				2.44	s	
				2.38 (18)	s	$C_3H(C\underline{H}_3)_2N_2$
				2.36	s	
				2.33	s	
				2.31	s	

Table 2 (*Contd.*)

X	Y	$\nu(NO)(cm^{-1})$		$\delta(RA)^{\underline{a}}$		Assignments	
		KBr	$CHCl_3$				
Cl	NHEt	1649	1662	12.29(1)		s;	NHEt
				5.86(1)		s	$C_3\underline{H}Me_2N_2$
				5.82(1)		s	
				5.80(1)		s	
				4.89(2)		AB pair,	δ(A)5.21, δ(B)4.57; J(AB)5.0Hz, $^3J(HH)$8Hz; $NHC\underline{H_2}Me$
				2.58	(18)	s	$C_3H(C\underline{H_3})_2N_2$
				2.48		s	
				2.37		s	
				2.35		s	
				2.33		s	
				1.36(3)		t;	$NHCH_2C\underline{H_3}$ $^3J(HH)$7.0Hz.
Cl	NMe_2	1645	1672	$5.89(1)^{\underline{d}}$		s	$C_3\underline{H}Me_2N_2$.
				5.88(1)		s	
				5.83(1)		s	
				4.35(3)		s	$N(C\underline{H_3})_2$
				3.26(3)		s	
				ca.2.4(18)		m;	$C_3H(C\underline{H_3})_2N_2$
Cl	NHPh	1654	1664	12.63(1)		s;	NHPh
				ca.7.25(5)		m;	$NHC_6\underline{H_5}$
				5.87(1)		s	$C_3\underline{H}Me_2N_2$
				5.85(1)		s	
				5.78(1)		s	
				2.68	(18)	s	$C_3H(C\underline{H_3})_2N_2$
				2.40		s	
				2.34		s	
				2.33		s	
				1.98		s	
Cl	NHC_6H_4Me	1653	1662	12.72(1)		s;	$\underline{NH}C_6H_4Me$
				7.30(4)		A_2B_2 mult;	δ(A)7.39, δ(B)7.21, J(AB)8.0Hz; $NHC_6\underline{H_4}Me$
				5.89(1)		s	$C_3\underline{H}Me_2N_2$
				5.87(1)		s	
				5.79(1)		s	
				2.67(3)		s	$C_3H(C\underline{H_3})_2N_2$
				2.38(12)		s	
				2.01(3)		s	
				2.36(3)		s;	$NHC_6H_4C\underline{H_3}$
Br	NHMe	1654	1667	12.57(1)		s;	$N\underline{H}Me$
				5.88(1)		s	$C_3\underline{H}Me_2N_2$
				5.83(2)		s	
				4.32(3)		d;	$NH(C\underline{H_3})$ $^3J(HH)$8.0Hz
				2.61	(18)	s	$C_3H(C\underline{H_3})_2N_2$
				2.50		s	
				2.40		s	
				2.37		s	
				2.36		s	
				2.35		s	
Br	NMe_2	1650	1659	5.92(1)		s	$C_3\underline{H}Me_2N_2$
				5.86(1)		s	
				5.80(1)		s	
				4.32(3)		s	$N(C\underline{H_3})_2$
				3.22(3)		s	
				ca.2.4(18)		m;	$C_3H(C\underline{H_3})_2N_2$
Cl	SBu^n	1662	1680	5.91(1)		s	$C_3\underline{H}(CH_3)_2N_2$
				5.80(2)		s	
				5.18(2)		m;	$SC\underline{H_2}Pr^n$, $^3J(HH)$7.0Hz
				2.54(3)		s	$C_3H(C\underline{H_3})_2N_2$
				2.45(3)		s	
				2.42(3)		s	
				2.33(6)		s	
				2.22(3)		s	
				2.06(2)		quint;	$SCH_2C\underline{H_2}Et$, $^3J(HH)$7.0Hz
				1.57(2)		sext;	$SCH_2CH_2C\underline{H_2}Me$, $^3J(HH)$7.0Hz
				1.01(3)		t;	$S(CH_2)_3C\underline{H_3}$ $^3J(HH)$8.0Hz.
Cl	SC_6H_{11}	1671	1678	5.90(1)		s	$C_3\underline{H}Me_2N_2$
				5.80(2)		s	
				2.55	(18)	s	$C_3H(C\underline{H_3})_2N_2$
				2.46		s	
				2.42		s	
				2.33		s	
				2.22		s	
				1.75	(10)	m;	SC_6H_{11}; $SC\underline{H}(CH_2)_5$ not observed

Table 2 (*Contd.*)

