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Reactions of the (μ-Hydrido)bis(μ-dimethyl sulfide)bis(trichlorotungstate(III)) Ion and Trichlorotungsten(III)bis(μ-dimethyl sulfide)(μ-hydrido)(dimethyl sulfide)dichlorotungsten(III)[1]

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Reactions of the compound $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_2(Me_2S)]$ (**1**) and salts of the derived anion $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_3]^-$ (**2**) are described in which several new W(III) compounds were prepared. Reactions of halocarbons with either **1** or **2** resulted in the replacement of the bridging hydride by halide, with retention of the confacial bioctahedral structure. Reaction of **1** with benzyl chloride gave rise to the compound $[PhCH_2(CH_3)_2S]^+[Cl_3W(\mu\text{-Cl})(\mu\text{-Me}_2S)_2WCl_3]^-$ (**3**), whose X-ray crystal structure was determined. This benzyldimethylsulfonium salt crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.094$ (1) Å, $b = 11.995$ (2) Å, $c = 14.845$ (4) Å, $\alpha = 69.53$ (2)°, $\beta = 66.49$ (2)°, $\gamma = 72.43$ (1)°, and $Z = 2$. The structure refined to $R = 0.052$ and $R_w = 0.066$ based on 5907 observed reflections. The confacial bioctahedral anion of **3** is very similar to that previously observed in **2**, but the W–W bond distance is lengthened by the presence of a bridging chloride in place of a μ-H group. Reactions of **1** with neutral ligands failed to displace the μ-H atom. For example reaction with pyridine resulted in the replacement of all the dimethyl sulfide ligands, but the μ-H is retained in an edge-sharing bioctahedral structure, $(py)_2Cl_2W(\mu\text{-H})(\mu\text{-Cl})WCl_2(py)_2$. Acetonitrile, however, only displaced the terminal dimethyl sulfide to yield the neutral complex $Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_2(MeCN)$.

Introduction

Synthetic pathways to tungsten(III) chemistry have proved to be relatively elusive, and as a consequence, the chemistry of tungsten(III) has been slower to develop than the corresponding chemistry of molybdenum.[2] In a number of cases, the reports of W(III) complexes have lacked structural data to verify their authenticity.[3] A recent publication by Chisholm and co-workers[4] referred to this problem in reporting the synthesis and characterization of $NaW_2Cl_7(THF)_5$, a complex that it is claimed will open a much easier route to $X_3W\equiv WX_3$ chemistry. We recently reported[5] the synthesis and properties of two compounds containing the moiety $[W^{III}(\mu\text{-H})(\mu\text{-Me}_2S)W^{III}]$, namely the neutral species $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_2(Me_2S)]$ (**1**) and salts of the derived anion $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_3]^-$ (**2**). We have found that, like $NaW_2Cl_7(THF)_5$, **1** and **2** can also be used to make an easy entry into the realm of tungsten(III) chemistry. Compound **1** is readily prepared from the reaction of $WCl_4(Me_2S)_2$ with triethylsilane, and the anion **2** is readily obtainable from **1** by a nucleophilic displacement reaction with chloride. In this paper we report some of the reactions of **1** and **2** that lead to new tungsten(III) species and in particular the compound $[PhCH_2(CH_3)_2S]^+[Cl_3W(\mu\text{-Cl})(\mu\text{-Me}_2S)_2WCl_3]^-$ (**3**), whose structure is described. By comparison of this structure with that of its μ-H analogue, $[Ph_4P]^+[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_3]^-$, we have been able to extend our interest in comparing the effects that bridging ligands have on metal–metal interactions in confacial bioctahedral (M_2L_9) structures.[6] M_2L_9 complexes have been analyzed previously from a theoretical standpoint by Hoffmann and Summerville[7] and by Cotton and co-workers.[8]

Results and Discussion

Reactions of $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_2(Me_2S)]$ (1) and the $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_3]^-$ Anion (2) with Halocarbons. The reactions of hydrido complexes with halocarbons have been studied

Table I. Atomic Positional Parameters for the Non-Hydrogen Atoms of the Anion $[Cl_3W(\mu\text{-Cl})(\mu\text{-Me}_2S)_2WCl_3]^-$ in **3**

atom	x/a	y/b	z/c
W(1)	0.02406 (4)	0.10511 (4)	0.23723 (3)
W(2)	0.23069 (4)	0.19190 (4)	0.13164 (3)
Cl(1)	0.0060 (3)	0.3136 (2)	0.1140 (2)
Cl(2)	−0.1739 (3)	0.1956 (3)	0.3565 (2)
Cl(3)	0.0303 (3)	−0.0930 (3)	0.3550 (2)
Cl(4)	−0.1213 (3)	0.0669 (3)	0.1697 (2)
Cl(5)	0.2674 (3)	0.3821 (3)	0.1337 (2)
Cl(6)	0.4526 (3)	0.0889 (3)	0.1401 (2)
Cl(7)	0.3140 (3)	0.2511 (3)	−0.0523 (2)
S(1)	0.2080 (3)	0.0086 (2)	0.1156 (2)
S(2)	0.1541 (3)	0.1454 (3)	0.3139 (2)
C(1)	0.1869 (12)	0.0043 (12)	0.0012 (9)
C(2)	0.3142 (12)	−0.1384 (11)	0.1493 (10)
C(3)	0.2463 (13)	0.0270 (13)	0.3920 (10)
C(4)	0.0864 (12)	0.2675 (12)	0.3780 (9)

