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Preliminary Communication

STABLE MONOMERIC MONOALKYLAMIDO, HYDRAZIDO(1-) AND MIXED ALKOXY COMPOUNDS OF MOLYBDENUM AND TUNGSTEN NITROSYLS

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Summary

The complexes $Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)XY$ ($[HB(3,5\text{-}Me_2C_3HN_2)_3]$= tris(3,5-dimethylpyrazolyl)borate; X = I or OR, R = alkyl; Y = NHR'. R = H, alkyl, NH_2, NMe_2, NHMePh, NHPh, CH_2CH_2OH or $N{:}CMe_2$) and $W[HB(3,5\text{-}Me_2C_3HN_2)_2\text{-}(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)](NO)XY$ (X = Br or OR, R = alkyl; Y = NHR', R' = H, alkyl, NH_2, NMe_2, NHPh, $CH_2CH_2NH_2$ or $N{:}CMe_2$) have been prepared, and the structures of representative examples determined crystallographically.

Monomeric monoalkylamido complexes of the transition metals, unlike their dialkylamido analogues,[1] are notoriously unstable, readily losing H^+ forming imido species and/or undergoing oligomerisation and polymerisation.[2] Mixed alkoxy-alkylamido and mixed alkoxy complexes likewise tend to be unstable, attempts to prepare them frequently resulting in ligand exchange and the formation of unmixed species. Such behaviour could be suppressed by combining the amido and/or alkoxy groups within a complex having an extremely bulky ligand, e.g. tris(3,5-dimethylpyrazolyl)borate, and an 'electron poor' metal, i.e. an early transition element binding π-acceptor and/or electronegative groups. Hydrazido(1-) complexes are also relatively rare, examples virtually being confined to certain tertiary phosphine, dithiocarbamato[3] and η^5-cyclopentadienyl[4] complexes of Mo and W. The factors likely to lead to the stabilisation of M-NHR (R = alkyl) groups should equally well apply to systems containing M-NHNRR'.

Accordingly, we have treated $Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)I_2$,[6] 1 (X = Y = I)[5] and the related $W[HB(3,5\text{-}Me_2C_3HN_2)_2(3,5\text{-}Me_2\text{-}4\text{-}Br\text{-}C_3N_2)](NO)Br_2$, 2 (X = Y = Br)[6ǂ] with primary amines at room temperature, and have obtained air- and moisture-stable red or magenta crystalline complexes, 1 (X = I, Y = NHR; R = Me, Et, C_6H_{11}) and 2 (X = Br, Y = NHR; R = Me, Pr^i or CH_2Ph). The related simple amino complexes 1 (X = I, Y = NH_2) and 2 (X = Br, Y = NH_2) were similarly produced using ammonia (d = 0.88). Secondary amines also react under similar conditions but if traces of alcohols are present, only the alkoxides 1 (X = I, Y = OR) and 2 (X = Br, Y = OR) are formed; the very unstable species 1 (X = I, Y = NMe_2) was detected spectroscopically in the absence of ROH. Remarkably, the dimethylamido group is displaced by primary amines affording, for example, 1 (X = I, Y = NHMe), a reaction which is very unusual in alkylamido chemistry. Treatment of 1 (X = I, Y = NHR) or 2 (X = Br, Y = NHR) with HX (X = halide) in aqueous acetone caused cleavage of the M-N bond and quantitative recovery of the amine as RNH_3^+. However, in the presence of Et_3N, 1 (X = I, Y = NH_2) and 2 (X = Br, Y = NH_2) reacted with acetone giving 1 (X = I, Y = $N{:}CMe_2$) and its tungsten analogue 2, as acetone solvates.

Reaction of 1 (X = Y = I) and of 2 (X = Y = Br) with hydrazines afforded the hydrazido(1-) compounds, 1 (X = I, Y = NHNRR'; R = R' = H or Me; R' = Ph) and 2 (X = Br, Y = NHNRR'; R = R' = Me; R = H, R' = Ph). These orange or red complexes are also air- and moisture-stable, although the simple hydrazides (Y = $NHNH_2$) decompose slowly in air (this can be arrested by formation of the respective hydrazones, Y = $NHN{:}CMe_2$, on treatment of the hydrazides with acetone). On reaction with HX

[ǂ] Prepared by bromination of $W[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)(CO)_2$ in benzene at room temperature. The analytical data for this and all other compounds described herein are entirely consistent with their formulations.