X	Y	ν(NO)(cm^{-1}) KBr	CHCl$_3$	δ(RA)[a]		Assignments
Cl	SCH$_2$Ph	1671	1684	ca.7.4(5)		m; $SCH_2\underline{C_6H_5}$
				6.32(2)		AB pair, δ(A)6.48, δ(B)6.15, J(AB)13.2Hz; SCH$_2$Ph
				5.90(1)		s
				5.86(1)		s $C_3\underline{H}Me_2N_2$
				5.84(1)		s
				2.50		s
				2.45		s
				2.42	(18)	s $C_3H(C\underline{H}_3)_2N_2$
				2.37		s
				2.30		s
Cl	SPh	1684	1691	7.89(2)		d; o-H, $SC_6\underline{H}_5$, ^3J(HH)7.0Hz
				7.55(2)		t; m-H, $SC_6\underline{H}_5$, ^3J(HH)7.0Hz
				7.37(1)		t; p-H, $SC_6\underline{H}_5$, ^3J(HH)7.0Hz
				5.92(1)		s
				5.83(1)		s $C_3\underline{H}Me_2N_2$
				5.78(1)		s
				2.53		s
				2.50		s
				2.45	(18)	s $C_3H(C\underline{H}_3)_2N_2$
				2.36		s
				2.02		s
Br	SBu^n	1665	1682	5.96(1)		s
				5.82(1)		s $C_3\underline{H}Me_2N_2$
				5.80(1)		s
				5.07(2)		m; SCH$_2$Pr^n; ^3J(HH)7.0Hz
				2.60(3)		s
				2.47(6)		s $C_3H(C\underline{H}_3)_2N_2$
				2.36(6)		s
				2.20(3)		s
				2.15(2)		quint; $SCH_2C\underline{H}_2Et$; ^3J(HH)8.0Hz
				1.57(2)		sext; $SCH_2CH_2C\underline{H}_2Me$; ^3J(HH)8.0Hz
				1.03(3)		t; $S(CH_2)_3C\underline{H}_3$ ^3J(HH)8.0Hz

[a] Recorded in CDCl$_3$ at 220 MHz, 37° using SiMe$_4$ as internal standard (rel. area);
[b] not recorded because of insolubility;
[c] Recorded in CDCl$_3$ at 400 MHz (Brucker FT instrument);
[d] Recorded in CD$_2$Cl$_2$ at 220 MHz.

halide or N- or S- ligand substituent effect on ν(NO) of the other monohalide complexes. In general ν(*NO*) in the amido and thiolato species averages 1664 and 1683 cm^{-1}, which is consistent with our observations elsewhere.[5]

The ^{1}H NMR spectra (Table 2) of the new complexes are generally unremarkable, and are consistent with the formulation of the new species. A group of signals in the region δ 2.7–1.9 is associated with the methyl groups of the pyrazolyl ring. The shape of these signals varies from compound to compound but in one complex (**1**; X=Y=Cl) it appears as a singlet. We have no explanation for this effect, but it is very useful for characterisation purposes. The group of signals occurring in the region δ 6.1–5.3 is due to the protons attached to C-4. In those complexes of the type (**1**; X=Y), the signals appear as a doublet of relative intensity 2:1. In the species where X ≠ Y, we would expect three singlets, since there is no plane of symmetry in the complexes, and this is usually observed. In two cases viz. (**1**; X=Cl, Y=SBu^n or SC$_6$H$_{11}$) only two resonances, of relative intensity 1:2, are observed and we assume this is due to accidental degeneracy; this effect has been noted before. In these complexes, as in all others reported previously, protons attached to the C atom α to the donor atom at Mo resonate at lower fields than expected, and we reiterate that this is probably due to the strong electron-withdrawing properties of the metal. The NH signals in the mono-alkyl and aryl-amides also resonate at low fields (δ 12.7–12.3) for the same reason. The signals due to the dimethylamido group in (**1**; X=Cl or Br, Y=NMe$_2$) appear as two singlets, because of the asymmetry of the complexes, and the lack of facile inversion at the amido N atom in these complexes.

Conclusion

The properties of the new complexes are generally very similar to those of their iodo-analogues. We have noted in a qualitative way that the apparent rates at which the monosubstituted fluoro-, chloro- and bromo-complexes were generally faster than those of the related iodo-complexes. While we believe that the mechanism of formation of the species (**1**; X=I, Y=OR, Y=OR, NHR or SR) from (**1**; X=Y=I)[8] involves prior one-electron transfer, we are not yet in a position to determine whether this occurs with the other dihalides. This possibility is being studied.

EXPERIMENTAL

The complex Mo{HB(Me$_2$pyz)$_3$}(NO)(CO)$_2$ was prepared as described elsewhere.[1,6] All reactions were carried out under nitrogen and in N$_2$-degassed solvents. All yields are quoted relative to the molybdenum-containing precursor. IR and ^{1}H NMR spectral data were obtained using PE 297 and PE 180 spectrophotometers, and PE R34 instruments, respectively. Molecular weights were determined osmometrically in chloroform.

