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Substitution Chemistry of the Doubly Bonded Ditungsten(IV) Ethoxide Complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2}$ toward Heterocyclic Tertiary Amines

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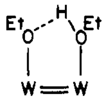
The displacement of the two ethanol ligands of $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2}$ (**1**) by pyridine (py), 4-methylpyridine (4-Mepy), or 4-phenylpyridine (4-Phpy) affords orange ditungsten(IV) complexes of the type $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2}$, where L = py (**3**), 4-Mepy (**4**), or 4-Phpy (**5**), in which a W–W double bond is believed to be retained. Complexes **3**–**5** possess quite different electrochemical redox behavior (in 0.2 M TBAH–$\mathrm{CH_2Cl_2}$) from that of **1**, specifically, two one-electron oxidations ($E_{1/2}$ values ca. +0.5 and +1.0 V vs. SCE) that are reversible or approach electrochemical reversibility, compared to an irreversible two-electron oxidation ($E_{p,a} \sim +0.9$ V vs. SCE) in the case of **1**. These differences can be related directly to the existence, in the case of **1**, of the coupled electrochemical–chemical (E–C) reaction sequence $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2} \xrightarrow{-2e^-(E)} [\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2}]^{2+} \xrightarrow{-2H^+(C)} \mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_4}$, which cannot occur with **3**–**5**. Electrochemical oxidation of 0.2 M TBAH–$\mathrm{CH_2Cl_2}$ solutions of **3**–**5** generates the ESR-active monocations. The reaction of **1** with 2-hydroxypyridine (Hhp) gives the hp-bridged complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(hp)_2}$ (**6**), which can be reduced chemically (with $(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Co}$) and electrochemically to its ESR-active monoanion. The species $[\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2}]^+$, where L = py, 4-Mepy, or 4-Phpy, and $[\mathrm{W_2Cl_4(\mu\text{-OEt})_2(hp)_2}]^-$, are formally derivatives of the $\mathrm{W_2}^{9+}$ and $\mathrm{W_2}^{7+}$ cores, respectively, which, on the basis of the existing MO treatment of molecules of this type, can be considered as examples of molecules possessing W–W bonds of order 1.5, albeit ones with different ground-state electronic configurations ($\sigma^2\pi^1$ and $\sigma^2\pi^2\delta^{*1}$).

Introduction

Studies on the alcohol–alkoxide exchange reactions of the doubly bonded ditungsten(IV) complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2}$ (**1**) have demonstrated[1] that the first step is the replacement of the two very labile ethanol ligands. This result has important ramifications in that the observed reductive coupling of ketones by this complex[2,3] is believed to proceed through the intermediacy of $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(ketone)_2}$.[3] Accordingly, we have sought to prepare stable complexes of the type $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2}$, with a view to characterizing as completely as possible such a group of complexes in which the type of hydrogen-bonded bridge (**2**)



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that exists in complex **1** and other compounds of this kind[1,4] is no longer possible. In view of the reports[5,6] that the pyridine-containing complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(py)_2}$ can be isolated, although it has not yet been fully characterized, we chose to focus our study upon complexes that contained pyridine ligands.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen gas, and all solvents were deoxygenated prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl. 2-Hydroxypyridine (Hhp) was purchased from Aldrich Chemical Co. and was sublimed prior to use. Pyridine was distilled from sodium metal, and 4-methylpyridine was distilled prior to use while 4-phenylpyridine was used without further purification. The complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2}$ was prepared by the literature method.[4]

(a) $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(py)_2}$ (3). Pyridine (0.52 mL, 6.45 mmol) was added to a slurry of 1.13 g (1.45 mmol) of $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2}$ in 30 mL of THF. The red solution was stirred at room temperature for 1 h, after which time the volume was reduced to ~10 mL and the reaction mixture filtered. The red precipitate was washed with 2 × 2 mL of a 1:1 hexane–diethyl ether mixture. A second crop of product could be obtained by treating the reaction filtrate with an excess of 1:1 hexane–diethyl ether and cooling it to 0 °C; yield 0.98 g (80%). Anal. Calcd for $\mathrm{C_{18}H_{30}Cl_4O_4N_2W_2}$: C, 25.47; H, 3.54; Cl, 16.75. Found: C, 25.69; H, 4.05; Cl, 16.38.

