DALTON COMMUNICATION

Synthesis of a rare tridentate dithiocarboxylato complex of molybdenum(IV) †

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Received 2nd April 2001, Accepted 22nd May 2001
First published as an Advance Article on the web 18th June 2001

Treating [Mo(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] with S$_8$ in tetrahydrofuran at reflux temperature affords [Mo(O)(κ^3-S$_2$CC$_6$H$_4$Me-4){κ^3-HB(pz)$_3$}] whose structure has been determined by X-ray diffraction.

The addition of elemental chalcogens to alkylidyne ligands generates either chalcogenobenzoyl or dichalcogenocarboxylate ligands depending on the alkylidyne complex. Thus, low-valent Group 6 alkylidyne complexes typically afford dichalcogenocarboxylates, M(κ^2-A$_2$CR),[1] whereas those of Group 8 form chalcogenobenzoyls M(η^2-ACR),[2] with no reported subsequent reactivity towards excess chalcogen. For example, [W(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (pz = pyrazol-1-yl)[3] and [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)][4] were converted to the dithiocarboxylato complexes [W(κ^2-S$_2$CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (**1**)[5] and [W(κ^2-S$_2$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] (**2**)[1] respectively (Fig. 1). The suspected intermediacy of chalcogenoacyls in the formation of such dichalcogenocarboxylates has since been established experimentally. It was recently reported that [M(η^2-ACC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (M = Mo, W; A = S, Se, all combinations), may be trapped by "Ru(CO)$_2$(η^5-C$_2$B$_9$H$_{11}$)" to afford [MRu(μ-1κ*C*$^{\alpha}$, 1:2κ*A*-ACC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo, W; A = S, Se, all combinations) (**3**).[6] Moreover Hill has recently employed methylthiirane as a chalcogen transfer reagent in a direct synthesis of [Mo(η^2-SCC$_6$H$_4$OMe-4)(CO)$_2${κ^3-HB(pz)$_3$}] (**4**) which may be subsequently converted to both *homo*- and *hetero*-dichalcogenocarboxylate species [Mo(κ^2-S(A)CC$_6$H$_4$OMe-4)(CO)$_2${κ^3-HB(pz)$_3$}] (A = S, Se) (**5**).[7,8] Here we report another facet to the reaction of the versatile alkylidyne fragment with chalcogens.

Treating [Mo(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] with elemental sulfur at reflux temperatures (tetrahydrofuran) proceeds cleanly over a period of 24 hours to provide a stable red complex in acceptable yield (43%) after chromatography. The infrared solution spectrum (CH_2Cl_2) indicates the loss of both carbonyl ligands. ^{1}H and ^{13}C{^{1}H} NMR data confirm the retention of both the HB(pz)$_3$ ligand and the tolyl group, with resonances for the latter characteristic of an AB quartet spin system. ‡ Since the formulation does not follow from spectroscopic data alone, a single crystal X-ray diffraction study was required. The crystallographic study unequivocally identified the compound as [Mo(O)(κ^3-S$_2$CC$_6$H$_4$Me-4){κ^3-HB(pz)$_3$}] (**6**) (Fig. 2) and represented the unprecedented conversion of an alkylidyne fragment to a rare example of a *mononuclear* tridentate dithiocarboxylato complex *via* well characterised intermediates (Scheme 1). § The oxo ligand is presumed to arise from oxidation or hydrolysis during the chromatographic purification.

Prior to this study the dithiobenzoato-*S*,*S*′ complex [Mo(O)(κ^3-S$_2$CC$_6$H$_5$)(κ^2-SS(S)CC$_6$H$_5$)][9] (**7**) and dithioacetato-*S*,*S*′