Mo{HB(Me$_2$pyz)$_3$}(NO)Cl$_2$ (**1**; X=Y=Cl)—*Method* 1. Nitrosyl chloride was generated *in situ*, and was bubbled through a dichloromethane solution of Mo{HB(Me$_2$pyz)$_3$}(NO)(CO)$_2$. The yellow-brown solution which formed was then evaporated to dryness *in vacuo*, and ethanol added in the cold. The slurry which formed was filtered, the *complex* being collected as a yellow powder. This could be recrystallised from toluene to give orange-red crystals (containing variable amounts of toluene of crystallisation) which, after repeated washing with n-pentane, changed to a yellow powder.

Method 2. Mo{HB(Me$_2$pyz)$_3$}(NO)(OEt)$_2$ was prepared as previously described, and dissolved in toluene. HCl gas was then bubbled through the stirred solution for 30 min during which time the colour of the solution became orange–red and some orange solid precipitated. The mixture was then refluxed for 30–45 min, filtered and allowed to cool slowly to room temperature. During this time, orange crystals separated which were collected by filtration, thoroughly washed with n-pentane, to afford the *complex* as a yellow powder (yield quantitative).

Mo{HB(Me$_2$pyz)$_3$}(NO)Br$_2$ (**1**; X=Y=Br). Nitrosyl bromide was generated in the same way as NOCl.[7] The red-brown gas was purified by passing through CaCl$_2$ and KCl, and was bubbled through a solution of Mo{HB(Me$_2$pyz)$_3$}(NO)(CO)$_2$ in dichloromethane. An orange solution quickly formed, and this was reduced in volume *in vacuo*. Ethanol was then added in the cold, causing precipitation of an orange powder. This was collected by filtration, recrystallised from toluene affording orange–red crystals of the toluene-solvated species. On repeated washing with n-pentane, the *complex* was obtained as an orange powder.

Mo{HB(Me$_2$pyz)$_3$}(NO)F$_2$, (**1**; X=Y=F). Mo{HB(Me$_2$pyz)$_3$}(NO)(OEt)$_2$ (0.3 g) was dissolved in dichloromethane (25 cm^3) and conc. HF (40% in water, 0.2 cm^3, PTFE beaker) was added. The mixture was stirred for 1 hr, and the solvent then removed *in vacuo* leaving the *complex* as a pale green powder (0.26 g, 90%).

Mo{HB(Me$_2$pyz)$_3$}(NO)F(OEt); (**1**; X=Y, Y=OEt). Mo{HB(Me$_2$pyz)$_3$}(NO)F$_2$ was suspended in ethanol and stirred at room temperature for 1 hr. The solvent was reduced in volume *in vacuo*, and the purple *complex* filtered off and dried *in vacuo*.

Mo{HB(Me$_2$pyz)$_3$}(NO)F(NHMe); (**1**; X=F, Y=NHMe). Mo{HB(Me$_2$pyz)$_3$}(NO)F$_2$ was suspended in methylamine and stirred at −10°C for 2 hr. The amine was then allowed to evaporate at room temperature, leaving the *complex* as a pale orange powder.

Mo{HB(Me$_2$pyz)$_3$}(NO)F(SBu^n); (**1**; X=F, Y=SBu^n). Mo{HB(Me$_2$pyz)$_3$}(NO)F$_2$ was suspended in *n*-heptane, and *n*-butanethiol (slight excess) added. The mixture was refluxed overnight and cooled, the brown *complex* being collected by filtration and dried *in vacuo*.

Mo{HB(Me$_2$pyz)$_3$}(NO)NHMe; (**1**; X=Cl, Y=NHMe). Mo{HB(Me$_2$pyz)$_3$}(NO)Cl$_2$ (0.3 g), dissolved in dichloromethane (30 cm^3), was treated with methylamine (33% ethanolic solution, 0.2 cm^3). The mixture was stirred at room temperature for 30 min during which time the solution became orange. The volume of solvent was reduced *in vacuo* to *ca.* 5 cm^3 and, after addition of diethylether, the precipitated [NH$_3$Me]Cl filtered off. The filtrate was reduced *in vacuo* to *ca.* 5 cm^3 whereupon the *complex* formed orange crystals (0.25 g, 83%).

The corresponding *ethyl*- and *n-butyl-amides* were obtained similarly as orange crystals (85 and 76% yields, respectively).