(b) $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(4\text{-}Mepy)_2}$ (4). This complex was prepared by using a procedure analogous to that described in part a; yield 63%. Anal. Calcd for $\mathrm{C_{20}H_{34}Cl_4O_4N_2W_2}$: C, 27.40; H, 3.88. Found: C, 27.37; H, 3.98.

(c) $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(4\text{-}Phpy)_2}$ (5). The reaction between $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2}$ and 4-phenylpyridine (1:2 stoichiometric proportions) was carried out by using a procedure similar to that described in part a; yield 82%. Anal. Calcd for $\mathrm{C_{30}H_{38}Cl_4O_4N_2W_2}$: C, 36.03; H, 3.83. Found: C, 35.85; H, 3.98.

(d) $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(hp)_2}$ (6). A solution containing 1.21 g (1.5 mmol) of freshly recrystallized $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2}$, 0.44 g (4.6 mmol) of 2-hydroxypyridine (Hhp), and 15 mL of $\mathrm{CHCl_3}$ was refluxed for 30 min and then cooled to room temperature; a small amount of orange solid was present at this stage. A quantity of tropylium hexafluorophosphate (0.3 g, 1.3 mmol) was added to the reaction mixture, which was then stirred for 30 min. The resulting orange precipitate was separated by filtration, washed with acetone, and vacuum dried. Further crops of product were obtained by removing the solvent under a stream of nitrogen gas and washing the precipitated orange solid with minimum volumes of acetone; yield 0.52 g (43%). Anal. Calcd for $\mathrm{C_{14}H_{18}Cl_4O_2N_2W_2}$: C, 21.32; H, 2.28; Cl, 18.00. Found: C, 21.27; H, 2.32; Cl, 17.59.

(e) $[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Co}][\mathrm{W_2Cl_4(\mu\text{-OEt})_2(hp)_2}]$ (7). A slurry consisting of 0.15 g (0.19 mmol) of $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(hp)_2}$ and 0.072 g (0.38 mmol) of cobaltocene in 10 mL of acetone was stirred for 15 min in a flask covered with aluminum foil. The reaction mixture was filtered under nitrogen and the black solid dried under vacuum; yield 0.13 g (68%). Anal. Calcd for $\mathrm{C_{24}H_{28}Cl_4CoN_2O_4W_2}$: C, 29.48; H, 2.87. Found: C, 30.48; H, 3.10. The slightly high C and H microanalyses for this air-sensitive product were in accord with contamination by a small amount of impurity whose identity is at present unknown.

(f) The Reaction of $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(4\text{-}Phpy)_2}$ with 2-Propanol. This complex (0.50 g, 0.50 mmol) was refluxed in 7 mL of 2-propanol for 10 min. The resulting mixture was cooled to room temperature and filtered, and the green solid was washed with hexane. The crude product was extracted into chloroform, the extract reduced to a small volume, and hexane added to precipitate a quantity of the complex $\mathrm{W_2Cl_4(\mu\text{-OEt})_2(O\text{-}\mathit{i}\text{-}Pr)_2(\mathit{i}\text{-}PrOH)_2}$; yield 0.08g (18%). The identity of this product was confirmed by a comparison of its cyclic voltammogram (recorded for a solution in 0.2 M TBAH–$\mathrm{CH_2Cl_2}$) and spectroscopic properties with those of an authentic sample.[1]

Physical Measurements. Infrared spectra as Nujol mulls were recorded in the region 4000–400 cm^{-1} with a Beckman IR-12 spectrophotometer and an IBM IR/32 spectrometer. Electronic absorption

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(1) Cotton, F. A.; Falvello, L. R.; Fredrich, M. F.; DeMarco, D.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 3088.

