A Molybdenum-95 and Nitrogen-14 Nuclear Magnetic Resonance Study of Six-co-ordinate Hydrotris(3,5-dimethyl-1-pyrazolyl)borate Complexes containing a Sixteen-electron {Mo(NO)}^{4} Core

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The mononitrosyl complexes [Mo{HB(Me$_2$pz)$_3$}(NO)XY] [HB(Me$_2$pz)$_3$$^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; X = Y = F, Cl, I, OEt, OPh, SPh, or NHPh; X = Cl, Y = SPh, OPh, OEt, NHC$_6$H$_4$Br-*p*, NHC$_6$H$_4$Me-*p*, or NHEt; X = I, Y = OPh, NHC$_6$H$_4$Me-*p*, NHEt, or NHNMe$_2$] have been studied in solution by ^{95}Mo and ^{14}N n.m.r. spectroscopy. The iodo complex, [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$], exhibits a ^{95}Mo resonance at δ 2 272, the most deshielded monomeric Mo^{II} resonance reported to date. Replacement of the iodo ligands of [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$] by other ligands increases the shielding of the ^{95}Mo nucleus according to the general trend, I$^-$ < Cl$^-$ < F$^-$ < thiolato < alkoxy < amido. A chemical shift range of δ 161—2 272 was observed for the complexes studied. The complexes exhibit an *inverse* halogen dependence of the chemical shift. The nitrosyl ligand ^{14}N chemical shifts follow the same shielding trend as the ^{95}Mo chemical shifts.

The tripodal ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(Me$_2$pz)$_3$$^-$, may be regarded as being formally isoelectronic with cyclopentadienide, C$_5$H$_5$$^-$ (cp), in that both ligands are uninegative six-electron donors which occupy three facial metal co-ordination sites.[1] Thus, complexes related to [Mo(cp)(CO)$_3$]$^-$, [Mo(cp)(NO)(CO)$_2$], and [{Mo(cp)(NO)I$_2$}$_2$], where HB(Me$_2$pz)$_3$$^-$ replaces cp, have been prepared.[2,3] However, there are important electronic and steric differences between these two ligand types. Replacement of cp by HB(Me$_2$pz)$_3$$^-$ in [Mo(cp)(NO)(CO)$_2$], for example, results in an average decrease of 22 cm^{-1} in ν_{CO} and ν_{NO}. Also, in complexes of HB(Me$_2$pz)$_3$$^-$, the 3-methyl groups of the ligand project across the metal, protecting it from dimerization reactions and restricting its co-ordination number to six. Consequently, although [{Mo(cp)(NO)I$_2$}$_2$] exists as a dimeric seven-co-ordinate complex having formally 18-electron molybdenum centres,[1,4] [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$] is a monomeric 16-electron system containing six-co-ordinate molybdenum.[3]

A variety of remarkably stable alkoxy, amido, and thiolato derivatives of [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$] have been prepared[1] and the steric properties of HB(Me$_2$pz)$_3$$^-$ are thought to play an important role in stabilizing these compounds. Formally, these monomeric complexes may be considered 16-electron Mo^{II} species although some structural features, *e.g.*, short Mo–OR bond distances,[1] are consistent with considerable *p*π–*d*π bonding which may offset the electron deficiency at the metal. In contrast, most of the cyclopentadienyl counterparts are dimeric 18-electron complexes. It would appear, therefore, that the steric demands of HB(Me$_2$pz)$_3$$^-$ are able to stabilize complexes in which the molybdenum centre is substantially electron deficient. The properties and reactivity of such metal centres are of particular interest.

Molybdenum-95 n.m.r. has proved to be a useful tool for characterizing many classes of molybdenum complexes[5] and a number of monomeric Mo^{II} complexes[6—10] and Mo^{II} metal–metal quadruply bonded dimers[11] have been studied by this technique. The monomeric Mo^{II} complexes exhibit resonances between δ 390 and −2 100, whereas the quadruply bonded Mo^{II} dimers display the most deshielded ^{95}Mo resonances known to date (δ 3 200—4 200). With the exception of [Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$X]$^-$ (X = F or Cl),[9] all previously studied Mo^{II} complexes exhibit a *normal* halogen dependence of the chemical shift,[12] *i.e.*, the shielding order for halogeno complexes is F$^-$ < Cl$^-$ < I$^-$. In view of the formal electron deficiency of the title complexes we have investigated their ^{95}Mo n.m.r. properties. The complexes exhibit broad, extremely deshielded resonances and an *inverse* halogen dependence of the chemical shifts. The ^{14}N resonances of the nitrosyl-N atoms follow the same general shielding pattern as the ^{95}Mo resonances.

