Communication

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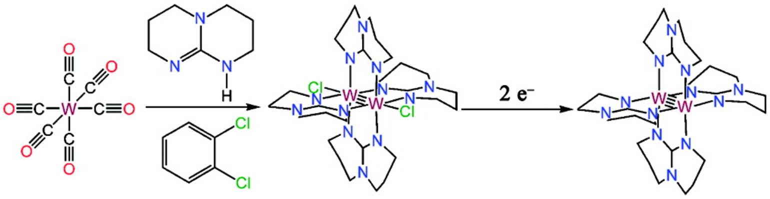

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COMMUNICATIONS

Expeditious Access to the Most Easily Ionized Closed-Shell Molecule, $W_2(hpp)_4$

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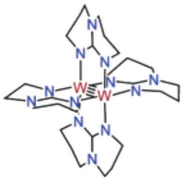
One of the special distinctions of chemistry is the ability of chemists to make new forms of matter with new properties. In contrast, physicists look for ultimate reasons why a *given* form of matter (including the cosmos as a whole) has the properties it does. The *ne plus ultra* of chemistry is not only to make a new form of matter, but to make it efficaciously. That point is illustrated by this communication.

Several years ago we reported that the molecule $W_2(hpp)_4$, **I** (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, **II**), has an onset ionization energy of only 3.51 eV, making it the most easily ionized stable molecule known.[1] Despite the fact that it has a closed-shell electronic structure, it is more easily ionized than such famously strong reducing agents as $(\eta^6\text{-}C_6Et_6)(\eta^5\text{-}C_5Me_5)Fe$ [2] and $(\eta^5\text{-}C_5Me_5)_2Co$,[3] which have a lone electron sitting outside of their closed shells and have ionization energies of 3.95 eV (onset) and 4.71 eV (vertical), respectively.[1] It even surpasses the cesium atom, commonly cited as the most easily oxidized of all neutral chemical entities,[4] by more than 0.35 eV. In the previous report[1] a theoretical explanation was also provided to account for the easy ionization of $W_2(hpp)_4$, which is characterized by a strong interaction of the hpp pπ orbitals with the δ orbitals of the quadruply bonded W_2^{4+} unit.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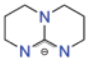
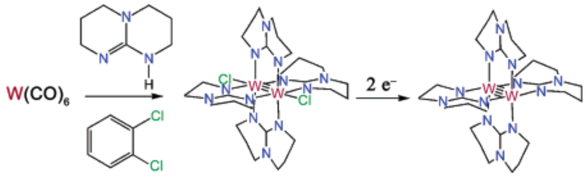

II

Despite the unique character and potential utility of $W_2(hpp)_4$ it would have limited importance if it could be obtained only by the difficult, laborious, and relatively low-yield route by which it was first obtained.[5] As shown in Chart 1, this route begins with two starting materials, $W(CO)_6$ and WCl_6 (which is inconvenient to handle and must be sublimed prior to its use), from which WCl_4 is made. The next two steps, which lead to $W_2(hpp)_4Cl_2$, are carried out in one pot, but the combined yield is low. The final step, reduction of $W_2(hpp)_4Cl_2$ to $W_2(hpp)_4$, can be carried out in essentially quantitative yield, although the isolated yield as crystalline material is smaller.[5b] The net yield, over three laborious stages, is 40−45%.

Subsequently, another route[6] was reported, but it is even less efficacious, as also shown in Chart 1. It employs the same starting materials, requires five steps, each in a separate vessel, with some highly reactive intermediates that require purification by sublimation,[7] and gives a net yield of $W_2(hpp)_4$ in solution of only ca. 30%. In the chart the typical yields are given either in bold or in italics in parentheses.

Even though $W_2(hpp)_4$ has great potential for use as a strong reducing agent, it is clear that the current methods of preparation would discourage most synthetic chemists from using it. Therefore, we decided to seek a convenient method of preparation using relatively inexpensive and easily handled starting materials. We recognized that in the method shown at the top of Chart 1 having an efficient preparation of $W_2(hpp)_4$ is equivalent to having an efficient preparation of $W_2(hpp)_4Cl_2$, because a one-step reaction with powerful reductants such as $NaHBEt_3$[8] or potassium metal[5b] with tetrahydrofuran as a solvent are very convenient and afford $W_2(hpp)_4$ in high yields. $W_2(hpp)_4Cl_2$ is a very desirable intermediate to work with since it is very stable, easily handled, and readily stockpiled for future use.

