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Reactions of the Gaseous Hydrogen Halides with Dimers of Molybdenum(II) and Tungsten(II) Containing the Anion of 2-Hydroxy-6-methylpyridine

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Whereas the reaction of the molybdenum(II) dimer $Mo_2(mhp)_4$ (where mhp represents the anion of 2-hydroxy-6-methylpyridine) with a cesium halide and a hydrogen halide gas in refluxing methanol produces the octahalodimolybdate(II) $Cs_4Mo_2X_8$ (X = Cl or Br), the related tungsten(II) dimer is oxidized to $Cs_3W_2X_9$. In the absence of CsX and in the presence of triethylphosphine, the $W_2(mhp)_4$ complex is still oxidized, but in this case the green methanolysis products $W_2X_4(OMe)_2(MeOH)_4$ precipitate. The use of other alcohols as the reaction solvent shows that this is a convenient synthetic route to W–W bonded dimers of the type $W_2X_4(OR)_2(ROH)_4$. There is no evidence for the formation of the $W_2X_8^{4-}$ anion from the reaction of $W_2(mhp)_4$ with HX in nonaqueous solvents.

Introduction

The discovery by Cotton and co-workers[1,2] that tungsten hexacarbonyl is oxidatively decarbonylated by 2-hydroxy-6-methylpyridine (Hmhp) and 2,4-dimethyl-6-hydroxypyrimidine (Hdmhp) in refluxing diglyme to produce the metal–metal bonded dimers $W_2(mhp)_4$ and $W_2(dmhp)_4$ is very important since it provides for the first time a direct and convenient entry into the chemistry of complexes containing tungsten–tungsten quadruple bonds. Such species have in the past been something of a rarity,[3] the $W_2Cl_8^{4-}$ anion, for example, having so far defied isolation in spite of the stability and ease of isolation of salts of the related molybdenum anion, $Mo_2Cl_8^{4-}$.[3]

Our interest in molecules such as $W_2(mhp)_4$ and $W_2(dmhp)_4$ stems from the possibility of using them as synthetic precursors to other tungsten dimers, particularly those which no longer contain an intramolecular bridging ligand system (e.g., $W_2X_8^{4-}$). Cotton et al.[4] have already demonstrated the synthetic utility of one of these dimers, namely, $W_2(mhp)_4$, by converting it to $W_2(map)_4$, a complex which contains the anion of 2-amino-6-methylpyridine (Hmap).

Following our earlier investigations[5-8] into the reactivity of the dimeric metal acetates $Mo_2(O_2CCH_3)_4$, $Re_2(O_2CCH_3)_4Cl_2$, and $Rh_2(O_2CCH_3)_4$ toward the gaseous hydrogen halides, we became interested in exploring the related reactions of some suitable metal–metal bonded tungsten dimer. Although $W_2(O_2CCH_3)_4$ has yet to be isolated and structurally characterized, the availability of complexes such as $W_2(mhp)_4$ now provides us with the opportunity to study the reactivity of a complex containing the W_2^{4+} core. The results of our studies into the reactions of $W_2(mhp)_4$ and its molybdenum analogue with the hydrogen halides in alcoholic media are now reported.

Experimental Section

Starting Materials. The complexes $Mo_2(mhp)_4$ and $W_2(mhp)_4$ were prepared by the standard literature procedure.[1] 2-Hydroxy-6-methylpyridine (Hmhp) and other reagents were obtained from commercial sources and were used as received. Diglyme was distilled over CaH_2 in a nitrogen atmosphere. All other solvents were dried over molecular sieves.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere, and solvents were deoxygenated by purging with N_2 gas prior to use.

A. Reactions of $Mo_2(mhp)_4$. (i) $Cs_4Mo_2Cl_8$. Finely ground $Mo_2(mhp)_4$ (0.65 g, 1.0 mmol) and CsCl (1.3 g, 7.7 mmol) were placed in a three-necked round-bottom flask which was then flushed with nitrogen for 30 min. A 25-mL sample of methanol was added, and the resulting suspension was refluxed while anhydrous HCl gas was bubbled through the reaction mixture. After 30 min, the reaction mixture was filtered and the resulting red solid (0.9 g) was washed with warm methanol and dried in vacuo; yield 84%. Anal. Calcd for $Cl_8Cs_4Mo_2$: Cl, 28.16. Found: Cl, 27.99.

(ii) $Cs_4Mo_2Br_8$. This complex could be obtained in 66% yield by using a procedure similar to that described in section A(i). Anal. Calcd for $Br_8Cs_4Mo_2$: Br, 46.91. Found: Br, 46.55.