extensively and often result in the reduction of the halocarbon and the incorporation of the halide into the metal complex.[9] Both terminal and bridging hydrides might be expected to be capable of participating in reactions of this type, but in most of the reported cases an anionic hydrido complex such as $HFe(CO)_4^-$ has been employed.[10–12] This is predicated by the nature of the reaction, since it would involve the nucleophilic transfer of hydride from a transition metal to an electrophilic carbon center.[10] Hence the hydrido ligand needs to be hydridic rather than protonic in character. A recent example involving neutral hydride complexes of an early heavy transition element was reported by Walton and co-workers,[13] who described the reactions of mono- and binuclear rhenium hydrides with halocarbons. It was therefore of interest to examine the reactions of **1** and **2** with selected halocarbons in order to ascertain whether the μ-H ligand in these complexes would be able to cleave a C–X bond and whether the confacial bioctahedral framework would remain intact during such a reaction. We have been unable to find any explicit example of this type of reaction in the literature.

Reaction of the neutral complex **1** with benzyl chloride in a 1,2-dichloroethane solution at 80 °C yielded an orange-red compound, which after recrystallization from dichloromethane proved

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Table II. Bond Distances (Å) and Bond Angles (deg) for the [Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]⁻ Anion in 3

	Distances		
		W(1)–W(2)	2.4772 (8)
W(1)–Cl(1)	2.513 (3)	W(2)–Cl(1)	2.499 (3)
W(1)–S(1)	2.380 (3)	W(2)–S(1)	2.363 (4)
W(1)–S(2)	2.371 (4)	W(2)–S(2)	2.380 (3)
W(1)–Cl(2)	2.395 (3)	W(2)–Cl(5)	2.424 (4)
W(1)–Cl(3)	2.387 (3)	W(2)–Cl(6)	2.389 (3)
W(1)–Cl(4)	2.401 (4)	W(2)–Cl(7)	2.400 (3)
S(1)–C(1)	1.81 (2)	S(2)–C(3)	1.80 (1)
S(1)–C(2)	1.80 (1)	S(2)–C(4)	1.80 (2)

	Angles		
W(1)–Cl(1)–W(2)	59.24 (6)	W(1)–S(2)–W(2)	62.85 (9)
W(1)–S(1)–W(2)	62.98 (8)		
Cl(1)–W(1)–S(1)	94.67 (8)	Cl(1)–W(2)–S(1)	95.4 (1)
Cl(1)–W(1)–S(2)	95.2 (1)	Cl(1)–W(2)–S(2)	95.29 (9)
S(1)–W(1)–S(2)	97.7 (1)	S(1)–W(2)–S(2)	97.9 (1)
Cl(1)–W(1)–Cl(2)	86.00 (8)	Cl(1)–W(2)–Cl(5)	85.9 (1)
Cl(1)–W(1)–Cl(3)	177.2 (1)	Cl(1)–W(2)–Cl(6)	175.7 (1)
Cl(1)–W(1)–Cl(4)	85.6 (1)	Cl(1)–W(2)–Cl(7)	85.24 (9)
S(1)–W(1)–Cl(2)	175.0 (1)	S(1)–W(2)–Cl(5)	175.21 (8)
S(1)–W(1)–Cl(3)	86.60 (9)	S(1)–W(2)–Cl(6)	87.7 (1)
S(1)–W(1)–Cl(4)	86.2 (4)	S(1)–W(2)–Cl(7)	86.2 (1)
S(2)–W(1)–Cl(2)	87.2 (1)	S(2)–W(2)–Cl(5)	86.5 (1)
S(2)–W(1)–Cl(3)	87.1 (1)	S(2)–W(2)–Cl(6)	87.2 (1)
S(2)–W(1)–Cl(4)	176.00 (9)	S(2)–W(2)–Cl(7)	175.8 (1)
Cl(2)–W(1)–Cl(3)	95.52 (9)	Cl(5)–W(2)–Cl(6)	90.8 (1)
Cl(2)–W(1)–Cl(4)	89.0 (1)	Cl(5)–W(2)–Cl(7)	89.3 (1)
Cl(3)–W(1)–Cl(4)	92.0 (1)	Cl(6)–W(2)–Cl(7)	92.0 (1)
C(1)–S(1)–C(2)	103.0 (7)	C(3)–S(2)–C(4)	103.5 (7)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for the Benzyldimethylsulfonium Cation in 3

	Distances		
S(3)–C(6)	1.80 (1)	S(3)–C(8)	1.80 (1)
S(3)–C(7)	1.79 (2)	C(8)–C(9)	1.49 (2)

	Angles		
C(6)–S(3)–C(7)	101.2 (8)	C(9)–C(8)–S(3)	113 (1)
C(6)–S(3)–C(8)	101.6 (6)	C(10)–C(9)–C(8)	121 (2)
C(7)–S(3)–C(8)	99.7 (7)	C(14)–C(9)–C(8)	120 (1)

Table IV. Selected Nonbonded Contacts for 3 (Å)