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Table I. ^1H NMR and Electronic Absorption Spectra of Pyridine Ligand Complexes of the Ditungsten(IV) Alkoxides

compd	^1H chem shifts,[a] δ				elec abs spectra, nm[b]
	phenyl/pyridine rings	$-CH_2-$ (bridge)	$-CH_2-$ (terminal)	$-CH_3$	
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(py)_2$ (3)	7.86 (d), 7.12 (t), 6.88 (t)	5.62 (q)	5.42 (q)	~1.40[c]	428 (5.3)
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Mepy)_2$ (4)	7.73 (d), 6.72 (d)	5.56 (q)	5.43 (q)	~1.40[c,d]	460 sh, 410 (5.2)
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Phpy)_2$ (5)	7.88 (d), 7.53 (d), 7.16 (d), 7.00 (s)	5.67 (q)	5.47 (q)	~1.40[c]	464 (6.3)
$W_2Cl_4(\mu\text{-}OEt)_2(hp)_2$ (6)	8.66 (d), 8.02 (t), 7.09 (m)	6.11 (q)		1.11 (t)	449 (2.7), 354 (14.1)

[a] All spectra were recorded at ambient temperature in $CDCl_3$ with the residual $CHCl_3$ protons as the internal reference. Abbreviations are as follows: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. [b] All spectra were recorded between 800 and 300 nm in CH_2Cl_2. Numbers in parentheses are molar extinction coefficients ($\epsilon_{max} \times 10^{-3}$). [c] Center of overlapping triplets due to bridging and terminal OEt ligands. [d] The resonance due to $-CH_3$ of the 4-Mepy ligand is at δ +2.39 (s).

Table II. Cyclic Voltammetric Data for Pyridine Ligand Complexes of the Ditungsten(IV) Alkoxides[a]

compd	$E_{1/2}$(ox)(2)	$E_{1/2}$(ox)(1)	$E_{1/2}$(red)(1)	$E_{1/2}$(red)(2)
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(py)_2$ (3)	+1.12 (100)	+0.54 (100)	−1.29[b]	
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Mepy)_2$ (4)	+1.08 (90)	+0.51 (90)	−1.32[b]	
$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Phpy)_2$ (5)	+1.09 (110)	+0.53 (110)	−1.28[b]	
$W_2Cl_4(\mu\text{-}OEt)_2(hp)_2$ (6)		+1.23 (100)	−0.39 (90)	−1.16 (100)

[a] In volts vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All data reported here were recorded at $v = 200$ mV/s. $E_{p,a} - E_{p,c}$ values are given in parentheses. [b] This reduction process is electrochemically irreversible (see Figure 1a) so that only the $E_{p,c}$ value is quoted.

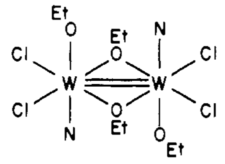
spectra of dichloromethane solutions were recorded by using a Hewlett-Packard 8450 UV–vis spectrophotometer in conjunction with a Hewlett-Packard 7225A plotter. The ^1H NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL-200 spectrometer using $CHCl_3$ as the internal reference. Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature and are uncorrected for junction potentials. All voltammetric measurements were made at a platinum-bead electrode in solutions deaerated with a stream of dry nitrogen gas. These cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7015B X-Y recorder. X-Band ESR spectra were recorded at −160 °C with dichloromethane solutions of the complexes by using a Varian E-109 spectrometer. Microanalyses were performed by Dr. C. S. Yeh and Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

Complexes with Monodentate Pyridine Ligands. The pyridine complex $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(py)_2$ has been reported to form[5] upon reacting the ethanol-containing complex $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ (**1**) with pyridine in chloroform solution at −78 °C. In neither this report[5] nor a later one from another group[6] was the yield of this product reported. Furthermore, these earlier investigations[5,6] provided very few details on the properties of this material with the exception of its IR spectrum[5] and the confirmation from a solution molecular weight determination[6] and a mass spectrum[5] that it is "dimeric". This is perhaps understandable since at the time the structural details of the precursor complex **1** had not yet been established.[4]