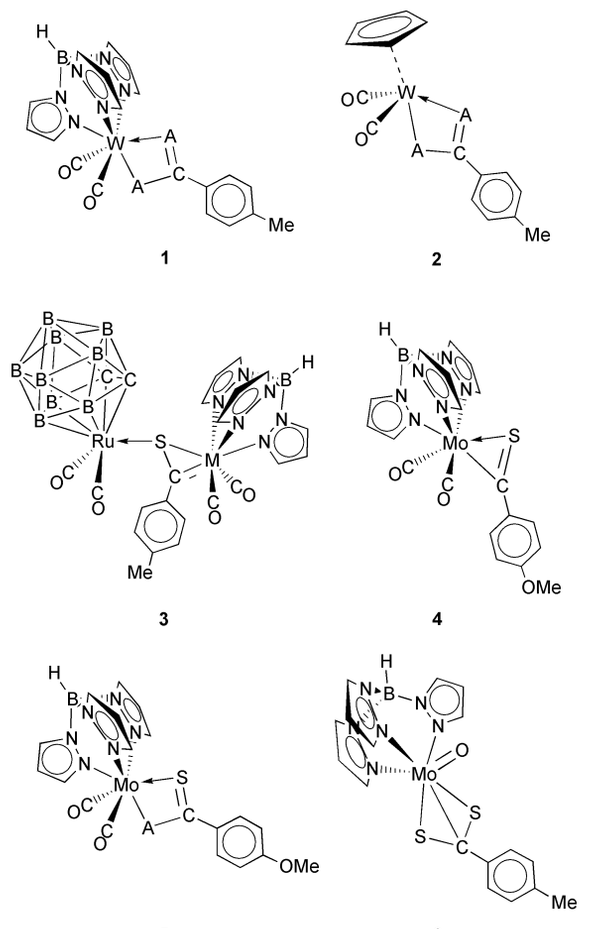


Fig. 1 Examples of η^2-thioacyl, η^2-dithiocarboxylato and κ^3-dithiocarboxylato complexes.

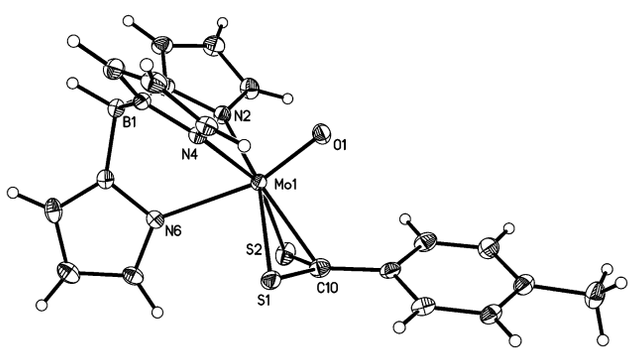


Fig. 2 Molecular structure of [Mo(O)(κ^3-S$_2$CC$_6$H$_4$Me-4){κ^3-HB(pz)$_3$}] with thermal ellipsoids shown at 40% probability level.

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b102947a/

DOI: 10.1039/b102947a

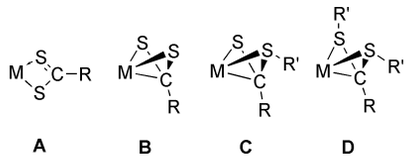
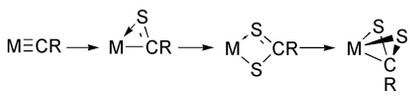


Fig. 3 Bonding in η^2-dithiocarboxylate (**A**), κ^3-dithiocarboxylate (**B**), κ^3-dithiocarboxylate ester (**C**) and dithioacetal carbanion (**D**) complexes.



Scheme 1 Stepwise reaction of the alkylidyne fragment (M≡CR) with S_8 showing known intermediates.