(iii) $[Bu_4N]_2Mo_4I_{11}$. A mixture of finely ground $Mo_2(mhp)_4$ (0.9 g, 1.44 mmol) and Bu_4NI (2.66 g, 7.2 mmol) was placed in a three-necked flask and flushed with nitrogen for 30 min. A 35-mL sample of tetrahydrofuran was added and the resulting mixture refluxed while anhydrous HI was bubbled through the solution. After 2.5 h, the reaction mixture was cooled and kept at 0 °C for 48 h. The resulting black crystals (0.57 g) were filtered off, washed with diethyl ether, and dried in vacuo; yield 38%. Anal. Calcd for $C_{32}H_{72}I_{11}Mo_2N_2$: C, 16.95; H, 3.17; I, 61.68. Found: C, 17.23; H, 3.39; I, 61.90.

B. Reactions of $W_2(mhp)_4$. (i) $Cs_3W_2Cl_9{\cdot}MeOH$. With a procedure similar to that described in section A(i), this green complex could be obtained in 81% yield. Anal. Calcd for $CH_4Cl_9Cs_3OW_2$: C, 1.07; H, 0.36; Cl, 28.55. Found: C, 1.07; H, 0.36; Cl, 28.45.

(ii) $Cs_3W_2Br_9{\cdot}MeOH$. The green complex of this stoichiometry was obtained in 46% yield by using a procedure analogous to section

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A(i). Anal. Calcd for $CH_4Br_9Cs_3OW_2$: Br, 47.3. Found: Br, 48.15.

(iii) $W_2Cl_4(OMe)_2(MeOH)_4$. The reaction between $W_2(mhp)_4$ and HCl gas in refluxing methanol was carried out by using a procedure analogous to that used in section A(i) except that a quantity of triethylphosphine (0.5 mL) was added in place of the CsCl. The resulting bright green insoluble complex was obtained in 50% yield. Anal. Calcd for $C_6H_{22}Cl_4O_6W_2$: C, 10.29; H, 3.14; Cl, 20.26. Found: C, 10.60; H, 3.00; Cl 20.93.

(iv) $W_2Br_4(OMe)_2(MeOH)_4$. The green complex approximating to this stoichiometry was obtained in 23% yield when a procedure analogous to that described in section B(iii) was followed. Anal. Calcd for $C_6H_{22}Br_4O_6W_2$: C, 8.21; H, 2.51; Br, 36.43. Found: C, 8.61; H, 2.36; Br 37.0.

(v) $W_2Cl_4(OEt)_2(EtOH)_4$. Using a procedure similar to that described in section B(iii), but with ethanol as the reaction solvent, afforded this green complex in 53% yield. Anal. Calcd for $C_{12}Cl_4H_{34}O_6W_2$: C, 18.37; H, 4.33; Cl, 18.10. Found: C, 18.58; H, 4.43; Cl 18.12.

Physical Measurements. Spectroscopic characterizations were carried out by using instrumentation described previously[5,9] with the exception of infrared spectra, which were obtained on a Digilab FtS 20B spectrometer.

Results and Discussion

The reactions between mixtures of $Mo_2(mhp)_4$, cesium halide, and gaseous HCl and HBr in refluxing methanol provide a convenient route to the well-known salts $Cs_4Mo_2X_8$ in yields in excess of 60%. The spectral properties of the samples prepared in the present work compare favorably with the published spectral data.[10-12] To confirm further the identity of these products, we converted both of them to phosphine derivatives of the type $Mo_2X_4(PR_3)_4$ by reaction with triethylphosphine in refluxing methanol. The latter complexes were characterized by a comparison of their infrared and electronic absorption spectra with samples of these complexes prepared from $K_4Mo_2Cl_8$ or β-MoX_2.[5]

The retention of the Mo_2^{4+} core in these reactions should be contrasted with the relative ease with which $Mo_2(O_2CCH_3)_4$ is oxidized under comparable reaction conditions.[7] Thus in the presence of appropriate tetra-*n*-butylammonium halide, the complexes $(n\text{-}Bu_4N)MoOCl_4$ and $(n\text{-}Bu_4N)Mo_2Br_6$ are isolated. Whether these differences reflect the greater sensitivity of $Mo_2(O_2CCH_3)_4$ to adventitious oxygen or are a consequence of different mechanisms for the displacement of the bridging acetate and mhp ligands by halide ion is uncertain at present.

