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A new reactivity pattern of low-valent transition-metal hydroxo complexes: straightforward synthesis of hydrosulfido complexes *via* reaction with carbon disulfide†

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A new basic transformation linking two important classes of transition metal compounds; namely, hydroxo and hydrosulfido complexes has been discovered.

Low-valent transition-metal complexes with terminal alkoxo, hydroxo and amido ligands attract considerable interest due to their involvement in industrially relevant or enzyme-catalyzed processes. The basic chemistry of these compounds remains little explored, mainly due to the difficulties encountered in their synthesis, and to the facile decomposition or oligomerisation pathways available.[1] While hydroxo and parent amido complexes are the less studied, recent pioneering works show that these derivatives are endowed with the higher reactivity and, therefore, are the more likely to reveal new reactivity patterns.[1,2]

We have recently found that octahedral [Mo(OR)(η^3-allyl)(CO)$_2$(N-N)] and [Re(OR)(CO)$_3$(N-N)] (N-N = 2,2′-bipyridine, bpy; 1,10-phenanthroline, phen) alkoxo complexes[3] and the related amido derivatives[4] do not possess coordination vacancies or labile ligands (a feature that prevents oligomerisation), react with electrophiles *via* direct attack by the undissociated –OR or –NR$_2$ ligand, and are about as reactive as the more studied group 6–8 complexes.[1,5] We have now initiated the extension of these studies to the homologous hydroxo complexes.[6]

Thus, [Mo(OH)(η^3-C$_3$H$_4$-2-Me)(CO)$_2$(phen)] (**1**) reacts with the stoichiometric amount of carbon disulfide in dichloromethane. The reaction is instantaneous at room temperature, is accompanied by gas evolution and its ^{1}H NMR monitoring in CD$_2$Cl$_2$ showed clean conversion to a single product, **3**, which displayed, in addition to the phen signals, a one-hydrogen singlet at -0.60 ppm.[7] Likewise, the reaction of [Re(OH)(CO)$_3$(bpy)] (**2**) with CS$_2$ afforded a single product **4**, which features a singlet at -2.43 ppm in ^{1}H NMR.[8] The two new products **3** and **4** were isolated in high yields by crystallization using slow diffusion of hexane into their CH$_2$Cl$_2$ solutions. Their structures could not be deduced from spectroscopic data alone and, therefore, were determined by single-crystal X-ray diffraction. The results, displayed in Fig. 1, indicated the [Mo(SH)(η^3-allyl)(CO)$_2$(phen)] (**3**) and [Re(SH)(CO)$_3$(bpy)] (**4**) compositions, and structures similar to those of the hydroxo precursors, *i.e.*, the M–S vector is orthogonal to a plane approximately defined by the N-N chelate and the two CO ligands.

The upfield singlets observed in the ^{1}H NMR spectra of **3** and **4** appear at chemical shifts close to previously reported hydrosulfido complexes.[9] Compounds **3** and **4** were independently prepared by the reactions of [MoCl(η^3-allyl)(CO)$_2$(phen)] and [Re(OTf)(CO)$_3$(bpy)] respectively with NaHS in CH$_2$Cl$_2$–MeOH.[10]

Interest in transition metal hydrosulfido complexes stems from their rich reactivity, the proposed role of M-SH moieties in hydrodesulfurization, and the presence of SH groups in metalloenzymes. The chemistry of hydrosulfido complexes has been dealt with in two very recent, comprehensive reviews.[9] Most synthetic approaches to these compounds employ either the reaction of H$_2$S with metal compounds containing basic ligands (including hydroxo groups),[12] or the reaction of alkaline hydrogenosulfides with metal halides. The synthesis of hydrosulfido complexes by reaction of hydroxo complexes and CS$_2$ has no precedent. We have previously found that the reactions of the methoxo complexes [Mo(OMe)(η^3-allyl)(CO)$_2$(phen)] and [Re(OMe)(CO)$_3$(bpy)] with CS$_2$ afforded the xanthato complexes resulting from the formal insertion of CS$_2$ into the M-O bonds.[3b] Similar insertions into the M-O bonds of the hydroxo complexes **1** and **2** would yield complexes with –SC(S)OH ligands, and subsequent extrusion of carbonyl sulfide, as depicted in Scheme 1, would yield the observed hydrosulfido complexes **3** and **4**.[13] The reaction would be in part driven by the favorable formation of the M–S bond at the expense of a M–O bond.[12]