In our hands, this complex (**3**) and its 4-methylpyridine (4-Mepy) (**4**) and 4-phenylpyridine (4-Phpy) (**5**) analogues can be prepared in good yield (>60%) from the reaction of **1** with the appropriate pyridine ligand in tetrahydrofuran at room temperature. These orange complexes have appreciable air stability; the 4-Phpy derivative **5** is seemingly stable for several days in the laboratory air. Thus, we cannot attribute the stability of the crystalline alcohol derivatives $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ to the presence of strong hydrogen-bonded alcohol–alkoxide bridges **2**,[4] since even when this bridge system has been disrupted (as in these pyridine derivatives), the ditungsten(IV) complexes are still quite stable in the solid state. As far as we can ascertain, the pyridine complex **3** prepared by us is the same as that prepared by Reagan and Brubaker,[5] at least insofar as the microanalytical data and IR spectral properties are concerned.

The ^1H NMR spectra of the pyridine ligand complexes **3–5** display two sets of methylene quartets (Table I) due to the bridging and terminal ethoxide ligands ($J \simeq 7$ Hz for each) and two overlapping triplets from the methyl protons of the two types of ethoxide ligands.[7] These assignments follow from those previously given for **1** and other complexes of this type,[1,4] namely, that the lower field methylene resonances can be attributed to the OEt bridges. However, note that the chemical shift difference between each pair of methylene resonances is much smaller than in the case of **1**. The integrated intensities of the ethoxide and pyridine ligands are in accord with the stoichiometry and structure we assign to these complexes:



3, N = py
4, N = 4-Mepy
5, N = 4-Phpy

In spite of the formal similarity between $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ and complexes **3–5**, the replacement of the ROH ligands by py, 4-Mepy, or 4-Phpy has a pronounced effect upon the electronic structure of the doubly bonded W_2^{8+} core. This is reflected by the electronic absorption spectral differences; viz., $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ possesses two characteristic electronic transitions between 800 and 300 nm with λ_{max} values in the ranges 742–730 and 433–420 nm,[1] whereas the pyridine ligand complexes (Table I) possess an intense absorption band ($\epsilon_{max} \sim (5\text{–}6) \times 10^3$) in the region between 465 and 410 nm.

An even more dramatic illustration of the difference is seen in the electrochemical redox properties of these complexes. The appropriate cyclic voltammetric data for 0.2 M tetra-*n*-

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(7) Note that the ^1H NMR spectrum we find for $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(py)_2$ differs in one important respect from that described by Reagan and Brubaker.[5] While we see two resolvable methylene quartets (due to the bridging and terminal ethoxide ligands), the earlier report[5] quotes but a single value of δ +5.88. It seems likely that the latter actually represents the *average* for the methylene quartets, although the reported[5] chemical shift differs significantly (by ~0.4 ppm) from that found by ourselves.

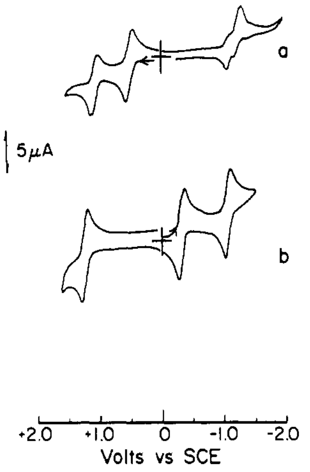


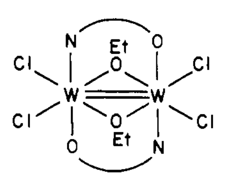
Figure 1. Cyclic voltammograms (at a Pt-bead electrode, ν = 200 mV/s) in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane: (a) $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(py)_2$; (b) $W_2Cl_4(\mu\text{-}OEt)_2(hp)_2$.