Our attempts to convert $Mo_2(mhp)_4$ to the analogous iodide $Cs_4Mo_2I_8$ failed. Only by changing to the tetra-*n*-butylammonium cation and by using tetrahydrofuran as the solvent did we isolate a pure product. This turned out to be the black crystalline cluster complex $(n\text{-}Bu_4N)_2Mo_4I_{11}$, a species which we had prepared[7] previously from $Mo_2(O_2CCH_3)_4$ and which had also been isolated independently by McCarley and coworkers.[13] The material prepared in the present investigation had spectroscopic properties (including its ESR and X-ray photoelectron spectra) identical with those of authentic samples of $(n\text{-}Bu_4N)_2Mo_4I_{11}$.[7]

Our ability to convert $Mo_2(mhp)_4$ into $Cs_4Mo_2X_8$ (X = Cl or Br) without any ensuing oxidation of the metal dimer unit prompted us to attempt the conversion of $W_2(mhp)_4$ to $Cs_4W_2X_8$. Regrettably, the reactions involving mixtures of $W_2(mhp)_4$, cesium halide, and a hydrogen halide in methanol led to the rapid precipitation of the methanol solvate of $Cs_3W_2X_9$ (X = Cl or Br) in good yield. The electronic absorption and vibrational spectral properties of these two complexes were in good agreement with literature data for these complex anions.[14-16] Furthermore, their X-ray photoelectron spectra (W $4f_{7/2}$ binding energy of 32.8 eV in each case) are in accord with literature data for $K_3W_2Cl_9$ and $(Bu_4N)_3W_2Cl_9$.[17]

In an attempt to prevent the oxidation of $W_2(mhp)_4$ to derivatives of the W_2^{6+} core, this complex was reacted with a hydrogen halide gas in methanol or ethanol in the presence of triethylphosphine. Our hope was that the phosphine would immediately complex any tungsten(II) halide intermediates which were formed and convert them to $W_2X_4(PEt_3)_4$, the tungsten analogues of the well-known class of molybdenum dimers of this type.[5,18,19] This strategy was unsuccessful as evidenced by our isolation of the green tungsten(III) alkoxy species $W_2X_4(OR)_2(ROH)_4$. Complexes of this type had previously been prepared by Clark and Wentworth[20] from reaction of the appropriate alcohol with $(n\text{-}Bu_4N)_3W_2Cl_9$. Accordingly, it seems likely that in the reaction of $W_2(mhp)_4$ with hydrogen halide, oxidation to tungsten(III) occurs extremely rapidly, possibly through the oxidative addition of HX across the tungsten–tungsten quadruple bond[21] rather than the initial formation of simple halide substitution product containing the W_2^{4+} core.[23]

As it turns out, our synthesis of $W_2X_4(OR)_2(ROH)_4$ constitutes a very convenient route to these complexes since this procedure is easily extended to the previously unknown bromide derivatives without changing the starting material. We believe that the phosphine reagent which is added to the $W_2(mhp)_4$/HX/ROH reaction mixture may promote the elimination of HX during the alcoholysis of the W–X bonds. When it is excluded from the reaction mixture, the tungsten(III) alkoxides do not precipitate.

The three complexes prepared in the present work, $W_2Cl_4(OR)_2(ROH)_4$ (R = Me or Et) and $W_2Br_4(OMe)_2(MeOH)_4$, had identical diffuse reflectance electronic absorption spectra (λ_{max} at 725–735 and 415–420 nm) which in turn resembled the spectra of chloroform solutions of $W_2Cl_4(OR)_2(ROH)_4$ reported by Clark and Wentworth.[20] The infrared spectra of the methoxy derivatives $W_2X_4(OMe)_2(MeOH)_4$ were identical in the region 4000–600 cm^{-1}, and a molecular weight determination of a chloroform solution of $W_2Cl_4(OEt)_2(EtOH)_4$ confirmed the dimeric nature of this complex (found, 778; calcd, 784).

The X-ray photoelectron spectra of these complexes reveal thereby demonstrating that these products are free of any high oxidation state tungsten oxide contaminants. The W $4f_{5/2}$ and $4f_{7/2}$ energies occur at 35.9–35.7 and 33.8–33.6 eV, respectively,[24] values which are somewhat higher than for the $W_2X_9^{3-}$

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(24) The C 1s energy of the methoxy and methanol carbon atoms of $W_2X_4(OMe)_2(MeOH)_4$ is located at 285.5 ± 0.1 eV. The full width at half-maximum (fwhm) values of the W 4f peaks are 1.4 ± 0.1 eV.