We now report a convenient, one-step, high-yield synthesis of $W_2(hpp)_4Cl_2$,[9,10] which works on a multigram scale. This is, in effect, a convenient, two-step, high-yield synthesis of $W_2(hpp)_4$. It uses only $W(CO)_6$ (an air-stable, relatively inexpensive, and easily handled compound) as the sole source of tungsten as shown in the equation below:



The use of $W(CO)_6$ came under consideration because it had previously been used to make quadruply bonded ditungsten compounds, notably with 2-hydroxy-6-methylpyridine,[11] 2-hydroxy-6-chloropyridine,[12] 2,4-dimethyl-6-hydroxypyrimidine,[13] and tetraphenylporphyrin.[14] These reactions with $W(CO)_6$ share the common feature of requiring vigorous reflux (180−200 °C) in a high-boiling solvent such as diglyme or Decalin. In addition to these older results, we also had in mind our recent isolation and characterization of a series of ditungsten compounds, resulting from the high-temperature reaction of $W(CO)_6$ with *N,N′*-di-*p*-anisylformamidine (HDAniF),[15] even though all of these compounds were edge-sharing bioctahedra and not the desired quadruply bonded tetragonal paddlewheel complexes. Some of the compounds identified in this earlier study revealed that the HDAniF ligand is susceptible to decomposition. Under harsh conditions hpp is a considerably more robust ligand,[16] and it is also capable of

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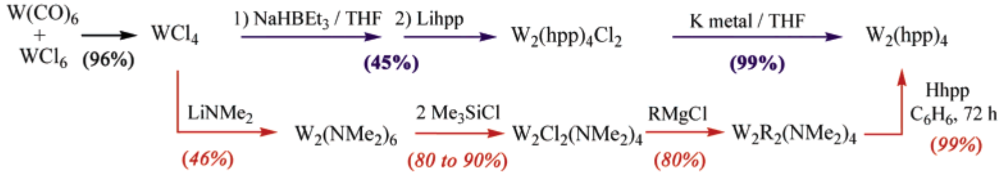
Chart 1



stabilizing oxidation states in dimetal complexes[17] that are not accessible with the formamidinates. A study of the reaction of $W(CO)_6$ with Hhpp, analogous to the recent report of reactions with HDAniF, was therefore undertaken. It was expected that reaction of $W(CO)_6$ with Hhpp might produce, at least initially, partial substitution products as has often been the case when group 6 metal carbonyls react with amidines. Apart from the production of W_2 products recently reported by us from reaction of $W(CO)_6$ with amidines, there were earlier reports of mixed amidinate/carbonyl products when $Cr(CO)_6$ and $Mo(CO)_6$ were used.[18,19] We therefore carried out our work in such a way as to be alert for such products in the reaction of $W(CO)_6$ with Hhpp, and this has led to the one-pot reaction which produces the $W_2(hpp)_4$ precursor, $W_2(hpp)_4Cl_2$, in more than 90% yield using only the commercially available and stable compounds $W(CO)_6$, Hhpp, and *o*-dichlorobenzene.[20] The latter acts not only as solvent but also as a source of chlorine atoms, and it is reduced to 2,2′-dichlorobiphenyl as shown by GC−MS.

Due to the poor solubility of $W_2(hpp)_4Cl_2$, no electrochemical measurements have been reported on it. However, the fact that the products of two chemical reductions exist, namely $W_2(hpp)_4Cl$[8] and $W_2(hpp)_4$, implies that two reversible reduction processes occur in this system. Changing the Cl^- counteranions for $TBPF^-$ [21] increased the solubility of the $W_2(hpp)_4{}^{2+}$ core and allowed the study of its electrochemical behavior. Differential pulse voltammetry upon $W_2(hpp)_4(TFPB)_2$ in THF shows two peaks at −0.94 and −1.78 V vs Ag/AgCl, which represent a reduction process with $E_{1/2}$ of −0.97 V for the first and −1.81 V for the second.[22] These are the most negative potentials recorded for any dimetal bonded species,[23] a fact which is reasonable since the fully reduced species $W_2(hpp)_4$ is the most easily ionized molecule in the gas-phase recorded to date. These electrode potentials confirm that $W_2(hpp)_4$ is a powerful reducing agent.