(X = halide), the hydrazine groups are apparently removed intact, and the parent molybdenum or tungsten dihalide is regenerated.

The facility with which Mo-N and W-N bonds in these systems can be formed is further demonstrated by the reaction of 1 (X = I, Y = OR; R = alkyl) and 2 (X = Br, Y = OEt) with primary amines at room temperature, when the mixed alkoxy-alkylamido species, 1 (X = NHR', Y = OR; R' = H, Me, Pr^i or CH_2Ph; R = Me or Pr^i) and 2 (X = NHR', Y = OEt; R' = Me or CH_2Ph) are formed. Bifunctional amines, e.g. $NH_2CH_2CH_2NH_2$, $NH_2CH_2CH_2OH$, etc., form monomeric amido complexes, e.g. 1 (X = I, Y = $NHCH_2CH_2OH$) and 2 (X = Br, Y = $NHCH_2CH_2NH_2$). There is a marked preference for N- rather than O-bonding in reactions involving $NH_2(CH_2)_nOH$ (n = 2, 3 or 4) and no evidence could be found in these, or the related diamine systems, for chelate ring formation or the production of homo-bimetallic species. The preference for N-bonding also extends to bifunctional ligands containing NH_2 and either S-S or SH groups.[7]

Treatment of 1 (X = I, Y = OEt or OPr^i) with silver(I) acetate in dichloromethane affords a green complex, probably $Mo[HB(3,5\text{-}Me_2C_3HN_2)_3]\text{-}(NO)(OR)(OAc)$.[††] This species reacts rapidly with alcohols forming symmetrical dialkoxides, e.g. 1 (X = Y = OEt or OPr^i), or, more interestingly, mixed alkoxides, 1 (X = OEt, Y = OPr^i). These pink complexes are also air- and water-stable, but react with acids, HX, releasing alcohols and forming $Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)X_2$ (X = Cl or Br).

The structures of 1 (X = I, Y = NHEt or NHNMePh) and 1 (X = Y = OEt, OPr^i and X = OEt, Y = OPr^i) have been determined crystallographically. Essential crystallographical information and important bond lengths are listed in the Table.

For each structural determination, data were collected on a Stöe Stadi-2 two-circle X-ray diffractometer and were corrected for the

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[††] IR and ^1H n.m.r. spectral data are consistent with this formulation, but due to facile hydrolysis, elemental analyses were not fully satisfactory.

Table:

Molecule	Space Group, Cell Dimensions and R-factor	Mo-Q[a]	Mo-N(O)	Mo-halide
1 (X=I, Y=NHEt)[b]	$P2_{1/a}$; monoclinic; a = 40.000(31) b = 12.751(10), c = 10.604(26)Å, β = 97.226(19)°, U = 5365(13)$Å^3$, Z=8, D_m = 1.67 g ml^{-1}, D_c = 1.43; R=0.0621, 3151 independent reflections	1.94 2.00	1.70 1.74	2.77 2.78
1 (X=I, NHNMePh)[b]	$B2_{1/c}$; monoclinic; a = 20.11(18), b = 19.67(17), c = 15.75(19)Å, β = 99.65 (17)°, U = 6141(108)$Å^3$, Z=8, D_m = 1.58, D_c = 1.54 (with 0.5 mol of CH_2Cl_2solvate per equiv. posn; R = 0.0973, 1474 independent reflections	1.92	1.73	2.79
1 (X=Y=OPr^i)	$P\bar{1}$; triclinic; a = 11.758(8), b = 14.403(9), c = 8.173(14)Å, α =97.90 (16), β = 77.296(26), γ = 96.523(7)°, U = 1332(3)$Å^3$, Z=2, D_m = 1.39 g ml^{-1}, D_c = 1.31; R=0.0398, 2605 independent reflections	1.90	1.76	
1 (X=Y=OEt)[c]	$P2_{1/n}$; monoclinic; a = 14.73, b = 21.09, c = 8.0 Å; β = 9480°; U = 2477 $Å^3$, Z=4, D_m = 1.36, D_c = 1.38	(1.90)	(1.76)	
1 (X=OEt, Y=OPr^i)	$P2_{1/n}$; monoclinic; a = 14.45(4), b = 21.68(6), c = 8.015(14)Å, β =96.08 (2)°; U = 24.97(10)$Å^3$, Z=4, D_m = 1.36, D_c = 1.36; R=0.0398, 2503 independent reflections	1.90	1.76	
1 (X=Cl, Y=OPr^i)[d]	ref. 5	1.86	1.76	2.38