Mo{HB(Me$_2$pyz)$_3$}(NO)Cl(NMe$_2$) (**1**; X=Cl, Y=NMe$_2$). To Mo{HB(Me$_2$pyz)$_3$}(NO)Cl$_2$ (0.3 g) dissolved in dichloromethane (20 cm^3) was added dimethylamine (0.1 cm^3). The colour of the solution immediately became orange and the mixture was stirred for 30 min. The volume of the solution was reduced *in vacuo* to *ca.* 5 cm^3, treated with diethylether which caused precipitation of [NH$_2$Me$_2$]Cl which was filtered off. The filtrate was slowly evaporated, effecting crystallisation of the orange *complex* (0.19 g, 61%).

Mo{HB(Me$_2$pyz)$_3$}(NO)Cl(NHPh); (**1**; X=Cl, Y=NHPh). A mixture of Mo{HB(Me$_2$pyz)$_3$}(NO)Cl$_2$ (0.3 g) and freshly redistilled aniline (0.1 ml) in dichloromethane (30 cm^3) was stirred overnight at room temperature. The solution had became yellow-brown, and the solvent was removed *in vacuo*. The residue was extracted with diethylether, the extract being filtered and allowed to cool at −5° until the *complex* had precipitated as a brown powder (0.26 g, 78%).

The related *p-toluidide*, Mo{HB(Me$_2$pyz)$_3$}(NO)Cl(NHC$_6$H$_4$Me), (**1**; X=Cl, Y=*p*-MeC$_6$H$_4$NH), was prepared similarly using *p*-toluidine (0.1 g) and was isolated as a brown powder (0.27 g, 79%).

Mo{HB(Me$_2$pyz)$_3$}(NO)Cl(SBu^n); (**1**; X=Cl, Y=SBu^n). A mixture of Mo{HB(Me$_2$pyz)$_3$}(NO)Cl$_2$ (0.3 g) and *n*-butanethiol (0.2 cm^3) in *n*-heptane (20 cm^3) was refluxed overnight. The yellow-black solution which had formed was reduced *in vacuo* to *ca.* 10 cm^3 and the *complex* allowed to form as black crystals which were collected by filtration (0.23 g, 74%).

The related complexes Mo{HB(Me$_2$pyz)$_3$}(NO)Cl(SR) R=C$_6$H$_{11}$, CH$_2$Ph *and* Ph) were prepared similarly, using C$_6$H$_{11}$SH (0.2 cm^3), PhCH$_2$SH (0.1 g) and PhSH (0.2 cm^3) and were isolated as black (R=Ph) or dark green (R=C$_6$H$_{11}$, CH$_2$Ph) crystals. The yields were 0.26 g (75%), 0.25 g (72%) and 0.27 g (80%) respectively, and the toluene-α-thiolate could be recrystallised from dichloromethane/*n*-hexane mixtures; giving black microcrystals.

Mo{HB(Me$_2$pyz)$_3$}(NO)Br(NHMe); (**1**; X=Br, Y=NHMe). To Mo{HB(Me$_2$pyz)$_3$}(NO)-Br$_2$ (0.3 g) dissolved in dichloromethane (20 cm^3) was added methylamine (33% solution in ethanol, 0.2 cm^3). The solution immediately became orange, and was stirred at room temperature for 30 min. The volume of the solvent was then reduced to *ca.* 5 cm^3, and diethylether was added causing precipitation of [NH$_3$Me]Br which was filtered off. The volume of the filtrate was slowly reduced *in vacuo* until crystallisation began, and the *complex* formed as orange crystals at −5° (0.20 g, 73%).

Mo{HB(Me$_2$pyz)$_3$}(NO)Br(NMe$_2$); (**1**; X=Br, Y=NMe$_2$). A mixture of Mo{HB(Me$_2$pyz)$_3$}(NO)Br$_2$ (0.3 g) and dimethylamine (0.2 cm^5) in dichloromethane (20 cm^3) was stirred for 10 min, during which time an orange solution rapidly formed. The volume of the solvent was reduced *in vacuo* to *ca.* 5 cm^3, and diethylether added causing precipitation of [NH$_2$Me$_2$]Br, which was filtered off. The filtrate was partially evaporated *in vacuo* and allowed to stand at −5° until the *complex* had formed as orange crystals (0.16 g, 57%).

Mo{HB(Me$_2$pyz)$_3$}(NO)Br(SBu^n); (**1**; X=Br, Y=SBu^n). A mixture of Mo{HB(Me$_2$pyz)$_3$}(NO)Br$_2$ (0.25 g) and *n*-butanethiol (0.2 cm^3) in *n*-heptane (20 cm^3) was refluxed overnight during which time a yellow–black solution had formed. The solvent was evaporated *in vacuo* to *ca.* 10 cm^3, and the complex precipitated as an olive-green powder (0.22 g, 71%).

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