Since the conversion of $W_2(hpp)_4Cl_2$ to $W_2(hpp)_4$ is simple and efficient, the way is now open for productive exploration of the chemistry of $W_2(hpp)_4$, a compound that ionizes easily but is stable in a vacuum to at least 300 °C. Early exploratory work has shown that $W_2(hpp)_4$ easily reduces TCNQ (TCNQ = 7,7,8,8-tetracyano-quinonedimethane), C_{60}, and halogenated species such as CH_2Cl_2.[5b] Finally, it should be noted that the synthetic chemist has rather few choices for strong chemical reducing agents that are soluble in organic solvents.[24] Thus, it is expected that $W_2(hpp)_4$ will now join the group of well-known reducing agents, e.g., $Cp^*{}_2Co$ and $Cp^*{}_2Cr$, the latter of which is competent even at reducing coordinated dinitrogen under mild conditions.[25,26]

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(9) $W_2(hpp)_4Cl_2$ was prepared in a Schlenk line equipped with a Hg bubbler. An oven-dried 100-mL Schlenk flask was charged with a stir bar, 1.00 g (2.84 mmol) of $W(CO)_6$, 0.90 g (6.47 mmol) of Hhpp, and 30 mL of degassed *o*-dichlorobenzene. The flask was then fitted with a water-cooled coldfinger. This mixture was vigorously refluxed under N_2 at 200 °C for 8 h and then cooled to ambient temperature. The brown-green precipitate that formed was collected by filtration and washed with 3 × 15 mL of CH_2Cl_2. Yield: 1.29 g, 92%. The properties are the same as those reported in ref 5a.
(10) The synthetic method is so easy that a satisfactory synthesis was carried out by students as part of an experiment in an undergraduate laboratory taught by two of the coauthors of this manuscript.
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(20) A series of other Whpp compounds which may also be obtained by reaction of $W(CO)_6$ with Hhpp at temperatures below 200 °C, hereby providing insight into the reaction pathway leading to $W_2(hpp)_4Cl_2$, will be reported elsewhere.
(21) Synthesis of $[W_2(hpp)_4](TFPB)_2$. A 100-mL Schlenk flask was charged with 0.100 g (0.10 mmol) of $W_2(hpp)_4Cl_2$ and 0.180 g (0.20 mmol) of $K^+(TFPB^-)$, and 15 mL of CH_2Cl_2. The resulting suspension was stirred for 8 h. The red solution was filtered through Celite and layered with 50 mL of isomeric hexanes. Large green-brown crystals were obtained in 48−72 h. Yield: 0.147 g, 55%. Absorption spectrum (CH_2Cl_2) λ_{max} (ϵ_M): 269 (33000), 280 (sh, 25000), 361 (33000). ESI$^+$−MS: *m/z* 460 ($M^{2+}/2$). Anal. Calcd. for $C_{30}H_{48}F_6N_{12}O_2PW_2$: C, 41.75; H, 2.74; N, 6.35. Found: C, 41.32; H, 2.91; N, 6.65. Note: K^+TFPB^- ($TFPB^-$ = tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate) was prepared according to a literature procedure. See: Buschmann, W. E.; Miller, J. S.; Bowman-James, K.; Miller, C. N. *Inorg. Synth.* **2002**, *33*, 83.
(22) The differential pulse voltammogram was recorded with a CH Instruments model-CHI620A electrochemical analyzer in 0.1 M Bu_4NPF_6 solution in CH_2Cl_2 with Pt working and auxiliary electrodes, a Ag/AgCl reference electrode. The potential values are referenced to the Ag/AgCl electrode, and under the present experimental conditions, the $E_{1/2}$ for the Fc^+/Fc couple consistently occurred at +440 mV vs Ag/AgCl (ca. 660 mV vs SHE).
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(26) As pointed out by a reviewer, an additional advantage of using unsaturated hpp ligands is that these species are less likely to be susceptible to secondary reactions such as nucleophilic attacks observed occasionally on the π systems of the rings of $Cp^*{}_2Co^+$.

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