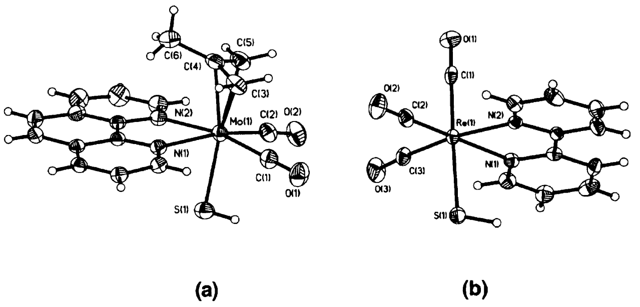
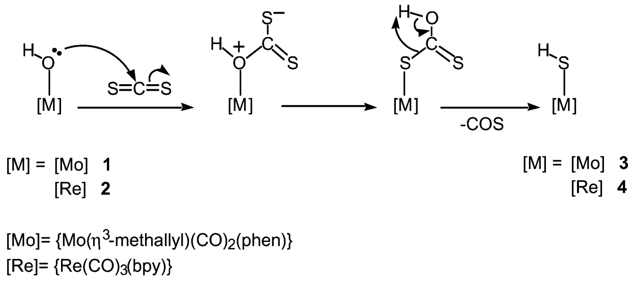


Fig. 1 Thermal ellipsoid (30%) plots of **3** (a) and **4** (b).[11]



Scheme 1

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† Complete details for the synthesis of all compounds, spectroscopic data and X-ray crystallographic data for [Mo(SH)(η^3-C$_3$H$_4$-2-Me)(CO)$_2$(phen)] (**3**) and [Re(SH)(CO)$_3$(bpy)] (**4**). See http://www.rsc.org/suppdata/cc/b2/b210860g/

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The intermediacy of unstable species with hydrogenodithiocarbonato ligands has been proposed in previously studied reactions of platinum hydroxo complexes with CS_2, although the final products of these reactions could not be characterized.[14] The formation of CS_2OH^- is considered to be the first step in the alkaline hydrolysis of CS_2;[15] interestingly, it features a high activation energy, in contrast with the fast reactions of **1** and **2** with CS_2 under mild conditions.

The interaction of carbon disulfide with transition metal compounds has been extensively studied. The homogeneous hydrogenolysis of CS_2 to H_2S catalyzed by a molybdenum sulfido-bridged dimeric complex (2–3 atm of H_2, 75 °C) has been proposed as a model for the industrially important heterogeneously-catalyzed hydrodesulfurization.[16] Previous transformations of C–S groups into HS groups at transition metal complexes involve either insertion of CS_2 into M–H bonds,[17] reaction of a cluster compound under strong conditions,[18] or reactions of dithiocarbonato,[19] dithiocarbamato[20] or phosphoniodithioformato[21] ligands.

To conclude, we have found that electronically and coordinatively saturated monomeric Mo(II) and Re(I) hydroxo complexes react under mild conditions with stoichiometric amounts of CS_2 to yield new hydrosulfido complexes. The reactions are both synthetically useful and unprecedented.