Experimental

The complexes used in this study were prepared according to methods described elsewhere.[3,13—20]

The n.m.r. spectra were obtained on a Bruker WM250 n.m.r. spectrometer. Dichloromethane, distilled from P$_2$O$_5$ prior to use, was used as a solvent in most cases. The 16.3-MHz ^{95}Mo n.m.r. spectra were measured with a 10-mm molybdenum probe. To reduce the effects of 'probe ringing' a Doty Scientific duplexer and preamplifier with a 16-MHz centre was inserted between the probe and the Bruker broadband preamplifier. The duplexer was gated off during the pulse and for 5 μs after the pulse. With this arrangement the preacquisition delay was reduced to 100 μs. The transmitter output was amplified with a Heathkit SB-201 (1 kW) linear amplifier. The input was attenuated to give a 26-μs 90° pulse. A 2 mol dm^{-3} Na$_2$[MoO$_4$] solution in D$_2$O, effective pH 11, was used as external standard (Ξ = 6.516 919 MHz). The ^{14}N spectra were measured at 18.1 MHz with a digitally selected 10-mm broadband probe (12.3—101 MHz) using the same experimental arrangement described above for ^{95}Mo. The chemical shifts are reported relative to neat nitromethane (Ξ = 7.226 326 MHz).

Results and Discussion

Molybdenum-95 and ^{14}N n.m.r. data for the [Mo{HB(Me$_2$pz)$_3$}(NO)XY] complexes and several related cp complexes are summarized in the Table. The [Mo{HB(Me$_2$pz)$_3$}(NO)XY] complexes exhibit the most deshielded resonances yet observed for any class of Mo^{II} monomer (Figure 1). Indeed, the chemical shift range of δ 161—2 272 overlaps by only *ca.* 230 p.p.m. the range previously defining the resonances of Mo^{II} monomers containing carbonyl[6—9] and isonitrile[10] ligands (δ 390[9] to

Table. Molybdenum-95 and ^{14}N n.m.r. data[a]

Compound	$\delta(^{95}Mo)$	Line-width (Hz)	$\delta(^{14}N)$	Line-width (Hz)
$[MoL(NO)I_2]$	2 272	1 800	46	100
$[\{Mo(cp)(NO)I_2\}_2]$[b]	−26	750		
$[MoL(NO)Cl_2]$	1 811	1 400	26	100
$[MoL(NO)F_2]$	1 274	1 490	14	130
$[MoL(NO)(SPh)_2]$	990	1 560	10	160
$[Mo(cp)(NO)(SPh)_2]$[c]	144	580	36	90
$[MoL(NO)(OPh)_2]$	624	1 600	11	120
$[MoL(NO)(OEt)_2]$	464	800	9	60
$[MoL(NO)(NHPh)_2]$	161	600	2	80
$[MoL(NO)Cl(SPh)]$	1 200	2 340	17	160
$[MoL(NO)Cl(OPh)]$	1 050	1 750	10	120
$[MoL(NO)Cl(OEt)]$	910	1 450	17	90
$[MoL(NO)Cl(NHC_6H_4Br\text{-}p)]$	539	1 500	11	100
$[MoL(NO)Cl(NHC_6H_4Me\text{-}p)]$	523	1 700	10	100
$[MoL(NO)Cl(NHEt)]$	404	1 000	10	60
$[MoL(NO)I(OPh)]$	1 179	1 600		
$[MoL(NO)I(NHC_6H_4Me\text{-}p)]$	568	1 350	13	100
$[MoL(NO)I(NHEt)]$	430	1 200	11	80
$[MoL(NO)I(NHNMe_2)]$	284	900	7	50

[a] In CH_2Cl_2 at ambient temperature, L = $HB(Me_2pz)_3$. [b] In $HCONMe_2$. [c] In $CDCl_3$.

