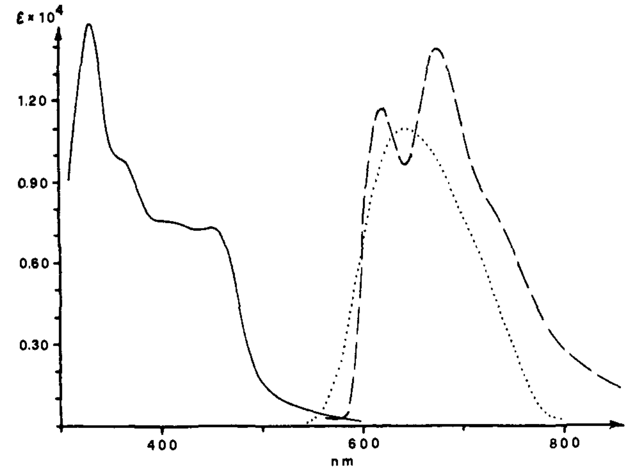

Figure 1. Absorption and emission spectra of $Ru(bipym)_3^{2+}$: —, absorption; ···, emission, aqueous solution 300 K; - - -, emission, solid complex 15 K.

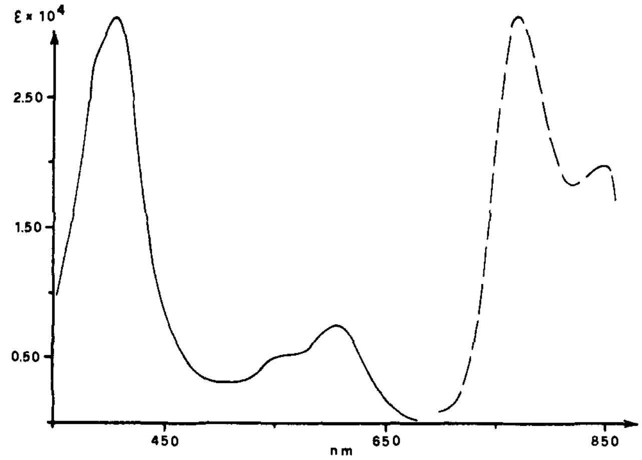

Figure 2. Absorption and emission spectra of $[(bipy)_2RubipymRu(bipy)_2]^{4+}$: —, absorption; - - -, emission, solid complex 15 K.

plexes did not show any reversible waves up to 1.3 V (vs. hydrogen). Spectrophotometric titration with Ce^{4+} indicates an oxidation rapidly followed by the reduction of the generated Ru(III) species by water. Formal reduction potentials were obtained from cyclic voltammograms on a Pt electrode in acetonitrile containing 0.1 M $[(n\text{-}Bu)_4N]PF_6$. Scan rates were varied between 100 and 500 mV/s. Owing to the onset of a steep increase of the base line at ~1.4 V, the cathodic and anodic waves were usually separated by more than 60 mV. Two well-defined waves were observed for the binuclear complex, the potential difference of 190 mV corresponding to a conproportionation constant of 1.63×10^3 for the generated mixed valence complex.[9] No reversible voltammogram was observed for the tetranuclear species IV. The formal reduction potentials (vs. hydrogen) of the various ruthenium(III)-bipyrimidine complexes are 1.64 V for I, 1.37 V for II, and 1.55 and 1.74 V for III. The value of 1.26 V for the $Ru(bipy)_3^{3+/2+}$ couple[4] was used to calibrate our measurements. The replacement of bipyridine by bipyrimidine thus shifts the reduction potential to considerably more positive values.