Cl(1)⋯S(1)	3.598 (4)	S(1)⋯Cl(3)	3.269 (3)
Cl(1)⋯S(2)	3.607 (4)	S(1)⋯Cl(4)	3.265 (4)
S(1)⋯S(2)	3.577 (5)	S(1)⋯Cl(6)	3.292 (5)
Cl(1)⋯Cl(2)	3.348 (3)	S(1)⋯Cl(7)	3.254 (4)
Cl(1)⋯Cl(4)	3.339 (5)	S(2)⋯Cl(2)	3.285 (4)
Cl(1)⋯Cl(5)	3.353 (5)	S(2)⋯Cl(3)	3.280 (5)
Cl(1)⋯Cl(7)	3.318 (3)	S(2)⋯Cl(5)	3.293 (4)
Cl(2)⋯Cl(3)	3.455 (4)	S(2)⋯Cl(6)	3.288 (4)
Cl(2)⋯Cl(4)	3.361 (5)	Cl(3)⋯Cl(4)	3.444 (5)
Cl(5)⋯Cl(7)	3.390 (5)	Cl(5)⋯Cl(6)	3.425 (4)
Cl(6)⋯Cl(7)	3.445 (5)		

to be the sulfonium salt of the μ-chloro anion derived from 1, viz. [PhCH₂(CH₃)₂S]⁺[Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]⁻·xCH₂Cl₂ (3). The expected production of toluene from the reduction of PhCH₂Cl by hydride was confirmed by a GC study of the reaction volatiles. Crystals of 3 suitable for an X-ray crystal structure determination were obtained from a CH₂Cl₂/hexane solution that had been cooled to ~–20 °C. X-ray crystallographic, IR, ¹H NMR, and mass spectroscopic analyses showed that the compound contains the sulfonium cation and ditungstate anion referred to above but, in addition, both dichloromethane and hydrogen chloride of crystallization. The complete formulation of 3 is thus [PhCH₂(CH₃)₂S]⁺[Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]·2CH₂Cl₂·0.5HCl. The positional parameters of the non-hydrogen atoms are given in Table I, while selected bond lengths and bond angles are listed in Tables II and III for the cation and the anion respectively. Important nonbonded contacts are given in Table IV, and the crystallographic parameters are given in Table V. The atoms are numbered according to the ORTEP diagrams (Figures 1 and 2). The structure of the benzyldimethylsulfonium cation

Table V. Crystallographic Data for [PhCH₂(CH₃)₂S][Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]·2CH₂Cl₂·0.5HCl

chemical formula:	fw: 1081.5
C₁₅H₂₉.₅S₃Cl₁₁.₅W₂	space group: P1̄
a = 11.094(1) Å	T = 22 °C
b = 11.995(2) Å	λ = 0.710 69 Å
c = 14.845(4) Å	ρcalcd = 2.16 g cm⁻³
α = 69.53(2)°	μ = 86.5 cm⁻¹
β = 66.49(2)°	transmission coeff = 0.322–0.219
γ = 72.43(1)°	R(F₀) = 0.052
V = 1667(2) Å³	Rw(F₀) = 0.066
Z = 2	
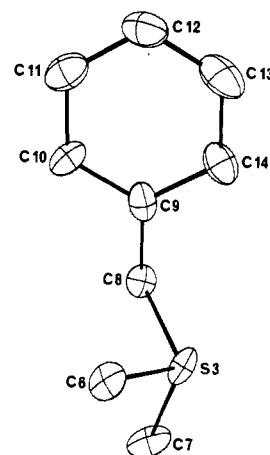
Figure 1. ORTEP plot of the [(PhCH₂)(CH₃)₂S]⁺ cation in the complex [(PhCH₂)(CH₃)₂S]⁺[Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]⁻·2CH₂Cl₂·0.5HCl (3), drawn at the 50% probability level.
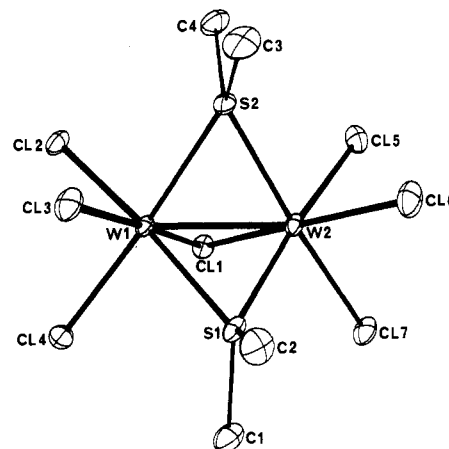
Figure 2. ORTEP plot of the anion [Cl₃W(μ-Cl)(μ-Me₂S)₂WCl₃]⁻ in 3, drawn at the 50% probability level.

(Figure 1) shows C–S bond lengths of 1.80 (1) Å and C–S–C bond angles in the range 99.7 (7)–101.6 (6)°. No previous report of the X-ray structure of this particular sulfonium ion seems to have been made. The confacial bioctahedral anion (Figure 2) can be compared directly with its μ-hydrido analogue, since they differ only in the identity of one of their bridging atoms. This therefore affords us with a rare opportunity to evaluate what structural changes accompany the replacement of one bridging ligand by another in a M₂L₉ complex. The W–W bond length in the anion of 3 is 2.4772 (8) Å, significantly longer than that in the μ-hydrido chloro anion 2 (2.410 (7) Å).⁵ These W–W bond length data can also be compared with those for related ditungsten(III) complexes, e.g. K₃W₂Cl₉ (2.409 (3) Å)¹⁴ and the [W₂Cl₇(THF)₂]⁻ anion (2.4028 (15) Å).⁴ Thus it might be concluded that a bridging hydride enhances metal–metal interactions in M₂L₉ complexes compared with bridging chloride. This observation is in agreement