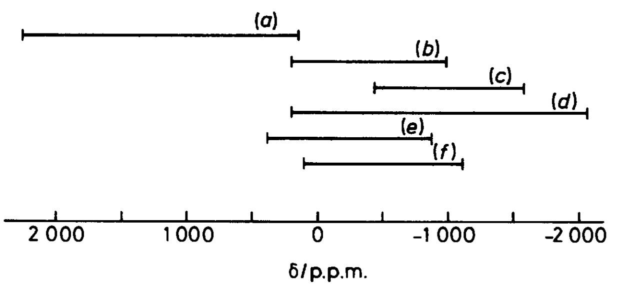

Figure 1. Chemical shift ranges for mononuclear nitrosyl–molybdenum and Mo^{II} complexes: (*a*) six-co-ordinate $\{Mo(NO)\}^4$, this work; (*b*) seven-co-ordinate $\{Mo(NO)\}^4$ and $\{Mo(NO)_2\}^6$, refs. 22 and 27; (*c*) $\{Mo(NO)\}^6$, refs. 29 and 30; (*d*) $Mo(CO)_3{}^{2+}$, refs. 6 and 7; (*e*) $Mo(CO)_2{}^{2+}$, ref. 9; (*f*) $Mo(CNR)_n{}^{2+}$ ref. 10. The notation used for the nitrosyl complexes follows that of J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339

−2 100 p.p.m.[6]). Hitherto, the most deshielded resonance known for monomeric Mo^{II} was exhibited by *cis*-$[Mo(S_2CNEt_2)_2(CO)_2]$, also a six-co-ordinate 16-electron complex.[9]

Comparison of the chemical shifts of analogous pairs of $HB(Me_2pz)_3{}^-$ and cp complexes, *e.g.*, the pairs $[MoL(CO)_2(NO)]$ and $[MoL(CO)_3]^-$ [L = $HB(Me_2pz)_3$ or cp], indicates that the resonances of the $HB(Me_2pz)_3{}^-$ complexes are deshielded by *ca.* 900 p.p.m. relative to those of analogous cp complexes.[5] However, the ligand deshielding effect of $HB(Me_2pz)_3{}^-$ does not fully account for the extreme deshielding of ^{95}Mo in the 16-electron complex, $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$, which is deshielded by 2 298 p.p.m. relative to the 18-electron complex, $[\{Mo(cp)(NO)I_2\}_2]$. The additional *ca.* 1 300 p.p.m. deshielding which is over and above that expected from ligand changes alone may be a consequence of the electron deficiency of the metal centre in the $HB(Me_2pz)_3{}^-$ complex. Although the uncertain nature of $[\{Mo(cp)(NO)I_2\}_2]$ in $HCONMe_2$ (one of the few solvents suitable for this complex) makes tenuous the conclusion above, a general deshielding of the electron-deficient $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ monomers compared to co-ordinatively saturated counterparts is evident from a comparison of the data summarized in Figure 1 with that available elsewhere.[5]

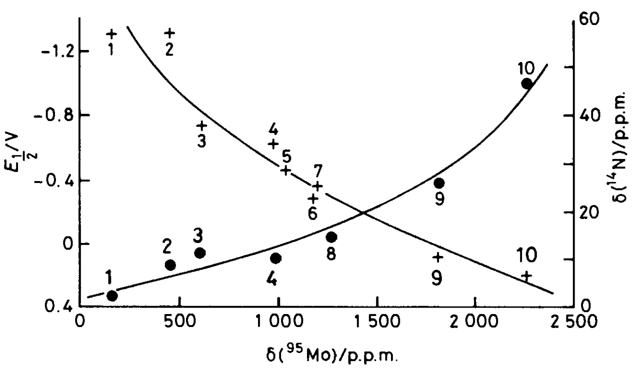

Figure 2. Plot of ^{95}Mo chemical shifts *versus* ^{14}N chemical shift (●) and reduction potential (+) for selected $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ complexes: X = Y = NHPh (1), OEt (2), OPh (3), SPh (4), F (8), Cl (9), I (10); X = Cl, Y = OPh (5), SPh (7); X = I, Y = OPh (6)

Replacement of the I^- ligands of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ by other ligands leads to increased nuclear shielding, the shielding order for the $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$ complexes being: X = Cl < F < SPh < OPh < OEt < NHPh. A similar shielding trend is observed in complexes of mixed ligands, $[Mo\{HB(Me_2pz)_3\}(NO)XY]$, *e.g.*, in the chloro complexes (X = Cl) the ligand-dependent shielding order is Y = SPh < OPh < OEt < NHC_6H_4Br-*p* < NHC_6H_4Me-*p* < NHEt.

