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The reaction of Molybdenum(VI) Dioxo Derivatives with Heterocumulenes

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The reactions of ArNSO (Ar = p-*MeC_6H_4) with* cis-*$Mo(O)_2(chel)_2$ (chel = S_2CNEt_2, $CH_3COCHCOCH_3$) give the molybdenum(VI) oxo-arylimido derivatives, $Mo(O)(NAr)(hel)_2$, and sulphur dioxide. From* cis-*$Mo(O)_2(S_2CNEt_2)_2$ and CyNCO (Cy = C_6H_{11}) the dimeric $Mo_2O_3(S_2CNEt_2)_4$ is obtained, with the concomitant formation of carbon dioxide and biuret, $(CyNHCO)_2NCy$. The spectroscopic properties of the molybdenum(VI) oxo-arylimido derivatives are reported and the possible reaction mechanisms are discussed.*

Introduction

The chemistry of the molybdenum(VI) dioxo derivatives, *cis*-$Mo(O)_2(S_2CNR_2)_2$, has been extensively investigated, particularly because they are possible models for molybdo-enzymes [1]. For these compounds a facile transfer of one oxygen atom to tertiary phosphines has been demonstrated [1].

Recently it has also been reported that treatment of *cis*-dioxobis(N,N-dimethyldithiocarbamato)molybdenum(VI) with phenylhydroxylamine, gives the molybdooxaziridine, $Mo(O)(PhNO)(S_2CNMe_2)_2$, and a seven-coordinate metal structure with η^2 bonding of the PhNO ligand has been proved by X-ray crystallography on a related derivative having pyridine-2,6-dicarboxylate as the anionic ligand [2, 3]. As a continuation of our studies on the synthesis and reactivity of arylimido complexes [4], we were investigating the interaction of organic nitrene precursors such as sulphinylamines, RNSO, and isocyanates, RNCO, with a series of *cis*-dioxomolybdenum(VI) derivatives. While our work was in progress [5], the synthesis of $Mo(O)(NPh)(S_2CNEt_2)_2$ from the reaction of $Mo(O)(S_2CNEt_2)_2$ and PhN_3 has been reported [6]. We report here on the synthesis and properties of related oxo-arylimido molybdenum(VI) derivatives, obtained by the reactions of *cis*-$Mo(O)_2(chel)_2$ (chel = S_2CNEt_2, $CH_3COCHCOCH_3$) with *p*-MeC_6H_4-NSO.

Experimental

$Mo(O)(NC_6H_4Me$-p$)(CH_3COCHCOCH_3)_2$, (I)

To *cis*-$Mo(O)_2(CH_3COCHCOCH_3)_2$ (1.5 g), *p*-MeC_6H_4NSO (5 ml) was added under a nitrogen atmosphere. The suspension was left under stirring at room temperature for one week; fresh sulphinylamine (0.5 ml) was added three times during the week in order to maintain a fluid solution. Nitrogen degassed ethyl ether was added to the resulting brown solution. The brick red precipitate was filtered off under a nitrogen atmosphere, washed with ethyl ether and dried *in vacuo*. m.p. = 122 °C (83% yields). *Anal.* Found: C, 48.9; H, 5.0; N, 3.3; O, 19.3; Mo, 23.0%; S, absent. $C_{17}H_{21}MoNO_5$ requires: C, 49.2; H, 5.1; N, 3.4; O, 19.3; Mo, 23.1%. I.r.: $\nu_{(Mo=O)}$ = 890(s), $\delta_{(p\text{-}Me)}$ = 820(m), cm^{-1} in nujol. ^1H n.m.r. in C_6D_6: $\tau_{(p\text{-}C_6H_4)}$, 2.66(2)–3.14(2) (J_{AB} = 8.4 Hz); $\tau_{(CH)}$, 4.7(1)–4.8(1); $\tau_{(p\text{-}CH_3)}$, 7.95(3); $\tau_{(CH_3)}$, 8.25(3)–8.29(3)–8.32(6). The mother liquor was evaporated under vacuum (0.1 mm); by adding n-hexane to the resulting oily residue under a nitrogen atmosphere, a dark brown precipitate was obtained. The absence of $\nu_{(Mo=O)}$ in the i.r. spectrum and the elemental analyses of this material suggested the formation of the bis-nitrene species, $Mo(NAr)_2(CH_3COCHCOCH_3)_2$; however we were unable to obtain this compound in an analytically pure form. Some reactions conducted at 60–80 °C did not give satisfactory results. The compound was stored in a nitrogen atmosphere.