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with the results of Cotton and co-workers,[8] who noted that the Mo–Mo bond shortens by at least 0.20 Å in going from [Mo$_2$Cl$_9$]$^{3-}$ to [Mo$_2$Cl$_8$H]$^{3-}$, an effect that they ascribed to the strong bonding of the H$^-$ ligand, its small size, and in particular the absence of filled p orbitals capable of donating charge to the metal–metal antibonding orbitals. This last argument is also stressed in the analysis of Hoffmann and Summerville.[7]

The structure of 3 also demonstrates the capability of thioethers to act as bridging ligands. The W–S$_{br}$ bond lengths are much shorter (2.363 (4)–2.380 (3) Å) than those normally observed for terminally bonded thioethers (e.g. 2.574 (9)–2.598 (6) Å in (Me$_2$S)Cl$_2$W(μ-S)(μ-SEt)$_2$WCl$_2$(Me$_2$S)[15]). For chloride ligands the reverse situation is observed in 3, which follows the normal pattern of terminally bonded Cl being more strongly bound than μ-Cl ligands. The angles subtended at the bridging atoms in 3 reflect the strong metal–metal interaction. They are considerably smaller than the 70.5° observed for a pure, undistorted confacial bioctahedral structure.[16]

The structure analysis shows, therefore, that the reaction of 1 with benzyl chloride replaced the bridging hydride by chloride, without disrupting the essential framework of the confacial bioctahedron. The metal–metal bond and the bridging dimethyl sulfides are retained.

The other feature of the reaction worthy of comment is the alkylation of the terminally coordinated Me$_2$S to form the sulfonium cation:
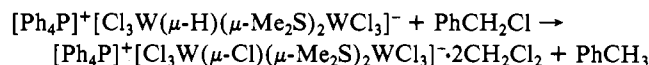
$$\text{W–SMe}_2 + \text{BzCl} \rightarrow \text{W–Cl} + \text{BzMe}_2\text{S}^+$$
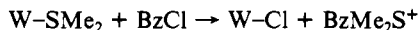
It is also notable that the bridging Me$_2$S is not affected in this way, presumably because its lone pairs are both involved in bonding to the metal, and hence the sulfur is devoid of any nucleophilic properties. Alternatively, the alkylation of Me$_2$S might occur in solution after dissociation of the ligand from the tungsten center has occurred.

The ^{1}H NMR spectrum of 3 is consistent with the structure established by crystallography, confirming the stability of this species in solution. The anion exhibits two singlets at δ 3.48 and 3.03 that can be attributed to the axial and equatorial protons of the μ-Me$_2$S ligands respectively, as illustrated in a Newman-type projection.

'a' axial
'e' equatorial
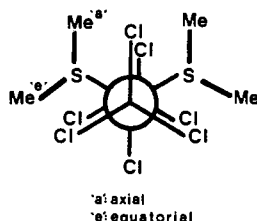
These resonances compare with those observed at δ 3.58 and 3.10 previously for the μ-hydrido chloro anion 2,[5] on which the present assignments are based.

As a sequel to the above study the analogous reaction involving the chloroanion [Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$]$^-$ was carried out. The product was the μ-Cl chloro anion:

[Ph$_4$P]$^+$[Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$]$^-$ + PhCH$_2$Cl $\rightarrow$

[Ph$_4$P]$^+$[Cl$_3$W(μ-Cl)(μ-Me$_2$S)$_2$WCl$_3$]$^-$·2CH$_2$Cl$_2$ + PhCH$_3$

The orange-red product was recrystallized from dichloromethane–hexane, and from its IR and ^{1}H NMR spectra, it was readily identified as the dichloromethane solvate of the tetraphenylphosphonium salt of 3. Again the product is notable in that it retains the W(μ-Me$_2$S)$_2$W moiety and simply arises from the replacement of hydride by chloride, derived from benzyl chloride (toluene was confirmed as a byproduct).

In view of the reactivity of benzyl chloride with both 1 and the anion 2, it was of interest to investigate the stability of these species

in the chlorocarbon solvents CH$_2$Cl$_2$, C$_2$H$_2$Cl$_4$, and C$_2$H$_4$Cl$_2$. At room temperature no reactions were observed over periods of several weeks, but salts of 2 were converted to salts of the anion 3 if the temperature of the solvent was raised. For example, [Ph$_4$P][Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$]·2CH$_2$Cl$_2$ was converted to its μ-chloro analogue after refluxing with C$_2$H$_4$Cl$_2$ for 30 h. The ^{1}H NMR spectra of the μ-Me$_2$S ligands provided an excellent probe for this study. In contrast to the reactivity of the anion 2 with halocarbon solvents, the neutral species 1 was observed to react only with benzyl chloride and not with 1,2-dichloromethane even after refluxing for ~10 days.

Other reactions of compound 1 with acidic molecules such as ethanethiol, 2-hydroxy-6-methylpyridine (Hmhp), and 2,4-dimethyl-6-hydroxypyrimidine (Hdmhp), all produced dihydrogen as expected, but the tungsten-containing products that resulted were somewhat intractable and could not be completely characterized. Reaction of 1 with diethyl disulfide yielded ethanethiol and a small amount of a material tentatively identified as Cl$_3$W-(μ-SEt)(μ-Me$_2$S)$_2$WCl$_2$(Me$_2$S). Acetonitrile was found to react with 1 to displace the terminal dimethyl sulfide, giving an insoluble purple solid, characterized as Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_2$(MeCN).

