The Synthesis and Characterization of μ-Hydrido-bis-(μ-sulphide)-ditungsten(III) Complexes: the *X*-Ray Crystal Structure of $[HPPh_3][Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]$

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Summary The reaction of $WCl_4(Me_2S)_2$ with Et_3SiH yields $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$ from which the anion $[Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]^-$ can be prepared; a single-crystal *X*-ray diffraction study of $[HPPh_3][Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]$ shows that these complexes possess a confacial bioctahedral framework with a formal W–W triple bond of length 2·410(7) Å.

IN spite of the current interest in the role of hydrido complexes in catalytic reactions,[1] little attention has been given to reactions between hydride and organosulphur ligands. Prompted by the observation that the loss of RCl from $WCl_5(SR)$ occurs *via* a carbonium ion mechanism,[2] we have investigated the possibility of inducing loss of RH from complexes of tungsten or molybdenum containing MH(SR) or $MH(SR_2)$ moieties. In our studies, we have examined the reaction of $WCl_4(Me_2S)_2$ with Et_3SiH (in an excess) in CH_2Cl_2 solution. The metathetical reaction yields as its major tungsten-containing product (60% yield) a diamagnetic purple solid which has been deduced to be $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$ (**1**). The analytical and spectroscopic data for this material support this formulation, and its reactions with Cl^- have been shown to liberate 1 mol. equiv. of Me_2S and salts with the $[Cl_3W(\mu\text{-}H)$-

(μ-$Me_2S)_2WCl_3]^-$ anion. The crystal structure† of $[HPPh_3]$-$[Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]$ (**2**) has been determined. These

$$Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$$
(**1**)

$$[HPPh_3][Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]$$
(**2**)

dimeric tungsten(III) complexes are the first examples of transition metal hydrido compounds known to have *simple* sulphide molecules co-ordinated to the metal centre(s), and they also belong to a very rare group of transition metal dimers in which the metal atoms are bridged by two simple sulphide ligands.[3–5]

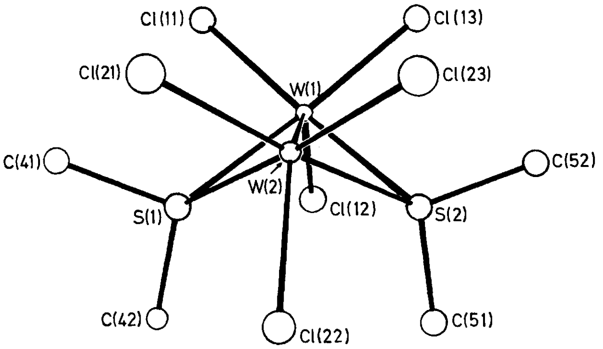

FIGURE. ORTEP drawing of the structure of the $[Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]^-$ anion. Important bond lengths and angles: W(1)–W(2), 2·410(7); W(1)–S(1), 2·37(3); W(1)–S(2), 2·38(3); W(1)–Cl(11) 2·40(3); W(1)–Cl(12), 2·40(4); W(1)–Cl(13), 2·36(3); W(2)–S(1), 2·39(4); W(2)–S(2), 2·35(3); W(2)–Cl(21), 2·40(3); W(2)–Cl(22), 2·46(2); W(2)–Cl(23), 2·39(3) Å; ∠W(1)–S(1)–W(2), 60·9(8); W(1)–S(2)–W(2), 61·2(8)°.

The ORTEP view of the anion of (**2**) (Figure) shows that it has a confacial bioctahedral structure with the vacant bridging site being occupied by the hydride, which was not located in this determination. The short W–W separation [2·410(7) Å] and the acute angles subtended at the μ-S atoms [60·9(8) and 61·2(8)°] are consistent with observations made on the isoelectronic and isostructural $W_2Cl_9^{3-}$ ion,[6] in which it is generally accepted that a formal triple bond exists.[7] The tungsten–sulphur bond lengths [2·35(3)—2·39(3) Å], although poorly defined in this preliminary structural study, are significantly shorter than those found in $(Me_2S)Cl_2W(\mu\text{-}SEt)_3WCl_2(SMe_2)$,[8] in which the Me_2S groups are terminally bonded to $W^{III/IV}$ [2·623(3) and 2·613(9) Å]. McCarley and co-workers found a similar feature in the complexes $(C_4H_8S)Br_2M(\mu\text{-}Br)_2(\mu\text{-}SC_4H_8)MBr_2(C_4H_8S)$ (M = Nb, Ta).[9]