$Mo(O)(NC_6H_4Me$-p$)(S_2CNEt_2)_2$, (II)

To dry benzene (45 ml), *cis*-$Mo(O)_2(S_2CNEt_2)_2$ (0.8 g) and *p*-MeC_6H_4NSO (1.45 g) were added under a nitrogen atmosphere. The pale brown solution was left under stirring for 64 hrs. The solution was decanted away and the oily, yellow insoluble residue was solidified by scratching with ethyl ether.

This material can be crystallized with difficulty from ethanol-ethyl ether, by cooling the solution at *ca.* −10 °C for several hours. Elemental analyses and spectroscopic data were in agreement with a formulation of this compounds as $Mo(O)(p\text{-}MeC_6H_4NSO)_2(S_2CNEt_2)_2$ (III) (6.5% yields). (Found: C, 41.1–39.2; H, 5.0–5.2; Mo, 13.9; N, 7.9–7.7; O, 6.8–7.4; S, 26.5%. $C_{24}H_{34}MoN_4O_3S_6$ requires: C, 40.3; H, 4.8; Mo, 13.5; N, 7.8; O, 6.7; S, 26.3%). *I.r.*: $\nu_{(ArNSO)}$ = 1275(m), 1215(m), 1030(s); $\nu_{(Mo=O)}$ = 880(m), $\delta_{(p\text{-}Me)}$ = 820(m) cm^{-1} in nujol. ^1H n.m.r. in $CDCl_3$: $\tau_{(p\text{-}C_6H_4)}$, quartet centered at 3.26(8); $\tau_{(CH_2)}$, quartet centered at 6.33(8); $\tau_{(p\text{-}CH_3)}$, 7.7(3)–7.9(3); $\tau_{(CH_3)}$, triplet centered at 8.7(12). The mother liquor was evaporated to a small volume; by adding n-hexane a brown, oily precipitate was obtained. The solution was decanted away and the oily residue was solidified by repeated washings with fresh n-hexane and by scratching. The dark brown product was crystallized from benzene–n-hexane. M.p. = 129 °C (66.5% yields). *Anal.* Found: C, 39.7; H, 5.6; N, 7.9; O, 3.5; Mo, 17.9%; $C_{17}H_{27}MoN_3OS_4$ requires: C, 39.8; H, 5.3; N, 8.2; O, 3.1; Mo, 18.7%. *I.r.*: $\nu_{(Mo=O)}$ = 870(s), $\delta_{(p\text{-}Me)}$ = 820(m), cm^{-1} in nujol. ^1H n.m.r. in C_6D_6: $\tau_{(p\text{-}C_6H_4)}$, 2.38(2)–3.16(2) (J_{AB} = 7.8 Hz); $\tau_{(CH_2)}$, quartet centered at 6.8(8); $\tau_{(p\text{-}CH_3)}$, 8.0(3); $\tau_{(CH_3)}$, triplet centered at 9.3(12).

When the same reaction was carried out on *cis*-$Mo(O)_2(S_2CNPh_2)_2$ we were unable to isolate a well characterizable product. On the other hand *cis*-$Mo(O)_2(oxine)_2$ (oxine-H = 8-hydroxyquinoline) did not react even at 60 °C in neat $p\text{-}MeC_6H_4NSO$ for 6 hrs.

$Mo(O)(p\text{-}MeC_6H_4NO)(S_2CNEt_2)_2$ (IV)

To CH_2Cl_2 (15 ml), *cis*-$Mo(O)_2(S_2CNEt_2)_2$ (0.614 g) and $p\text{-}MeC_6H_4NHOH$ (0.214 g) were added under a nitrogen atmosphere and with magnetical stirring. After 30 min dry $MgSO_4$ (0.39 g) was added. After 5 min the red solution was filtered and evaporated to dryness. The red-brown residue was crystallized from ethyl ether–n-hexane, to give the pure product. M.p. = 75–80 °C. *Anal.* Found: C, 39.0; H, 5.1; N, 7.9%. $C_{17}H_{27}MoN_3O_2S_4$ requires: C, 38.6; H, 5.1; N, 7.9%. *I.r.*: $\nu_{(Mo=O)}$ = 940(s), $\delta_{(p\text{-}Me)}$ = 820(m), cm^{-1} in nujol. ^1H n.m.r. in $CDCl_3$: $\tau_{(p\text{-}C_6H_4)}$, quartet centered at 2.7(4); $\tau_{(CH_2)}$, complex multiplet at *ca.* 4.2(8); $\tau_{(p\text{-}CH_3)}$, 7.66(3); $\tau_{(CH_3)}$, complex multiplet at *ca.* 8.66(12).