The anion 2 could not be induced to undergo any of these reactions, thereby suggesting that the mechanism of the attack of the above reagents on 1 involves the initial displacement of its terminal dimethyl sulfide. In all the reactions in which hydrogen was produced, we identified free dimethyl sulfide as a byproduct, tending to confirm this interpretation.

Reactions with Pyridine: Synthesis of W$_2$Cl$_5$H(py)$_4$. Both the neutral compound 1 and the salts of its μ-hydrido chloro anion 2 reacted with neat pyridine at ambient temperature to yield identical products. These light brown, insoluble materials were shown by infrared spectroscopy to contain both free and coordinated pyridine (see Experimental Section for details). The spectra also showed the presence of W–Cl bonds, but indicated that all the coordinated dimethyl sulfide in the starting materials had been displaced. The free pyridine was removable by heating to 80 °C in vacuo or by stirring with acetonitrile or dichloromethane at room temperature. With the exception of a band at 1509 cm^{-1}, the spectrum of this product, 4, was almost identical with that of the ditungsten(III) compound (py)$_2$Cl$_2$W(μ-Cl)$_2$WCl$_2$(py)$_2$. This species was reported by Wentworth and co-workers in 1967,[17] and the structure was later published by Jackson and Streib.[18] Together with the elemental analyses (Experimental Section), the infrared spectrum of 4 is consistent with its formulation as (py)$_2$Cl$_2$W(μ-Cl)(μ-H)WCl$_2$(py)$_2$, since the band at 1510 cm^{-1} is in the range characteristic of bridging hydride–metal stretching frequencies.[19] This assignment was confirmed by repeating the synthesis using the μ-D analogue of 1 as the reaction starting material whereupon the band at 1510 cm^{-1} was replaced by one at 1097 cm^{-1}. The spectrum of the reaction product was otherwise identical with that of 4. The insolubility of these complexes has precluded the acquisition of further spectroscopic data and the growing of X-ray quality crystals, but there can be little doubt that these products are *trans*-dichloro-*cis*-bis(pyridine)tungsten(III) (μ-chloro)(μ-hydrido)-*cis*-dichloro-*trans*-bis(pyridine)tungstate(III) and its μ-D analogue, respectively. The implications of this structure are that in this reaction the W–(μ-Me$_2$S)$_2$–W entity, which was preserved in all the previously described reactions, was cleaved in this case. Conversely, the μ-hydrido ligand is retained. These results can be contrasted with those of San Filippo and Schaefer King, who studied the reactions of pyridine with Mo$_2$X$_8$H^{3-} and Mo$_2$X$_9$$^{3-}$ (X = Cl, Br).[20] They found that, depending on the reaction temperature, either Mo$_2$X$_4$(py)$_2$ or *mer*-MoX$_3$(py)$_3$ was produced. The μ-H moiety was thus invariably displaced from the Mo$_2$X$_8$H^{3-} ion.

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Experimental Section

The starting materials 1 and 2 were prepared as described in ref 4; a freshly prepared sample of 1 was always used, since it loses terminal dimethyl sulfide over extended time periods. All handling procedures were carried out in an atmosphere of pure, dry nitrogen, by using standard Schlenk tube and glovebox techniques.

Reagents, sources, and drying procedures/agents were as follows: 2-hydroxy-6-methylpyridine and 2,4-dimethyl-6-hydroxypyrimidine (Aldrich), used as received; diethyl disulfide (Eastman-Kodak), benzyl chloride (Aldrich), dried over Ca turnings; acetonitrile (Fisher), dried over P_2O_5 then CaH_2. Mass spectra were obtained by using a Varian MAT CH-5 spectrometer operating in the 70-eV electron-impact mode; gas chromatographic analysis for dihydrogen liberated in some of the experiments was accomplished on a Hewlett-Packard 5700 A instrument equipped with a Porapak-Q column and a TCD. ^1H NMR spectra were obtained with a Varian XL-200 spectrometer.

Preparation of $[Me_2SCH_2Ph][Cl_3W(\mu\text{-}Cl)(\mu\text{-}Me_2S)_2WCl_3]\cdot2CH_2Cl_2\cdot0.5HCl$. To a stirring, turbid purple solution of 1 (0.36 g, 0.49 mmol), in $C_2H_4Cl_2$ ($\sim$40 mL) was slowly added neat benzyl chloride (2 mL). After being stirred at room temperature for $\sim$10 min, the mixture was brought to a gentle reflux, whereupon the color changed from purple to orange-red. After 2 h no further changes in color were noted, and the solution was allowed to cool to room temperature. The solution was then filtered to yield a clear orange-red liquid. A small amount of a blue-black solid, which could not be identified, remained on the frit. The solution was evaporated to dryness under vacuum, and the resultant red, glassy solid was redissolved in CH_2Cl_2 ($\sim$25 mL). Hexane ($\sim$5 mL) was slowly added, and after cooling ($\sim$-20 °C) for 48 h, orange-red platelets of the compound later identified as 3 were produced (yield: 0.37 g). IR data (2000–250 cm^{-1}, KBr disk): 1489 (w), 1448 (mw), 1400 (m) [1413 (sh)], 1330 (w), 1309 (w), 1291 (w) [1287 (sh)], 1262 (mw), 1197 (vw), 1155 (vw, br), 1075 (vw), 1025 (ms), 995 (mw), 970 (w, br), 927 (w, br), 770 (w), 725 (mw), 702 (mw), 652 (vw), 567 (vw, br), 467 (vw), 307 (s), 295 (ms). The ^1H NMR spectrum of 3 ($C_2D_2Cl_4$ solution) consists of a multiplet at δ 7.32–7.54 and a singlet at δ 4.54, assigned respectively to the protons of the phenyl group and the methylene group protons of the benzyl portion of the cation, and a singlet at δ 2.77 due to the methyl groups of the cation. A singlet at δ 5.24 is due to the solvated CH_2Cl_2, while the two singlets at δ 3.48 and 3.03 are assigned to the equatorial and axial methyl groups, respectively, of the bridging Me_2S groups.[5]