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A Quadruple Bond between Tungsten Atoms in an Air-Stable Compound

Sir:

The ability of transition metal atoms to form homonuclear multiple bonds (double,[1] triple,[2] and quadruple[3]) was first recognized, thus initiating an entirely new phase of transition metal chemistry, a relatively short time ago, but rapid progress has already been made in exploring this field.[4] The formation of quadruple bonds, which is restricted, so far as is presently known, to certain of the transition elements, mainly Re,[4] Mo,[4] Cr,[4] and Tc,[5] was only recently demonstrated for tungsten by the unequivocal characterization of the $[W_2Me_{8-x}Cl_x]^{4-}$ ions ($x = \sim 2.5$[6] or 0[7]), compounds of which are exceedingly reactive and thermally sensitive. We report here a method of preparation and proof of structure for a compound containing a quadruple W-W bond that is stable in air at ambient temperature, namely, $W_2(C_8H_8)_3$.

The existence of several compounds with the formula $M_2(C_8H_8)_3$ (M = Ti, V, Cr, Mo, W) was first announced a number of years ago.[8] However, except for $Ti_2(C_8H_8)_3$ no preparative methods nor any identifying physical or chemical properties were revealed. The structure of $Ti_2(C_8H_8)_3$, in which there is no M-M bond, was reported[9] in 1966. It was only with the report[10] last year that $Cr_2(C_8H_8)_3$ has a structure indicative of the presence of a quadruple Cr-Cr bond (but this report again reveals nothing about the preparation or other properties of the compound) that we became interested in the structure of $W_2(C_8H_8)_3$. It was possible (as Brauer and Kruger[10] themselves stated) that the molybdenum and tungsten compounds would be likely to have similar molecular structures. Our keen, long-standing[6,7,11] interest in the question of the stability of quadruple W-W bonds led us to examine the preparation and structure of $W_2(C_8H_8)_3$.

The preparation is quite simple. The reaction of WCl_4 with 2 molar equiv of $K_2C_8H_8$ in THF gave an intensely green solution from which a moderate yield of black crystals was obtained after removal of solvent and recrystallization from toluene. The mass spectrum has a prominent parent ion peak (m/e 680). The crystals appear to be stable in air for periods of at least a week.

Although the molecular structure of $W_2(C_8H_8)_3$ is quite similar to that of $Cr_2(C_8H_8)_3$ (vide infra) the compounds are not isomorphous. For $W_2(C_8H_8)_3$ we have space group $I\bar{4}$, $a = 15.820$ (3) Å, $c = 15.041$ (3) Å, $Z = 8$, meaning that the entire molecule constitutes the asymmetric unit. Using 2063 unique reflections with $I > 3\sigma(I)$ we have solved and refined the structure to convergence using anisotropic temperature parameters for all atoms. A spherical crystal was used to expedite the making of accurate absorption corrections, and both enantiomorphs were tested. The residuals obtained with the correct one ($R_1 = 0.038$, $R_2 = 0.048$) are significantly (*ca.* 0.006) lower than for the other one.

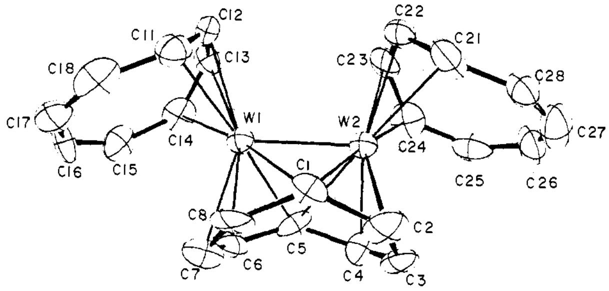

Figure 1. The molecular structure of $W_2(C_8H_8)_3$. In this ORTEP drawing each atom is represented by a scaled outline of its ellipsoid of thermal vibration.

Regrettably, the carbon atom positions,[12] and hence all the molecular parameters except the W–W distance have relatively large esds (e.g., 0.04 Å for C–C) because the intensities of all reflections are so dominated by the contribution of the tungsten atoms. Nonetheless, as shown in Figure 1, the molecular structure is of the same type as that reported for $Cr_2(C_8H_8)_3$ and the bonding can be viewed in the same way.

The bond order is believed to be 4 (as also suggested for the Cr compound[10]) because the diamagnetism requires it to be either 4 or 2, and a double bond would be expected to be much longer (Cf. 2.48–2.50 Å for Re=Re bonds).