Reaction of cis–*$Mo(O)_2(S_2CNEt_2)_2$ with CyNCO ($Cy = C_6H_{11}$)*

To dry benzene (45 ml), *cis*-$Mo(O)_2(S_2CNEt_2)_2$ (0.6 g) and freshly distilled CyNCO (0.85 g) were added under a nitrogen atmosphere. The suspension was left under stirring for three days with a slow flux of nitrogen. Analyses of the gas revealed the formation of large amounts of carbon dioxide. The violet precipitate was filtered off. This material was treated with ethanol (40 ml) and left under stirring for 15 minutes. The violet, insoluble product was crystallized from CH_2Cl_2–n-hexane and was shown to be $Mo_2O_3(S_2CNEt_2)_4$ by its i.r. spectrum, identical to that of an authentic sample [7] and elemental analyses. (Found: C, 28.8; H, 4.9; N, 6.3; Mo, 24.9%. $C_{20}H_{40}Mo_2N_4O_3S_8$ requires: C, 28.8; H, 4.8; N, 6.7; Mo, 23.1%). The ethanol washing was evaporated to dryness. The light brown residue was shown to be the cyclohexyl biuret, $(CyNHCO)_2NCy$, by its i.r. spectrum identical to that of an authentic sample [8].

Reaction of (I) with HBF_4

To ethanol (10 ml), compound (I) (0.1 g) and HBF_4 (two drops of a 40% solution in water) were added under a nitrogen atmosphere. The initial red suspension became a colourless solution. A saturated solution of $NaBPh_4$ in ethanol (*ca.* 5 ml) was added. It was evaporated to a small volume. By adding water (30 ml) a white precipitate was formed. It was shown to be the tetraphenylborate salt of $p\text{-}MeC_6H_4NH_2$, by comparison of its i.r. spectrum with that of an authentic sample.

Results

By reaction at room temperature of *cis*-$Mo(O)_2(chel)_2$ (chel = $CH_3COCHCOCH_3$, S_2CNEt_2) with $p\text{-}MeC_6H_4NSO$ under a nitrogen atmosphere, a slow reaction takes place giving sulphur dioxide and the corresponding molybdenum(VI) oxo-arylimido derivatives (eqn. 1):

$$cis\text{-}Mo(O)_2(chel)_2 + ArNSO \rightarrow Mo(O)(NAr)(chel)_2 + SO_2 \qquad (1)$$

Ar = $p\text{-}MeC_6H_4$
chel = $CH_3COCHCOCH_3$, (I); S_2CNEt_2, (II)

These reactions require the appropriate experimental conditions in order to give the desired product. Moreover they are sensitive to the nature of the substituents of the chelating ligand, since in the case of the phenyl dithiocarbamate derivative we were unable to obtain the corresponding arylimido complex.

For the dark brown dithiocarbamate derivative (II), a single $\nu_{(Mo=O)}$ = 870 cm^{-1} is observed in the i.r. spectrum and the ^1H n.m.r. spectrum of this compound has shown equivalent ethyl groups, with the other signals in the expected position and ratio. For the brick-red acetylacetonate derivative (I), which also shows a single $\nu_{(Mo=O)}$ = 890 cm^{-1} in the i.r. spectrum, the ^1H n.m.r. spectrum has clearly indicated two non equivalent chelating ligands (see Experimental).

A molecular model with the arylimido and the oxygen ligands in a *cis* position was consistent with –CH– groups of the acetylacetonate ligands in different chemical environments.

During the reaction which leads to (II) small amounts of a yellow product, insoluble in the reaction medium, were always obtained. The elemental analyses suggest the formula, $Mo(O)(p\text{-}MeC_6H_4NSO)_2(S_2CNEt_2)_2$ (III). In the i.r. spectrum a band was observed at 880 cm^{-1}, attributable to $\nu_{(Mo=O)}$, while medium-strong absorptions associated with the ArNSO ligand were detected at 1275, 1215 and 1030 cm^{-1} (the absorptions due to the $Mo(S_2CNEt_2)_2$ fragment were similar to those observed in *cis*-$Mo(O)_2(S_2CNEt_2)_2$ and in compound (II)). These absorptions are lower than those detected in rhodium(I) complexes having the sulphinylamine coordinated *via* the S-atom [9b]. On the other hand, a sulphinylamine coordinated *via* the π N = S system should exhibit $\nu_{(N-S)}$ at around 910–960 cm^{-1} [9a, b]. On the basis of these data it is difficult to propose a reasonable structure for compound (III), which also shows two well distinct signals in the ^1H n.m.r. spectrum due to the *para* substitutent of the ArNSO ligands. Moreover this compound was shown to be a conductor in ethanol and in nitrobenzene (Λ_M = 33.8 and 26.4 respectively, calculated for a monomeric derivative).