The complex is diamagnetic and moderately stable to air in the solid state. It is soluble in polar organic solvents, such as MeCN, acetone, and chlorocarbons. Chemical analyses were not reproducible, due to the loss of the solvate molecules, HCl and CH_2Cl_2. The HCl could not be detected in the ^1H NMR spectrum but was detected by mass spectroscopy on the solid. A GC study of the reaction solvent confirmed the production of toluene from the reduction of benzyl chloride.

Reflux Reaction of $[Ph_4P]^+[Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]^-\cdot2CH_2Cl_2$ with 1,2-Dichloroethane. The above-mentioned salt (0.12 g) was dissolved in 1,2-dichloroethane ($\sim$20 mL), and the solution was heated in an evacuated, sealed Pyrex tube at 90 °C for 30 h. The solution, originally purple in color, changed to orange-red, and after cooling to 20 °C, the solvent was removed by evacuation. The resultant glassy solid was recrystallized from CH_2Cl_2, to yield 0.11 g of an orange-red microcrystalline material identified as $[Ph_4P]^+[Cl_3W(\mu\text{-}Cl)(\mu\text{-}Me_2S)_2WCl_3]^-\cdot nCH_2Cl_2$, where n = 0.25–2.00. The ^1H NMR spectrum ($C_2D_2Cl_4$ solution) consisted of a multiplet at δ 7.43–7.85 due to the tetraphenylphosphonium cation, a singlet at δ 5.24 that arises from the solvating dichloromethane, and two singlets at δ 3.44 and 2.99 assignable to the two sets of methyl groups of the bridging dimethyl sulfides, in equatorial and axial positions respectively. The integrated intensities were totally consistent with this interpretation and were used to assess the amount of solvate dichloromethane in each sample. The slow loss of this solvent as soon as the sample was removed from solution precluded the acquisition of good elemental analyses.

Preparation of $(py)_2Cl_2W(\mu\text{-}H)(\mu\text{-}Cl)WCl_2(py)_2$. To 0.49 g (0.67 mmol) of $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$ (*1*) was added $\sim$50 mL of dry pyridine, and the mixture was stirred at room temperature under nitrogen. After only 5 min a brown solid was seen to have been formed, but the stirring was continued for a further 12 h. Dimethyl sulfide was identified as a reaction product by a ^1H NMR study of the solution. The brown solid was filtered off and dried under vacuum, (yield: 0.48 g). The extreme insolubility of this product restricted its characterization to the use of IR spectroscopy and elemental analysis. The IR spectrum suggested the presence of both free and coordinated pyridine,[17,21] and the analyses were consistent with the formulation $(py)_2Cl_2W(\mu\text{-}H)(\mu\text{-}Cl)$-

$WCl_2(py)_2\cdot2py$. IR data (cm^{-1}, KBr disk): 1601 (ms), 1578 (m), 1566 (m), 1535 (m, br) (due to μ-H), 1485 (ms), 1480 (sh), 1446 (s), 1435 (s), 1361 (mw), 1353 (sh), 1219 (m), 1154 (m), 1148 (sh), 1071 (ms), 1050 (mw), 1031 (mw), 1010 (m), 1002 (sh), 992 (m), 886 (vw), 873 (vw), 766 (s), 752 (ms), 712 (s), 695 (vs), 641 (w), 645 (sh), 606 (w), 444 (mw), 402 (w), 320 (ms), 274 (s). Anal. Calcd for $W_2Cl_5N_6C_{30}H_{31}$: Cl, 17.37; N, 8.23; C, 35.31; H, 3.06. Found: Cl, 17.7; N, 8.43; C, 35.5; H, 3.08.

The free pyridine was found to be easily removed by stirring the brown solid in a solvent such as dichloromethane, or more conveniently, by heating to $\sim$80 °C in vacuo. Under these conditions, for example, a sample of 0.31 g (0.30 mmol) of the pyridine solvate lost the pyridine quantitatively over a 5-h period to yield 0.25 g (0.30 mmol) of the compound $(py)_2Cl_2W(\mu\text{-}H)(\mu\text{-}Cl)WCl_2(py)_2$ (4). This olive green-brown solid was as insoluble as its solvated precursor, and hence its characterization was also restricted to IR spectra and elemental analysis. Anal. Calcd for $W_2Cl_5N_4C_{20}H_{21}$: N, 6.50; C, 27.26; H, 2.40. Found: N, 6.91; C, 27.26; H, 2.45. IR data (cm^{-1}): 1601 (ms), 1510 (m, br), 1482 (ms), 1445 (s), 1350 (vw), 1230 (vw, sh), 1212 (m), 1150 (w), 1061 (m), 1045 (m), 1008 (m), 970 (vw), 942 (vw), 815 (vw), 758 (s), 690 (s), 640 (mw), 444 (w), 319 (m), 298 (m), 274 (ms).