butylammonium hexafluorophosphate–dichloromethane solutions of the complexes **3**–**5** are given in Table II. These three complexes exhibit almost identical redox behavior, the cyclic voltammogram shown in Figure 1a being truly representative of this class of molecules. The characteristic features are as follows: (1) two one-electron oxidations (at ca. +0.5 and +1.0 V vs. SCE) that meet the usual criteria, with our experimental setup, of being electrochemically reversible or, at least, approaching reversibility,[8,9] and (2) an irreversible one-electron reduction that appears in the vicinity of −1.3 V vs. SCE. Actually there is evidence for two sets of coupled processes occurring close together within the potential range −1.05 to −1.35 V (see Figure 1a). We do not yet understand the relationship between them and accordingly have chosen not to pursue a study of the reduction chemistry at this time. However, of special significance as far as the present study is concerned is the recognition that the pyridine complexes **3**–**5** possess two one-electron oxidations, whereas the alkoxide–alcohol complexes $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ exhibit a single irreversible two-electron oxidation whose potential (∼ +0.9 V) is between those of the former. This irreversible electrochemical process is followed by the formation of the ditungsten(V) product $W_2Cl_4(\mu\text{-}OR)_2(OR)_4$,[1,4] a reaction course not open to **3**–**5**. These electrochemical differences reflect very nicely how the existence of coupled electrochemical–chemical processes are dependent upon the nature of L (i.e., upon whether L is an alcohol or a pyridine ligand).

The electrolysis of solutions of **3**–**5** in 0.2 M TBAH–CH_2Cl_2 at ca. +0.7 V generates yellow solutions of the monocations that exhibit characteristic and virtually identical ESR spectra (at −160 °C), viz., for **3**, g_1 = 1.88, g_2 = 1.70, and g_3 = 1.66, while for **5**, g_1 = 1.87, g_2 = 1.70, and g_3 = 1.66.[10] These solutions, which can be re-reduced electrochemically to the neutral ditungsten(IV) parent compounds **3**–**5**, have CV's identical with those of the latter (Figure 1a and Table II), with the exception that the couple at ca. +0.5 V now corresponds to a one-electron reduction.

Thus, the preceding results indicate that with $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2L_2$, where L = py, 4-Mepy, or 4-Phpy, we have a class of molecules that like $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ possess tungsten–tungsten double bonds, although the chemistry is dictated to some extent by whether alcohol or pyridine ligands occupy the most labile coordination sites. We note that it is possible to convert the 4-Phpy complex **5** to $W_2Cl_4(\mu\text{-}OEt)_2(O\text{-}i\text{-}Pr)_2(i\text{-}PrOH)_2$ upon heating it in neat 2-propanol. Although a significant amount of decomposition occurs during the course of this reaction, this conversion is in accord with the retention of the doubly bonded W_2^{8+} core within complexes **1**, **3**, **4**, and **5**.

A Complex Containing the Bridging 2-Hydroxypyridine Ligand. In view of the relative ease with which alcohol and alkoxide exchange takes place with the terminal ligands of **1**,[1] we felt that reaction of **1** with 2-hydroxypyridine might displace not only the EtOH ligands but also the terminal OEt groups. This indeed occurs to give the complex $W_2Cl_4(\mu\text{-}OEt)_2(hp)_2$ (**6**), which we believe possesses the structure depicted, where N–O represents the bridging hp ligand, a familiar bonding mode for hp and other ligands of this type in multiply bonded dimetal complexes.[11] The ¹H NMR spectrum of **6** (Table I) is fully in accord with this structure, a single methylene quartet (δ +6.11) and methyl triplet (δ +1.11) being assignable to the remaining (bridging) ethoxide ligands. Like the other pyridine ligand complexes, **6** possesses a band close to 450 nm in its electronic absorption spectrum but, in addition, shows an additional intense feature at 354 nm that can be attributable (tentatively) to a W → hp(π^*) charge-transfer transition.



