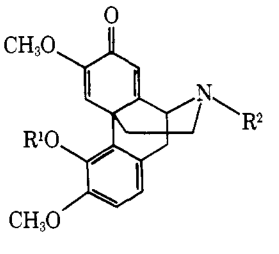
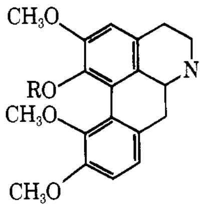
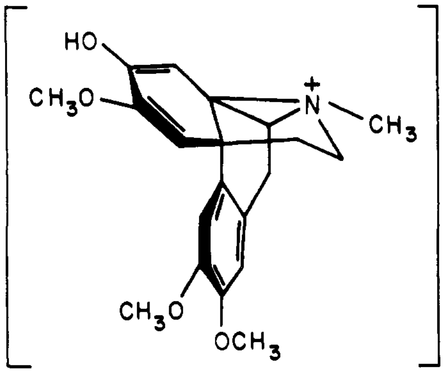


11a, $R^1 = H$; $R^2 = COOEt$
b, $R^1 = CH_3$; $R^2 = COOEt$
c, $R^1 = R^2 = CH_3$



12a, R = H
b, $R = CH_3$

The acid-catalyzed rearrangements of morphinandienones thus follow two principal routes, one which leads to dibenzazonine derivatives (e.g., **1** → **2** → **4**), and a second which leads to aporphines (e.g., **1** → **9** → **10**). The rearrangement to aporphines appears to be favored in reactions involving substrates and conditions which may enhance the participation of the nitrogen free electron pair, possibly through the intermediacy of a species such as **13**.[20] Examination of the molecular model of **13** indicates that stereoelectronic factors favor migration of the aryl group, to yield a proerythrinadienone intermediate. In contrast, those acid-catalyzed rearrangements of morphinandienones whch involve minimal nitrogen participation (e.g., with boron trifluoride salts or amide derivatives) result in migration of the alkyl group, to yield neospirine derivatives.



13

Biosynthetic studies have demonstrated that (±)-reticuline (**5d**) is a precursor of the aporphine alkaloids (+)-bulbocapnine,[21] (+)-isoboldine,[22] and (+)-magnoflorine,[23] and these results have been interpreted as indicative of a "direct-coupling" mechanism. The in vivo conversion of (±)-reticuline (**5d**) to morphinandienones has also been demonstrated.[24] In view of the newly discovered facile in vitro conversion of morphinandienones to aporphines, biosynthetic experiments are underway to explore the possibility that morphinandienones may as well be in vivo precursors of aporphine alkaloids.

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New Metalloorganic Compounds of Tungsten(III)

Sir:

The high stability and number of chromium(III) complexes have no counterpart in the chemistry of molybdenum and tungsten.[1] For example[1] the only pure halo compounds of tungsten(III) are $W_2X_9^{3-}$ salts where X = Cl and Br. We wish now (i) to report a simple synthesis of tungsten(III) dialkylamides and our characterization of these compounds and (ii) to indicate how these compounds afford synthetic routes to an extensive chemistry of tungsten(III) which was hitherto unknown.

Previously we reported[2] that the reaction of $LiNMe_2$ with a variety of tungsten halides led to either pure $W(NMe_2)_6$ or mixtures of $W(NMe_2)_6$ and $W_2(NMe_2)_6$. However, we were unable to isolate pure $W_2(NMe_2)_6$ from these W(III)-W(VI) mixtures by classical techniques. An examination of the mixed W(III)-W(VI) dimethylamides by X-ray diffraction techniques showed that the two dimethylamides cocrystallized. The unit cell contained two dimers, $W_2(NMe_2)_6$, and one monomer, $W(NMe_2)_6$. This study was significant in providing the first structurally characterized molecule with an unbridged triple bond between two tungsten atoms. However, W(III)-W(VI) dimethylamide samples were not amenable for the development of the chemistry of tungsten(III). Since $W(NMe_2)_6$ is an extremely sterically congested molecule, we thought that synthetic procedures which had formerly yielded the highest $W_2(NMe_2)_6$ to $W(NMe_2)_6$ ratio would further favor the formation of $W_2(NR_2)_6$ at the expense of $W(NR_2)_6$ if other lithium dialkylamides $LiNR_2$ were employed (these are inherently more bulky than $^-NMe_2$). We have now found that this is indeed the case. The reaction of decomposed $WCl_4(OEt_2)_2$[3] with LiNMeEt or $LiNEt_2$ (4 equiv) in THF-hexane leads to the isolation of the appropriate W(III) dialkylamides upon sublimation, 120-150°, 10^{-4} cm Hg, as pale-yellow crystalline solids. These compounds are oxygen and moisture sensitive, diamagnetic, and show

