Bis(organodiazenido)-complexes of Molybdenum

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Summary We report a general method for the preparation of a rare class of compounds, bis(diazenido)-complexes $[Mo(N_2R^1)_2(S_2CNR^2{}_2)]$ where R^1 and R^2 are the same or different alkyl or aryl groups; some intermediates in the preparative reactions are also described.

BIS(ORGANODIAZENIDO)-COMPLEXES are very rare, and to date only $[Mo(N_2Ph)_2(8\text{-hydroxyquinolate})_2]$,[1] $[RuCl(N_2Ar)_2(PPh_3)_2]^+$,[2] $[Mn(CO)(N_2Ph)_2(PPh_3)_2]$,[3] and $[Mo(C_5H_5)(N_2Ph)(N_2Ar)(PPh_3)]^+$ (Ar = aryl)[4] have been described. The reaction of $[MoO_2(dtc)_2]$ (dtc = dithiocarbamato-ligand) with an excess of mono-organohydrazine hydrochlorides, $RNHNH_2HCl$, in the presence of Na(dtc) in methanol solution in air leads to mono(diazenido)-complexes $[Mo(N_2R)(dtc)_3]$.[5] We now find that in the absence of Na(dtc), bis(diazenido)-complexes $[Mo(N_2R)_2(dtc)_2]$ are the principal products.

In this way we have prepared $[Mo(N_2Ph)_2(dtc)_2]$, (dtc = S_2CNEt_2 or $S_2C\overline{N[CH_2]_4C}H_2$) and $[Mo(N_2R)_2(S_2CNMe_2)_2]$ (R = Me, Ph, p-BrC_6H_4, or p-$MeOC_6H_4$). The compound $[Mo(N_2Me)_2(S_2CNMe_2)_2]$ is the first reported bis(methyldiazenido)-complex. On the basis of the eighteen-electron rule, these Mo^{IV} complexes would be expected to have two linear Mo–N–N groups.

The i.r. spectrum of the methyldiazenido-compound shows two bands (1604, 1662 cm^{-1}) assignable to $\nu(N{=}N)$, suggesting a *cis*-arrangement of diazenido-groups. In the other complexes this region is masked by aryl vibrations. The spectrum also shows a single strong band at *ca.* 980 cm^{-1} consistent with the dtc ligands being bidentate.[6] The ^1H n.m.r. spectrum of $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ in solution in CD_2Cl_2 at 25 °C shows two singlets from the dtc methyl groups at τ 6·58 and 6·64. These arise because the general configuration of the complex is *cis* and there are thus two kinds of methyl group present. The spectra are temperature dependent, the values of the dtc methyl shifts depending upon the substituent R in the N_2R groups, and for R = Me at 25 °C all the dtc methyl groups are equivalent. The analogous compound $[Mo(NO)_2(S_2CNMe_2)_2]$, which has linear Mo–N–O systems, is also fluxional.[7] It is possible that the *cis*-diazenido groups are joined to yield a tetrazene ligand, but the mass spectrum of $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ which shows fragments with *m/e* corresponding to $[Mo(N_2Ph)_2(dtc)_2]^+$, $[Mo(N_2Ph)(dtc)_2]^+$, and $[Mo(dtc)_2]^+$ lends little credence to this.

The preparative reaction has not yet been fully investigated. Condensation of an organohydrazine with an Mo=O function should lead to a hydrazido(2−)-complex containing the grouping Mo=N–NHR, and subsequent conversion into a diazenido-ligand requires a two-electron ligand-oxidation. Since only one electron per ligand is removed by the metal, the other oxidant is presumably the air. Thus, if the preparative reactions are carried out under dinitrogen, complexes which we formulated as $[Mo(N_2R)(NHNHR)(dtc)_2]$ can be isolated in specific cases (R = Me, Ph, p-ClC_6H_4, BuOCO, EtOCO, or PhOCO; dtc = S_2CNMe_2). Several of these can be converted into $[Mo(N_2R)_2(dtc)_2]$ by exposing their solutions to air. The structural assignment as $Mo(N_2R)(N_2H_2R)$ rather than $Mo(NNHR)_2$ rests principally on ^1H n.m.r. data. Thus the spectrum of $[Mo(N_2CO_2Bu^t)(N_2H_2CO_2Bu^t)(S_2CNMe_2)_2]$ in

CD_2Cl_2 at 25 °C shows 4 inequivalent methyl (τ 6·56, 6·60, 6·62, and 6·72), 2 t-butyl (τ 9·48 and 9·56) and 2 N-*H* protons (τ 2·88 and 4·84). In the ^{13}C n.m.r. spectrum the two carbonyl carbons and the *C*Me_3 carbons also have different shifts. These spectra are more compatible with the proposed structure than any other. Work is continuing to confirm the structures.

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