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One striking difference between the hp-bridged complex **6** and the three other pyridine ligand complexes **3**–**5** is seen in a comparison of their electrochemical properties (Table II and Figure 1). Instead of two oxidations and one reduction being observed within the potential range +1.6 to −1.6 V, as in the case for **3**–**5**, complex **6** possesses one oxidation and two reductions. It is as if comparable redox processes are shifted by ca. 0.8 V to more positive potentials in **6** compared to those in **3**–**5**, thereby making a second reduction much more accessible and shifting the second oxidation >+1.8 V, beyond the range of our measurements in 0.2 M TBAH–CH_2Cl_2. The reduction at −0.39 V was shown by coulometry to correspond to a one-electron process. Bulk electrolysis at a potential of −0.5 V caused the solution to change color from a pale orange to an intense blue. Cyclic voltammetry on the solution following electrolysis showed that the $[W_2Cl_4(\mu\text{-}OEt)_2(hp)_2]^-$ anion had been generated. This solution had an electronic absorption spectrum that exhibited an intense band at 587 nm ($\epsilon_{max} > 2.5 \times 10^3$) and an ESR spectrum (at −160 °C) with three *g* values (g_1 = 1.93, g_2 = 1.86, and g_3 = 1.62). The g_2 feature was very broad and showed some unresolved splitting that might be attributable to nitrogen hyperfine splitting.

The accessibility of this reduction suggested that we might be able to generate the anion chemically.[12] This was accomplished by using acetone solutions of cobaltocene to yield dark purple-black $[(\eta^5\text{-}C_5H_5)_2Co][W_2Cl_4(\mu\text{-}OEt)_2(hp)_2]$ (**7**). Dichloromethane solutions of this complex exhibit electronic

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(8) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(9) For each couple, $i_{p,a}/i_{p,c}$ = 1 (or very close to unity) and $i_p/v^{1/2}$ ratios were constant in the sweep rate range 50–400 mV/s in accord with diffusion control. At v = 200 mV/s, the potential separation between the coupled anodic and cathodic peaks was close to 100 mV and increased slightly with an increase in scan rate.

(10) When dichloromethane solutions of $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Phpy)_2$ were treated with 1 equiv of $NOPF_6$ (used here as an oxidant), solutions containing the monocation could be generated (as characterized by CV) although our attempts to isolate pure samples of $[W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(4\text{-}Phpy)_2]PF_6$ have so far failed.

(11) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(12) Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

absorption and ESR spectral properties identical with those shown by solutions containing the electrochemically generated anion. The electrochemical properties of 7 confirmed its identity. A CV showed that it possessed the expected two one-electron oxidations and a one-electron reduction, together with a couple at –0.90 V due to cobaltocene/cobaltocenium.[12]

Note that, in the preparative procedure used to obtain the neutral complex 6 (see Experimental Section), we found some reduction to the monoanion occurred in the reaction mixture. Hence we added a quantity of tropylium hexafluorophosphate[13] to reoxidize the anion back to the neutral complex and thereby enhance its yield.

Our attempts to develope the redox chemistry of 6 further by generating the monocation upon oxidizing its solutions in 0.2 M TBAH–CH_2Cl_2 at +1.40 V led to decomposition to give unidentified species.

Concluding Remarks

The reactions of several pyridine ligands (py, 4-Mepy, 4-Phpy, or Hhp) with $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ give the doubly bonded ditungsten(IV) complexes $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2$, where L = py, 4-Mepy, or 4-Phpy, and $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$, which exhibit well-defined redox chemistry. In the case of $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2$, electrochemical oxidation to the paramagnetic monocations can be achieved, whereas $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$ is easily reduced (chemically and electrochemically) to its monoanion. The oxidation to $[W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2]^+$ represents, on the basis of the Fenske–Hall molecular orbital treatment of molecules of this type,[4] the loss of an electron from the π-bonding HOMO and a configuration change from $\sigma^2\pi^2$ (double bond) to $\sigma^2\pi^1$. Thus, such cations may represent examples of W–W bonds of order 1.5. On the other hand, reduction of $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$ to $[W_2Cl_4(\mu\text{-OEt})_2(hp)_2]^-$, if this involves the addition of an electron to a δ^* orbital (the predicted LUMO),[4] also represents formally the formation of a W–W bond of order 1.5, although one that is clearly of a different type, viz. $\sigma^2\pi^2\delta^{*1}$.

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Registry No. 1, 78350-74-0; 3, 91551-22-3; 3 (monocation), 91551-28-9; 4, 91551-23-4; 4 (monocation), 91551-29-0; 5, 91551-24-5; 5 (monocation), 91551-30-3; 6, 91551-25-6; 7, 91551-27-8; $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-}Pr)_2(i\text{-}PrOH)_2$, 85202-62-6; W, 7440-33-7.