The presence of the hydride ligand in (**1**) and (**2**) is confirmed by the spectroscopic data in the Table. The ^1H n.m.r. signal of the μ-H in (**1**) and (**2**) is at an unexpectedly low-field position, but similar observations have been reported recently for other hydrido-bridged dimers of the early transition metals[11,12] (see Table for example). The unusual temperature dependence of the chemical shift for the μ-H resonance in (**1**) and (**2**) is probably due to a temperature-dependent anisotropy in the metal–metal bond, and the fact that the coupling between the ^{183}W nuclei and the μ-H in these complexes is invariant with temperature suggests that the W–H–W moiety remains intact under all temperature conditions.[12]

In view of the potential reactivity of μ-hydrido complexes, we have carried out preliminary studies on (**1**). For example, it has been shown that Et_2S_2 is reduced by (**1**) to EtSH, with the concomitant formation of the μ-SEt analogue of (**1**).

The reaction between $WCl_4(Me_2S)_2$ and Et_3SiH deserves further comment. The production of (**1**) involves the reduction of W^{IV} to W^{III} *via* the reductive elimination of H_2 or HCl (identified by g.c.–m.s.) from non-isolable reactive intermediates $WCl_{(4-n)}H_n(Me_2S)_2$. Of more interest, however, to our original hypothesis, is the generation of small quantities of CH_4 during the reaction (CH_3D when

TABLE. Spectroscopic data for μ-hydrido and μ-deuterido complexes.

Compound	ν_{sym} (M–H–M) or ν_{sym} (M–D–M)/cm^{-1}	ν_{asym} (M–H–M) or ν_{asym}(M–D–M)/cm^{-1}	$\delta(\mu\text{-}^1H)$ or $\delta(\mu\text{-}^2H)$	$J(^{183}W\text{–}^1H)$ or $J(^{183}W\text{–}^2H)$/Hz
(**1**)	1637	1243	+3·76 (+20 °C) +3·35 (−80 °C)	109*
(**2**) ($HPPh_3^+$ cation)	1675	1285	+3·60 (+20 °C) +3·24 (−80 °C)	109*
(**1d**)[a]	1148	889	+3·7 (+23 °C)	17
(**2d**)[a] ($HPPh_3^+$ cation)	1162	920	+3·5 (+20 °C)	17
(**3**)[b]	1538	1240	—	—
(**3d**)[b]	1120	896	—	—
(**4**)[c]	—	—	+7·87 (+60 to −60 °C)	96*
(**4d**)[c]	—	—	+7·90 (+16 °C)	16

* These values are independent of temperature.

[a] (**1d**) and (**2d**) are the deuterio-analogues of (**1**) and (**2**); (**1d**) prepared from $WCl_4(Me_2S)_2 + Et_3SiD$; (**2d**) from (**1d**) by displacement of Me_2S by Cl^-. [b] (**3**) = $[Cl_3W(\mu\text{-}H)(\mu\text{-}Cl)_2WCl_3]^{3-}$, (**3d**) = $[Cl_3W(\mu\text{-}D)(\mu\text{-}Cl)_2WCl_3]^{3-}$, see ref. 10. [c] (**4**) = $[W_2(\mu\text{-}H)(OPr^i)_7]_2$, (**4d**) = $[W_2(\mu\text{-}D)(OPr^i)_7]_2$, see ref. 12.

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† *Crystal data:* $[HPPh_3][Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]$, triclinic, space group $P\bar{1}$; a = 9·282(5), b = 13·310(5), c = 13·114(7) Å; α = 111·32(4), β = 91·99(4), γ = 93·50(4)°; U = 1504 Å^3; D_c (+25 °C) = 2·01 g cm^{-3}; Z = 2. Of the 2789 reflections collected at −100(5) °C on a CAD-4 diffractometer using Mo-K_α radiation in the range 2° $\leqslant \theta \leqslant$ 20°, only 783 had $I > 2{\cdot}5\,\sigma(I)$. The structure was solved by heavy atom methods and refined by full-matrix least squares techniques. The phenyl ring carbon atoms were refined as rigid bodies. The paucity of data precluded attempts to introduce anisotropic thermal parameters. Final agreement factor R = 0·078; goodness-of-fit = 0·998.

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Et_3SiD is used). Although not apparently related to the synthetic pathway of (**1**), it must arise from a reaction between the methyl group of a Me_2S ligand, and the introduced hydride at the metal centre(s). This aspect of the reaction is still under investigation.

The financial support of Imperial Oil Ltd. and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. The authors thank Drs. M. Sisley, P. W. Codding, R. T. Oakley, R. Yamdagni, and V. D. Patel, and Mr. K. B. Burgess for helpful discussions and/or experimental assistance.

(*Received*, 28*th July* 1981; *Com.* 921.)

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