[a] Mo-N (amido or hydrazido) or Mo-O distance; [b] The quoted R is an interim value; [c] Molecule isomorphous with 1 (X=OEt, Y=OPr^i); [d] Mo[HB(3,5-Me_2-4-ClC_3N_2]$_3$(NO)Cl(OPr^i), ref. 5.

usual effects and for absorption. The structures were solved by standard crystallographic methods and were refined by block-diagonal least-squares. Except in the case of 1 (X = I, Y = NHNMePh), allowance was made for anisotropic thermal vibration of all non-hydrogen atoms and the hydrogen atoms were placed at stereochemically accepted positions.

Each molecule has an overall octahedral geometry with the tris-(3,5-dimethylpyrazolyl)borato ligand adopting the usual facial coordination geometry. In all cases, the Mo - N - O linkage is essentially linear (maximum deviation from co-linearity is 5.3°).

The structure of the mixed alkoxide 1 (X = OEt, Y = OPr^i) shows clear disorder of the alkyl groups with α-carbon atoms carrying a half-population methyl group as substituent. The close approach of these two half-population carbon atoms (3.0 Å) precludes the possibility that the sample crystal is a crystalline form of the diisopropoxide complex 1 (X = Y = OPr^i). The structure of 1 (X = Y = OEt) was not directly determined but was proved to be isomorphous (from unit cell measurements and from relative intensity determinations from film data) with that of the mixed alkoxide 1 (X = OEt, Y = OPr^i) by replacement of the two half-population methyl groups by hydrogen atoms.

The structure of the amido complex 1 (X = I, Y = NHEt) comprises two symmetry-independent molecules which only significantly differ in the one structural parameter (Mo-N-C angle: 135 and 150°).

In both the amido and hydrazido complexes, which formally contain Mo^{III}, the Mo-N distances are significantly shorter than those in $Mo_2(OSiMe_3)_6(NHMe_2)_2$ (Mo^{III}, 2.28 Å),[8] and $Mo_2(NMe_2)_6$ (Mo^{III}, 1.98 Å)[9], but comparable with the Mo(1)-N(1) distance in $\{Mo(\eta^5\text{-}C_5H_5)I(NO)\}_2NNMe_2$ (Mo^{III}, 1.92 Å)[4] and in $Mo(NMe_2)_4$ (Mo^{IV}, 1.92 Å).[10] These data clearly indicate that there is significant p_π-d_π bonding between the N atom and the metal. The N-N distance in the hydrazido(1-) species is 1.35 Å which is noticeably shorter than the comparable distances in $\{Mo(\eta^5\text{-}C_5H_5)I(NO)\}_2NNMe_2$, but in the same region as those in hydrazido(2-) complexes of Mo and W.[3] Thus, it would appear that the electron-withdrawing effect of the

$[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)I$ moiety causes not only multiple bonding between the metal and the adjacent N atom, but also facilitates mesomeric release of electrons from the NMePh group. Multiple bonding also exists between the Mo and O atoms in the alkoxide complexes, but the Mo-O distances are slightly longer than that observed in $Mo[HB(3,5\text{-}Me_3\text{-}4\text{-}ClC_3N_2)_3](NO)Cl(OPr^i)$ (1.86 Å).[5] They are also longer than those in $Mo_2(OCH_2Bu^t)_6$ (Mo^{III}, 1.88 Å [11], $[Mo(NO)(OPr^i)_3]_2$ (Mo^{III}, 1.85-1.86 Å).[12] and $[Mo(OPr^i)_4]_2$ (Mo^{IV}, 1.87-1.88 Å).[12] An increase in the Mo-O distances in going from the chloro-isopropoxide to the bis-alkoxides might be expected because of the replacement of the highly electronegative Cl by the potentially more electron-releasing OR group.

The stability of these complexes can readily be ascribed to the steric protection afforded by the bulky tris(pyrazolyl)borato ligand, as seen in the dispositions of the amido, hydrazido and alkoxy groups with respect to that ligand, and to the very strongly electron-withdrawing effect of the $Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)$ group which causes multiple bonding between the Mo and N- or O-donor atoms.

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