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[13] Tropylium hexafluorophosphate is, on the basis of its electrochemical properties, a suitable oxidant for this purpose. See footnote 11 in: Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 169.

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New Bromo Complexes of Osmium(IV) and Osmium(III): $[Os_2Br_{10}]^{2-}$ and $OsBr_3(PPh_3)_2(CH_3CN)$

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When $(n\text{-}Bu_4N)_2[OsBr_6]$ is refluxed in trifluoroacetic acid for several hours, it is converted in about 80% yield to $(n\text{-}Bu_4N)_2[Os_2Br_{10}]$ (1). When 1 is warmed in acetonitrile containing additional PPh_3, $OsBr_3(PPh_3)_2(CH_3CN)$ (2) is obtained in yields around 30%. Compound 1, a black crystalline solid, has been shown by X-ray crystallography to contain edge-sharing bioctahedral $[Br_4Os(\mu\text{-}Br)_2OsBr_4]^{2-}$ anions. These reside on crystallographic inversion centers and have essentially D_{2h} symmetry. The Os–Os distance is 3.788 (3) Å, and other important average dimensions are Os–(μ-Br) = 2.544 [4] Å, Os–Br(terminal) = 2.454 [5] Å, and Os–Br–Os = 96.3 (1)°. The structure indicates that Os–Os bonding does not occur although the compound is only feebly paramagnetic. Compound 1 crystallizes in space group $P2_1/n$ with unit cell dimensions a = 12.186 (4) Å, b = 16.528 (4) Å, c = 12.908 (4) Å, β = 103.02 (2)°, V = 2532 (3) Å^3, and Z = 2. Compound 2 consists of approximately octahedral molecules in which the bromine atoms are meridional and the Ph_3P ligands occupy trans positions above and below the $OsBr_3(CH_3CN)$ plane. The important bond distances are Os–Br = 2.481 (1), 2.499 (1) (trans Br's), 2.499 (1) Å (trans to CH_3CN), Os–P = 2.418 (2), 2.419 (2) Å, and Os–N = 2.024 (10) Å. Compound 2 crystallizes in space group $P2_1/n$ with the following unit cell dimensions: a = 10.210 (2) Å, b = 15.308 (3) Å, c = 23.122 (3) Å, β = 91.15 (3)°, V = 3613 (2) Å^3, Z = 4.

Introduction

The hexahaloosmates(IV) and their derivatives play a leading role in the chemistry of tetravalent osmium,[2,3] and for this reason the $[OsX_6]^{2-}$ ions have already been extensively studied both chemically and physically. In spite of this, it has not previously been observed that $[OsX_6]^{2-}$ ions can dimerize with attendant loss of halide ions to give a binuclear product. We report here the preparation and characterization of the $[Os_2Br_{10}]^{2-}$ ion. In the course of studying the chemical reactivity of this new complex anion, we have found that it reacts wth triphenylphosphine in acetonitrile to give the osmium(III) complex $OsBr_3(PPh_3)_2(CH_3CN)$, the chloro analogue of which is already known.[4-6] In this paper we present full preparative and crystallographic details for the two new compounds $(n\text{-}Bu_4N)_2[Os_2Br_{10}]$ (1) and $OsBr_3(PPh_3)_2(CH_3CN)$ (2).

Experimental Section

Preparation of $(n\text{-}Bu_4N)_2[Os_2Br_{10}]$ (1). The starting material, $(n\text{-}Bu_4N)_2[OsBr_6]$, was prepared by a method in the literature.[3] Two grams (1.73 mmol) of $(n\text{-}Bu_4N)_2[OsBr_6]$ and 15 mL of trifluoroacetic acid were placed in a 50-mL round-bottom flask equipped with a condenser and stirring bar. The mixture was heated to reflux, and a black solid began to form. Refluxing was continued for about 2 h at which time there appeared to be no further formation of precipitate, and the supernatant liquid was either pale yellow or pale red. The black solid was isolated by filtration and dried under vacuum.

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