The quadruple W–W bond in this case has a length of 2.375 (1) Å, which is ~0.12 Å longer than that in the $[W_2Me_{8-x}Cl_x]^{4-}$ ion. The length of the quadruple Cr–Cr bond in $Cr_2(C_8H_8)_3$, 2.214 (1) Å, exceeds that in the $Cr_2Me_8^{4-}$ ion,[13] 1.980 (5) Å, by an even greater amount.

We see here further examples of the fact that, for these M–M multiple bonds, bonds of a given order may vary considerably in length as the character of the ligands changes. It is notable that the quadruple W–W bond here is actually longer than the triple W–W bonds in the many W_2X_6 (X = CH_2SiMe_3, NR_2) compounds and their derivatives[14] recently described. The lengths of multiple M–M bonds seem to depend in part on the number of electrons formally occupying the orbitals of each metal atom. Thus, the $M_2X_8^{4-}$ ions contain 16-electron species (and the metal atoms in W_2X_6 molecules have only 12 electrons), whereas in the $M_2(C_8H_8)_3$ molecules (as well as the $CpM(CO)_2{\equiv}M(CO)_2Cp$ molecules, which have relatively long triple bonds[15]) we are dealing with 18-electron cases.

The ^{13}C and ^{1}H NMR spectra of $W_2(C_8H_8)_3$ at ambient temperature each contain one intense, sharp line for the 16 carbon or hydrogen atoms of the two η^4-C_8H_8 rings, which are evidently "whizzing" as rings so bound are well known to do.[16] However, we also see signals for the third ring that are consistent with its being stereochemically rigid. These observations are in contrast to the report by Timms and Turney[17] (who recently reported the preparation of $Cr_2(C_8H_8)_3$ by a metal vapor reaction) that the ^{13}C and ^{1}H spectra each consisted of only one resonance.[18]

Note Added in Proof. A neutron diffraction study, with J. M. Williams and A. Schultz, Argonne National Laboratory, is nearly complete, and has fully confirmed and extended the results of the x-ray work.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

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Exceedingly Short Metal-to-Metal Multiple Bonds

Sir:

Over the past decade, a facet of transition-metal chemistry first recognized[1-3] only in the early 1960s, namely, the ability of transition metal atoms to form multiple bonds, has experienced vigorous (lately, exponential) growth.[4] This growth has been highlighted by the discovery of hundreds of compounds containing triple and quadruple bonds[5] and by the development of an increasingly sophisticated understanding of the nature of these bonds.[6-9]

A natural question in this connection is how short may such multiple M–M bonds be? In terms of directly measured bond lengths in isolable compounds the shortest such bonds so far reported are to be found in several chromium[10] compounds, where Cr–Cr distances of 1.96–1.98 Å are found, and in several dimolybdenum compounds,[10] where Mo–Mo distances of ~2.09 Å are found.

Astonishingly short as these distances may seem, they are by no means the shortest possible. We report here the preparation and structural characterization of analogous dichromium and dimolybdenum compounds in which there are M–M distances that are *substantially* shorter than those mentioned above.

The reaction of 2,6-dimethoxyphenyllithium, (DMP-Li) with $Cr_2(O_2CCH_3)_4$ followed by suitable workup allows the isolation, in good yield, of red-orange and red crystalline products. These products are thermally stable at ambient temperature and only moderately air sensitive. They are crystallographically isomorphous and belong to space group $Pn2_1a$ with $Z = 4$ and the following unit cell dimensions: for $Cr_2(C_8H_9O_2)_4$, $a = 16.266$ (3), $b = 16.560$ (3), $c = 11.350$ (1) Å; for $Mo_2(C_8H_9O_2)_4$, $a = 16.576$ (3), $b = 16.436$ (5), $c = 11.546$ (3) Å. The chemical compositions are confirmed by the successful solution and refinement of the crystal structures.[11a]

The molecular structure of the chromium compound is shown in Figure 1. No crystallographic symmetry is imposed on the molecule, but it has approximately C_{2h} symmetry. Each DMP ligand is bidentate and bridging and they are arranged