In order to confirm the assignment of the band at 1535 cm^{-1} (solvated material) or 1510 cm^{-1} (unsolvated material) to a W–(μ-H)–W stretching vibration, the analogous deuterio complexes were prepared from the reaction of pyridine with $Cl_3W(\mu\text{-}D)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$, which had been prepared previously.[5] The initial product was a pyridine solvate, whose IR spectrum was identical with that of its ^1H analogue except for the presence of a band at 1110 cm^{-1}, which moved to 1090 cm^{-1} upon removal of the solvating pyridine. The broad band at 1535/1510 cm^{-1} assigned to the μ-H species of 4 in its solvated and unsolvated forms, respectively, is absent in the deuterio complexes, thus confirming the presence of the bridging hydride.[18]

Synthesis of $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(MeCN)$. To a stirring, turbid solution of 1 (0.18 g, 0.25 mmol) in CH_2Cl_2 ($\sim$50 mL) was slowly added neat acetonitrile (0.5 mL). No immediate change in the appearance of the reaction mixture was noticed, but after $\sim$12 h a dark purple solid had precipitated. This material was removed by filtration, washed with CH_2Cl_2 (3 $\times$ 5 mL), and dried in vacuo at 60 °C for several hours. Yield: 0.15 g. A GC study of the reaction solution after removal of the solid product confirmed that dimethyl sulfide had been displaced from 1, and elemental analysis of the purple solid, coupled with its IR spectrum, revealed that its likely identity was $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2$-(MeCN). Anal. Calcd for $W_2Cl_5S_2NC_6H_{16}$: W, 51.69; Cl, 24.92; N, 1.97; C, 10.13; H, 2.27. Found: W, 50.84; Cl, 24.87; N, 1.66; C, 10.00; H, 2.25. IR data (KBr disk, 2500–250 cm^{-1}): 2303 (mw), 2288 (m) [$\nu(C\equiv N)$ of coordinated MeCN], 1685 (w) [$\nu_{sym}(W—H—W)$], 1410 (m), 1357 (mw), 1317 (mw), 1300 (mw), 1260 (m) [$\nu_{asym}(W—H—W)$], 1030 (ms), 740 (mw), 350 (m), 312 (vs) [290 (sh)]. The low solubility of this compound in common organic solvents restricted the scope of further studies on this material.

Reactions of $[Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)]$ with Acidic Molecules. Several reactions were carried out to investigate the hydridic character of the bridging hydrogen in 1. The methodology employed was similar in each case, and only the reaction between 1 and 2-hydroxy-6-methylpyridine (Hmhp) will be described here. To a solution of 1 (0.29 g, 0.40 mmol) in dichloromethane was added Hmhp (0.05 g, 0.41 mmol), dissolved in $\sim$10 mL of the same solvent. The solution was stirred at ambient temperature for 1 h, during which time its color darkened. A GC analysis of the reaction flask atmosphere showed that dihydrogen and Me_2S were evolved. The reaction solution was filtered, and the dark purple filtrate was evaporated to dryness. The glassy purple product was redissolved in CH_2Cl_2 ($\sim$ 50 mL) and reprecipitated at -20 °C after the addition of hexane ($\sim$12 mL). Yield: 0.19 g. Elemental analyses were consistent with the formulation $\{W_2Cl_5(mhp)(Me_2S)_2\}_n$. Anal. Calcd for $W_2Cl_5S_2NOC_{10}H_{18}$: Cl, 22.80; C, 15.45; H, 2.33. Found: Cl, 22.0; C, 15.02; H, 2.59. The IR spectrum of this product was independent of the hydride isotopic composition of 1, suggesting the complete loss of the μ-hydrido ligand. The complex was soluble in several chlorocarbon solvents, giving deep purple solutions. ^1H NMR spectra confirmed the presence of both the mhp anion and dimethyl sulfide in the complex in the Me_2S:mhp ratio 2:1 [δ 7.86 (doublet of doublets), 6.93 (d), 6.72 (d), 3.74–1.96 (variable collection of singlets)]. The lack of reproducibility of the high-field part of the spectrum suggests that a number of isomeric forms of a polynuclear complex might be present in the product, but the ratio of the higher field resonances to the resonances in the aromatic region was consistently ca. 5:1. We therefore suggest a tetrameric structure (i.e. n = 2 in the empirical formula), but we were unable to grow crystals suitable for an X-ray structural analysis.

X-ray Analysis of 3. The crystallographic data and experimental details are given in Tables V and S4 (supplementary material). The

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crystal chosen for data collection was removed from the mother liquor and immediately mounted and covered with epoxy resin to prevent loss of solvent of crystallization. It was then transferred to a CAD4F diffractometer, and the cell constants were determined from 25 accurately centered reflections (17.7 < θ < 26.2). The cell was identified as triclinic by using the indexing routines of the instrument, and space group $P\bar{1}$ was chosen on the basis of the centric distribution of the E values.[22] The successful solution of the structure supported this choice. Intensity data were obtained by using the ω–2θ scan mode and were corrected for background, Lorentz and polarization effects. Three standard reflections were monitored every 2000 s, but no systematic decay in their intensities were observed. The program CADABS[23] was used to correct for absorption.