derivative $[Fe(\kappa^3\text{-}S_2CMe)(\kappa^1\text{-}dppm)(\eta\text{-}C_5H_5)]$[10] (**8**) represented the only crystallographically characterised examples of the basic tridentate κ^3-S_2CR dithiocarboxylato ligand (**B**). Comparable architectures have been reported for tridentate dithiocarboxylic ester (κ^3-R′S(S)CR) (**C**),[11] dithioacetal carbanion (κ^3-$(R'S)_2CR$) (**D**),[11,12] phosphinodithioformato (κ^3-S_2CPR_3) and phosphinothioformate ester (κ^3-R′S(S)CPR_3) complexes.[13] In all cases the butterfly motif observed for complexes with a κ^3-S_2C core differs dramatically from related mononuclear κ^2-S_2C (**A**) complexes such as **2** wherein the MS_2C unit is approximately planar (Fig. 3).[1] For the family of tridentate ligands, κ^3-S_2CR (**B**), κ^3-R′S(S)CR (**C**), κ^3-$(R'S)_2CR$ (**D**), the small M–S–C angle (CSD[14] range 63.05–55.50°, mean 58.51°) is associated with short M–C separations (CSD range 2.215–2.038 Å, mean 2.145 Å). Comparison of these parameters for the present example (**6**) (62.95(14)°, 63.05(14)°; 2.222(4) Å) and the most closely related complex $[Mo(O)(\kappa^3\text{-}S_2CC_6H_5)(\kappa^2\text{-}SS(S)CC_6H_5)]$ (**7**) (63.05°, 63.37°; 2.217(3) Å) suggests the sterically demanding $HB(pz)_3$ ligand has little influence on the overall geometry.

This study identifies a novel synthetic route to a complex containing a κ^3-S_2CR moiety via the conversion of an alkylidyne ligand. We are currently exploring related transformations.

Acknowledgements

We thank the ERDF Centre for 21st Century Materials at the University of Durham for funding (J. M. M.).

Notes and references

‡ Data for **6**: $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{\kappa^3\text{-}HB(pz)_3\}]$ (0.1 g) and sulfur (0.01 g) in tetrahydrofuran (25 cm^3) was brought to reflux and heating continued for 24 h. The solvent was removed, the residue redissolved in 1 cm^3 of dichloromethane and chromatographed (silica gel, hexane–dichloromethane, 4:1). The red eluate was collected, solvent removed *in vacuo* and the residue crystallised from pentane–chloroform 4:1. Yield 0.045 g (43%). Found: C, 41.55; H, 3.53; N, 17.32. $C_{17}H_{17}BMoN_6OS_2$ requires C, 41.30; H, 3.47; N, 17.01%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.39 [s, 3H, Me], 5.82, 6.44 [apparent triplet × 2, 1:2, 3H, H^4, pz, ^3J(HH) = 2 Hz], 7.09, 7.92 [$(AB)_2$, 4H, C_6H_4, J(AB) = 8 Hz], 6.95, 7.33, 7.87, 8.25 [d × 4, 1:1:2:2, 6H, $H^{3,5}$pz, ^3J(HH) = 2 Hz]; ^{13}C{1H} NMR ($CDCl_3$, 25 °C): δ 147.1, 143.7 [2:1, C^3 pz], 140.7 [C^3 C_6H_4], 136.7, 133.1 [2:1, C^5 pz], 128.0, 126.0 [C_6H_4], 106.7, 104.1 [2:1, C^4 pz], 21.1 [C_6H_4Me].

§ Crystal data for **6** $C_{17}H_{17}BMoN_6OS_2$, M = 492.24, monoclinic, space group $C2/c$, a = 25.788(5), b = 8.499(2), c = 18.441(4) Å, β = 100.269(4)°, U = 3977.0(15) Å^3, Z = 8, D_c = 1.644 Mg m^{-3}, μ(Mo-Kα) = 0.890 mm^{-1}, F(000) = 1984. A pale orange thin plate of dimensions 0.24 × 0.22 × 0.02 mm^3 was used. 4928 independent reflections were measured on a Smart 1k CCD diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71093 Å, T = 150(2) K) using 0.3° ω scans. The structure was solved by direct methods and all non-hydrogen atoms refined anisotropically using full matrix least squares based on F^2 and absorption corrected data to give R_1 = 4.59% and wR_2 = 9.88% [4068 observed reflections, $|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 57°$, 257 parameters]. CCDC reference number 164197. See http://www.rsc.org/suppdata/dt/b1/b102947a/ for crystallographic data in CIF or other electronic format.

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