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anions. The Cl 2p binding-energy spectra of the two chloride complexes are each characterized by a very well-resolved Cl $2p_{1/2,3/2}$ doublet (the Cl $2p_{3/2}$ component is located at 198.2 eV for $W_2Cl_4(OMe)_2(MeOH)_4$ and 197.9 eV for $W_2Cl_4(OEt)_2(EtOH)_4$) which is a good indication that only a single type of chlorine environment[25] is present within these complexes. This supports an alkoxy-bridged structure rather than a halogen-bridged structure for $W_2X_4(OR)_2(ROH)_4$.

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Registry No. $Mo_2(mhp)_4$, 67634-80-4; $W_2(mhp)_4$, 67634-84-8; $Cs_4Mo_2Cl_8$, 55937-61-6; $Cs_4Mo_2Br_8$, 41772-62-7; $[Bu_4N]_2Mo_4I_{11}$, 68024-65-7; $Cs_3W_2Cl_9$, 23403-18-1; $Cs_3W_2Br_9$, 72332-25-3; $W_2Cl_4(OMe)_2(MeOH)_4$, 12552-15-7; $W_2Br_4(OMe)_2(MeOH)_4$, 72301-56-5; $W_2Cl_4(OEt)_2(EtOH)_4$, 72301-57-6.

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Reactions of Metal Carbonyl Derivatives. 23.[1] Donor Behavior of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H, CH_3) toward Various Rhodium and Iridium Complexes and the Role of the Solvent in the Type of Product Formed. Reversible Uptake of Carbon Monoxide and Dihydrogen by the Nonclosed Trinuclear Species $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (M′ = Rh, Ir)[2]

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The metal-containing phosphine $[P(C_6H_5)_2ML_n]$ ($ML_n = Fe(CO)_2(\eta\text{-}C_5H_4R)$ (R = H or CH_3)) reacts with various compounds of rhodium in alcohol, including $[RhCl_3{\cdot}3H_2O]$ and $[\{Rh(C_8H_{12})Cl\}_2]$, to produce in each case, when present in slight excess, a cationic species of stoichiometry $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$, having a nonclosed structure in which the iron and rhodium atoms are bridged by a carbonyl as well as by a phosphino group. The iridium analogue is formed in the corresponding reaction involving $[Ir(C_8H_{12})(solvent)_x]^+$ but not $[\{Ir(C_8H_{12})Cl\}_2]$. Coordinating solvents such as tetrahydrofuran, acetone, diglyme, methanol, and acetonitrile react reversibly with these cationic species to afford products containing terminal carbonyls only. Controlled addition of $P(OCH_3)_3$, $P(C_6H_5)_3$, halide ions, or pseudohalide ions to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ leads to the formation of simple adducts of the parent compound, in which the bridged structure is retained, while treatment of $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (M′ = Rh, Ir) with carbon monoxide in dichloromethane or chloroform gives rise to a compound characterized as $[M'(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$. Whereas the carbonylation of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ is reversible, that involving the iridium species is irreversible. Hydrogen also reacts with $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ although high pressures are required for the rhodium reaction. Treatment of $[\{Rh(CO)_2Cl\}_2]$ or $[\{Rh(C_8H_{12})Cl\}_2]$ with $[P(C_6H_5)_2ML_n]$ in benzene affords neutral $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ which can be converted to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ by treatment with silver ions. The iridium compound $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ is obtained similarly from $[\{Ir(C_8H_{12})Cl\}_2]$. Reaction of $[RhL'_2(solvent)_x]^+$ or $[Rh(C_8H_{12})L'_2]^+$ ($L' = P(OC_6H_5)_3$, $P(CH_3)_2C_6H_5$; $2L' = C_8H_{12}$ or $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$) with an equimolar amount of $[P(C_6H_5)_2ML_n]$ in alcohol gives a dinuclear product, $[RhL'_2\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}]^+$, which, similar to the trinuclear species, contains both a bridging carbonyl and a bridging phosphino group. The donor properties of $[SR'ML_n]$ ($R' = C_2H_5$, $t\text{-}C_4H_9$, C_6H_5) toward various rhodium derivatives are also described.

Metal-cluster complexes are receiving much attention of late. This can be attributed to their potential as models for metal surfaces in heterogeneous catalysis[4,5] as well as to the highly fascinating and novel chemistry already discovered for a number of them.[4-12] Support for their utilization as models is provided by recent observations that certain metal-cluster derivatives are effective homogeneous catalysts for a number of processes which, until these particular discoveries, could only be catalyzed by heterogeneous systems. For instance $[Os_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ have been found to homogeneously catalyze the reduction of carbon monoxide by dihydrogen to methane,[13] a reaction readily promoted by nickel surfaces[14] and for which mononuclear homogeneous catalysts have thus far not been reported.[15] Furthermore ruthenium and mixed iron/ruthenium carbonyl clusters, in the presence of a base,

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