The origin of this complex is also uncertain. We thought that the SO_2 formed in reaction (1) could reduce the starting bis oxo compound to give the mono oxo species, $Mo(O)(S_2CNEt_2)_2$ which could then coordinate the ArNSO present in solution, as it does with other unsaturated ligands [10]. However, when we have carried out reaction (1) under an atmosphere of sulphur dioxide only the dimeric $Mo_2O_3(S_2CNEt_2)_4$ was obtained. On the other hand, the amounts of compound (III) do not increase, even for very long reaction times, thus excluding a subsequent reaction between compound (II) and ArNSO.

Although compounds (I) and (II) have been fully and satisfactorily characterized, in order to exclude unambiguously the presence in compound (II) of an arylnitroso ligand we have also carried out the synthesis of the corresponding molybdooxaziridine by the route reported by Sharpless [2] (eqn. 2):

$$cis\text{-}Mo(O)_2(S_2CNEt_2)_2 + ArNHOH \rightarrow Mo(O)(ArNO)(S_2CNEt_2)_2 + H_2O \quad (2)$$

$Ar = p\text{-}MeC_6H_4$ (IV)

The red-brown molybdooxaziridine (IV) thus obtained showed $\nu_{(Mo=O)}$ = 940 cm^{-1}, distinctly different from the $\nu_{(Mo=O)}$ observed in the arylimido complex. The different nature of (II) and (IV) was also confirmed by comparison of their ^1H n.m.r. spectra. Since aliphatic sulphinylamines are very sensitive to moisture, we have also attempted the reaction of *cis*-$Mo(O)_2(S_2CNEt_2)_2$ with CyNCO (Cy = C_6H_{11}) another possible nitrene precursor which tolerates the presence of adventitious moisture (eqn. 3):

$$cis\text{-}Mo(O)_2(S_2CNEt_2)_2 + CyNCO \xrightarrow{\text{benzene}}$$
$$\{Mo(O)(NCy)(S_2CNEt_2)_2\} + CO_2 \xrightarrow[H]{CyNCO}$$
$$\{Mo(O)(S_2CNEt_2)_2\} + CyNHCONHCy$$
$$\xrightarrow[cis\text{-}Mo(O)_2(S_2CNEt_2)_2]{CyNCO} Mo_2O_3(S_2CNEt_2)_4 + (CyNHCO)_2NCy \quad (3)$$

However in this case the molybdenum containing product was only $Mo_2O_3(S_2CNEt_2)_4$. We believe that the alkylimido molybdenum derivative is intermediately formed, but it probably further reacts at the RN center with CyNCO, giving urea and the mono-oxo species. The reaction between the mono-oxo derivative with the starting bis-oxo compound gives the dimeric molybdenum product [7], while the urea by reaction with excess CyNCO gives the biuret, and these are the actual final products together with carbon dioxide.

We have studied the reactivity of compounds (I) and (II) towards various molecules [11]. We mention here only the reaction between (I) and HBF_4 in ethanol suspension. By adding $NaBPh_4$ to the resulting clear solution only the BPh_4^- salt of $p\text{-}MeC_6H_4NH_2$ was obtained. Although no molybdenum derivative could be isolated, this reaction has some significance since it is known that an imido ligand triply bonded to a metal is protected from the attack by a proton [12].

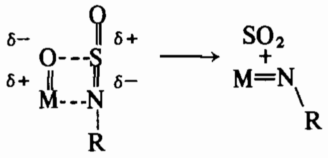
Conclusions

Sulphinylamines appear to be useful precursors of arylimido complexes in their reactions with metal oxo derivatives [8]. On considering the sulphur–nitrogen bond polarized as $-\overset{\delta-}{N}-\overset{\delta+}{S}-$ in view of the reactions of sulphinylamines with HX (X = OH, halogen) or RSH compounds [13] (eqn. 4):

$$R{-}N{=}SO + 2HX \rightarrow RNH_2 + SOX_2$$

$$R{-}N{=}SO + RSH \rightarrow R{-}NH{-}S(O){-}SR \quad (4)$$

the formation of a four member metallocycle intermediate seems likely (eqn. 5)



(5)

This finds support on some recent observations on the reactions of olefins with metal-oxo derivatives [14].

Finally the protonation reaction observed for compound (I) and the reactivity of (I) in several reactions [11], suggest that the arylimido ligand is bent (two electron donor), while the oxo ligand acts as a four electron donor in order to give an 18-electron complex [6].

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