The positions of the W atoms were obtained from a three-dimensional Patterson synthesis, and structure factor and difference Fourier calculations were used to locate the remaining non-hydrogen atoms. The structure was refined by full-matrix least-squares techniques based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w is defined as $[\sigma^2(F_o) + 0.002F_o^2]^{-1}$. Scattering factors were taken from Cromer and Mann,[24] and anomalous dispersion corrections were included for all non-hydrogen atoms.[25] A refinement of the population parameters for the non-hydrogen atoms of the CH_2Cl_2 and HCl molecules revealed that there are

two independent dichloromethane molecules, and half of a molecule of HCl per asymmetric unit. All the hydrogen atoms, except that of the HCl half-molecule, were located in a difference Fourier map. These were included in calculated positions with isotropic thermal parameters set to be 10% greater than the B_{eq} of the carbon atom to which they were bonded. The model converged with a maximum shift-to-error of 0.229 (z of W(2)) and an average value of 0.036. Several peaks of no chemical significance were found in the final difference map within 0.8–0.9 Å of the tungsten atoms. The Cl atom of the HCl half-molecule was found to be very close (1.99 (2) Å) to the carbon of one of the CH_2Cl_2 molecules, and within 1.83 (1) Å of the Cl of its symmetry-related other half-molecule of HCl. It is possible[26] that both the solvate sites may be partially occupied by CH_2Cl_2 and HCl, which would explain this close C···Cl contact, but we cannot be certain of this point. However, in spite of this disorder problem it does not affect the structural data for the focal part of the structure, namely the ditungstate anion, which has no close contacts with the solvate molecules.

Supplementary Material Available: Listings of positional parameters for the non-hydrogen atoms of the cation and of the solvate molecules (Table S1), anisotropic thermal parameters for all non-hydrogen atoms (Table S2), positional parameters and isotropic thermal parameters for hydrogen atoms (Table S3), and crystallographic parameters (Table S4) and a figure showing the contents of the unit cell (Figure S1) for complex **3** (5 pages); listing of observed and calculated structure factors (Table S5) (36 pages). Ordering information is given on any current masthead page.

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Ligand Substitution in Manganese(I) Carbonyl Complexes Mn(CO)5X (X = Cl, Br): Activation Parameters and X-ray Structure of Mn(CO)3(dab)Cl (dab = Biacetyl Bis(phenylimine))

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Visible spectrophotometry at ambient and elevated pressure has been applied to study the kinetics of ligand substitution in pentacarbonylhalomanganese(I) complexes Mn(CO)5X (X = Cl, Br) by bidentate diimine ligands LL (dab (biacetyl bis(phenylimine)), dab-Cl (biacetyl bis(4-chlorophenylimine)), dab-OCH3 (biacetyl bis(4-methoxyphenylimine)), bpy (2,2'-bipyridine), and phen (1,10-phenanthroline)) in the solvents toluene and 1,2-dichloroethane (1,2-DE). The rate of formation of the product Mn(CO)3(LL)X is in most cases governed by a one-term rate law, rate = k[Mn(CO)5X], and in some cases by a two-term rate law, rate = $(k + k_{LL}[LL])$[Mn(CO)5X]. Rate constant k is independent of the nature of the incoming ligand LL. The occurrence of a minor second-order contribution k_{LL}[LL] in some of the systems is attributed to decomposition reactions at higher temperatures or to the effect of water as introduced in the form of phen·H_2O. The activation parameters as derived from the temperature and pressure dependence of rate constant k in toluene are $\Delta H^* = 24.5 \pm 0.9$ kcal mol^{-1}, $\Delta S^* = 8.8 \pm 3.0$ eu, $\Delta V^* = 20.6 \pm 0.4$ cm^3 mol^{-1} (system Mn(CO)5Cl/dab), $\Delta H^* = 24.4 \pm 1.6$ kcal mol^{-1}, $\Delta S^* = 3.7 \pm 5.3$ eu (system Mn(CO)5Br/dab), and $\Delta H^* = 26.2 \pm 0.5$ kcal mol^{-1}, $\Delta S^* = 9.9 \pm 1.6$ eu (system Mn(CO)5Br/dab-OCH3). The results support the operation of a limiting dissociative (D) mechanism with k describing the rate of dissociation of a cis-CO ligand from Mn(CO)5X. Ligand substitution in Mn(CO)5Cl is faster than that in Mn(CO)5Br by a factor of 10. As compared to toluene the solvent 1,2-DE reduces the reactivity of Mn(CO)5Br by a factor of 2.2. The product Mn(CO)3(dab)Cl [C19H16ClMnN2O3] crystallizes in the monoclinic space group $P2_1/m$ with $a = 878.0$ (2) pm, $b = 1852.3$ (3) pm, $c = 622.1$ (1) pm, $\beta = 101.950$ (5)°, and $Z = 2$. The ligands around the manganese form a slightly distorted octahedron with a facial arrangement of the three CO groups.

Introduction

The kinetics and mechanism of ligand substitution in pentacarbonylhalomanganese(I) complexes Mn(CO)5X have been studied extensively. The results of carbon monoxide exchange

with isotopically labeled CO proved the operation of a limiting dissociative (D) mechanism with labilization of the CO ligands cis to X.[2–9] The substitution of monodentate ligands L for CO

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