The complexes $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$ (X = F, Cl, or I), $[Mo\{HB(Me_2pz)_3\}(NO)X(NHEt)]$, $[Mo\{HB(Me_2pz)_3\}(NO)X(NHC_6H_4Me\text{-}p)]$, and $[Mo\{HB(Me_2pz)_3\}(NO)X(OPh)]$ (X = Cl or I) display an inverse halogen dependence of the chemical shift,[12] *i.e.*, shielding of the ^{95}Mo nuclei increases in the order X = I < Cl < F. An inverse halogen dependence of the chemical shift has been observed for high-valent molybdenum complexes containing *cis*-$MoO_2{}^{2+}$, MoO^{4+}, $Mo(NPh)^{4+}$, and MoO^{2+} fragments.[21–23] Also, a recent study of complexes containing the *cis*-$Mo(CO)_2{}^{2+}$ fragment revealed an inverse halogen dependence of their chemical shifts.[9] In contrast, a normal halogen dependence of the chemical shift is displayed by other Mo^{II} and Mo^0 complexes such as $[Mo(cp)(CO)_3X]$,[6] $[Mo(CNCMe_3)_6X]^+$,[10] $[Mo_2X_8]^{4-}$,[11] $[Mo(CO)_5X]^-$,[24–26] and for complexes containing *cis*-$Mo(NO)_2{}^{2+}$ fragments.[27]

The ^{95}Mo n.m.r. linewidths exhibited by the complexes $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ are large (600—2 340 Hz), a consequence of rapid quadrupole relaxation of the ^{95}Mo nuclei. The observation of such broad signals is made even more difficult by 'probe ringing' at the frequencies employed for ^{95}Mo n.m.r. The combination of short ^{95}Mo relaxation times and the need for a preacquisition delay to allow for the decay of probe ringing present several experimental difficulties for observing broad ^{95}Mo resonances. We recently described[23] a reliable methodology for the observation of resonances with linewidths up to *ca.* 5 000 Hz, and emphasized that minimum probe ringing, a short preacquisition delay and the use of highly concentrated samples in low-viscosity solvents are critical to successful observation of broad resonances. Only limited ^{95}Mo n.m.r. data are reported herein because the low solubility of several $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ complexes prevented reliable measurement of their ^{95}Mo n.m.r. spectra.

The ^{14}N n.m.r. chemical shifts of the nitrosyl nitrogen in the $HB(Me_2pz)_3{}^-$ complexes follow the same general shielding pattern as the ^{95}Mo n.m.r. chemical shifts. The chemical shifts for the nitrosyl nitrogens in the $HB(Me_2pz)_3{}^-$ complexes vary in the range δ 2—46 and are within the range established for linear nitrosyl groups.[28–30] There appears to be a broad correlation of the ^{95}Mo and ^{14}N chemical shifts as shown in Figure 2. A linear fit of the data is only of moderate quality. There also appears to be a similarly broad correlation of the ^{95}Mo chemical shifts with the reduction potentials of the complexes,[31] a relationship also represented in Figure 2.

In conclusion, formally electron-deficient complexes of the type $[\mathrm{Mo}\{\mathrm{HB(Me_2pz)_3}\}(\mathrm{NO})XY]$ exhibit broad, extremely deshielded ^{95}Mo resonances which are quite difficult to observe in most cases due to low solubility levels. The magnitudes of the chemical shifts appear to be related to the electron deficiency of the ^{95}Mo centres. The chemical shift range is extensive (2 110 p.p.m.); the chemical shifts are ligand dependent and show an inverse halogen dependence, in contrast to those of related Mo^{II} complexes. Further, an inverse relationship between the ^{95}Mo chemical shifts and reduction potentials, and a direct relationship between the ^{95}Mo and ^{14}N chemical shifts, is consistent with all three parameters reflecting the relative electron deficiency of the metal centres.

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