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6 The hydroxo complex $[Mo(OH)(\eta^3\text{-}C_3H_4\text{-}2\text{-}Me)(CO)_2(phen)]$ (**1**) has been recently obtained: (*a*) D. Morales, M. E. N. Clemente, J. Pérez, L. Riera, V. Riera and D. Miguel, *Organometallics*, 2002, **21**, 4934; The complex $[Re(OTf)(CO)_3(bpy)]$ (**2**) is analogous to the previously known hydroxo complex $[Re(OH)(CO)_3(bpy')]$ (bpy′ = 4,4′-dimethyl-2,2′-bipyridine) (*b*) D. H. Gibson and X. Yin, *J. Am. Chem. Soc.*, 1998, **120**, 11200. Full details are given as Supplementary Information†.

7 Reaction of **1** with CS_2. To a solution of **1** (0.050 g, 0.124 mmol) in CH_2Cl_2, CS_2 (9 μL, 0.124 mmol) was added. After 5 minutes stirring at room temperature, the volatiles were evaporated under reduced pressure and the residue was washed with hexane (3 × 15 mL). Slow diffusion of hexane into a solution of $[Mo(SH)(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)]$(**3**) in CH_2Cl_2 (10 mL) at −30 °C afforded dark red crystals of **3**. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.045 g, 87%. IR(CH_2Cl_2): 1940, 1857 (ν_{CO}); (KBr): 2359 (ν_{SH}). ^1H NMR(CD_2Cl_2): 9.01, 8.45 [m, 2H each, phen] 7.95 [s, 2H, phen], 7.79 [m, 2H, phen], 2.86 [s, 2H, H_{syn}], 1.58 [s, 2H, H_{anti}], 0.62 [s, 3H, $\eta^3\text{-}C_3H_4\text{-}CH_3\text{-}2$], −0.60 [s, 1H, S*H*]. Full details are given as Supplementary Information†.

8 Reaction of **2** with CS_2. To a solution of **2** (0.080 g, 0.179 mmol) in CH_2Cl_2 (20 mL), CS_2 (13 μL, 0.179 mmol) was added causing an immediate color change from orange to red. The resulting solution was concentrated under reduced pressure to a volume of 5 mL and layered with hexane, affording crystals of **4**, one of which was used for the structure determination by X-ray diffraction. Yield: 0.070 g, 84 %. IR(CH_2Cl_2): 2011, 1910, 1891 (ν_{CO}). ^1H NMR(CD_2Cl_2): 9.01, 8.22, 8.05 and 7.50 [m, 2H each, bpy], −2.43 [s(br), 1H, S*H*]. Full details are given as Supplementary Information†. The analogous reaction of $[Re(OH)(CO)_3(bpy')]$ with CS_2 is included in the Supplementary Information†.

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11 X-ray data for **3**. $C_{18}H_{16}MoN_2O_2S$: crystal dimensions 0.14 × 0.16 × 0.21 mm³, monoclinic, space group $P2(1)/n$, a = 8.6005 (10) Å, b = 15.0923 (17) Å, c = 13.5883 (15) Å, β = 101.228 (2) °, V = 1730.0 (3) Å³, Z = 4, T = 299 (2) K. A total of 2498 unique reflections ($2.04 \leq \theta \leq 23.28°$) was measured. Full-matrix least-squares refinement on F^2 (221 variables) converged to R = 0.0296, *wR2* = 0.0787. X-ray data for **4**, $C_{13}H_9N_2O_3ReS$: crystal dimensions 0.05 × 0.11 × 0.17 mm³, triclinic, space group $P\bar{1}$, a = 8.174 (5) Å, b = 8.372 (5) Å, c = 10.931 (7) Å, α = 100.773 (9)°, β = 103.413 (9)°, γ = 93.959 (9)°, V = 709.8 (8) Å³, Z = 2, T = 299 (2) K. A total of 2051 unique reflections ($1.96 \leq \theta \leq 23.62°$) was measured. Full-matrix least-squares refinement on F^2 (185 variables) converged to R = 0.0279, *wR2* = 0.0662. CCDC reference numbers 193532 and 193533. See http://www.rsc.org/suppdata/cc/b2/b210860g/ for crystallographic files in CIF or other electronic format.

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