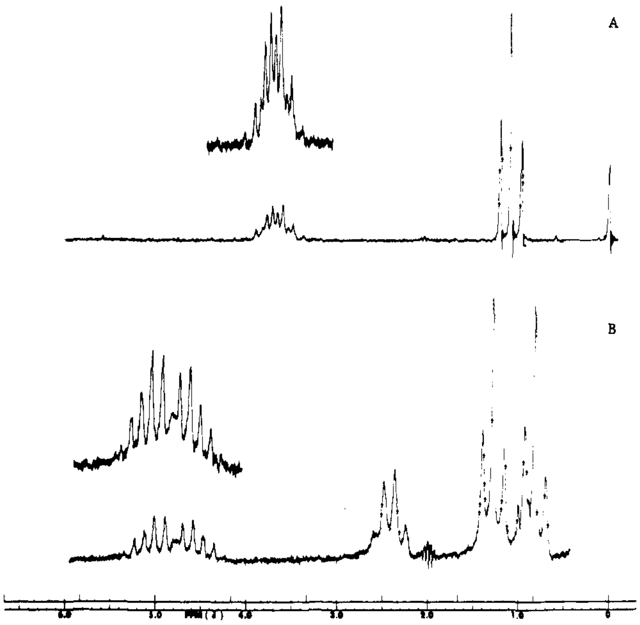

Figure 1. ^{1}H NMR spectra of $W_2(NEt_2)_4Cl_2$ recorded in toluene-d_8 at 60 MHz: A at 116° and B at −32°.

$W_2(NR_2)_6^+$ and only other W_2-metal-containing ions in the mass spectrum. The ^{1}H NMR spectra of these compounds reveal the temperature-dependent rate of exchange of proximal and distal alkyl groups analogous to that observed for $M_2(NMe_2)_6$ (M = Mo, W).[2,4] $W_2(NMeEt)_6$ adopts a ground state configuration with six proximal-methyl and six distal-ethyl groups.[5]

During the course of our systematic study of the reactions of tungsten halides with $LiNMe_2$ we have found that WCl_4, freshly prepared according to the method of McCarley,[6] reacts with $LiNMe_2$ (4 equiv) to give pure $W_2(NMe_2)_6$. It is not obvious why this should be so, especially since $WCl_4(OEt_2)_2$ reacts to give only $W(NMe_2)_6$ and decomposed $WCl_4(OEt_2)_2$ gives mixtures of $W_2(NMe_2)_6$ and $W(NMe_2)_6$. However, these observations are reproducible.

It is thus possible to prepare analytically pure samples[7] of $W_2(NMe_2)_6$, $W_2(NMeEt)_6$, and $W_2(NEt_2)_6$ in yields ca. 40% based on tungsten. We have isolated a mixed chloro(dialkylamido)tungsten(III) compound, $W_2(NEt_2)_4Cl_2$,[8] from reactions involving deficiencies of $LiNEt_2$. $W_2(NEt_2)_4Cl_2$ is a red, volatile (120°, 10^{-4} cm Hg), air-sensitive crystalline solid and is appreciably more soluble in hydrocarbon solvents than $W_2(NEt_2)_6$. It is diamagnetic, dimeric, and shows $W_2(NEt_2)_4Cl_2^+$ and many other W_2-containing ions in the mass spectrum. The high and low temperature limiting spectra of $W_2(NEt_2)_4Cl_2$ in toluene-d_8, shown in Figure 1, clearly indicate (i) the temperature-dependent rate of proximal and distal alkyl exchange and the large diamagnetic anisotropy induced by the W–W triple bond and (ii) the inequivalence of the methylene protons even at the high temperature limit. The magnetic inequivalence of the proximal methylene protons in the low temperature limiting spectrum is particularly pronounced. The ^{1}H NMR data together with other observations lead us to suggest an anti-ethane-like structure for the $ClN_2W{\equiv}WN_2Cl$ moiety. We are currently extending our synthetic efforts using more sterically demanding $^-NR_2$ groups with the hope of isolating monomeric three-coordinate tungsten(III) compounds (cf.[9] $Cr(N\text{-}i\text{-}Pr_2)_3$).

Tungsten(III) dialkylamides react with alcohols, ROH, in hydrocarbon solvents to give alkoxides $W(OR)_3$. The nature of the alkoxide is dependent on the steric properties of the alkyl group R. Small alkyl groups, such as methyl, give black polymeric nonvolatile alkoxides which are insoluble in hydrocarbon solvents. Bulky alkyl groups, such as t-Bu and $SiMe_3$, give orange volatile[10] diamagnetic dimeric compounds. Spectroscopic data are consistent with an unbridged $(RO)_3W{\equiv}W(OR)_3$ structure. It is interesting to note that $W_2(OSiMe_3)_6$ forms adducts with small donor molecules, e.g., $W_2(OSiMe_3)_6(HNMe_2)_2$, which is a purple diamagnetic dimeric crystalline solid and is initially formed in the reaction between $W_2(NMe_2)_6$ and Me_3SiOH. The coordinated amine is readily released under vacuum at elevated temperatures (>50°).

$W_2(O\text{-}t\text{-}Bu)_6$ reacts reversibly with carbon dioxide in toluene at room temperature to give a green diamagnetic dimeric alkoxide(alkylcarbonate) $W_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$, which has been isolated as an analytically pure crystalline compound from cooled toluene solutions in the presence of an atmosphere of CO_2. When this compound is redissolved in the absence of CO_2, $W_2(O\text{-}t\text{-}Bu)_6$ is regenerated.

$W_2(NMe_2)_6$ and $W_2(NMeEt)_6$ react rapidly with CO_2, COS, and CS_2 (in excess) in benzene at room temperature to give the appropriate tungsten(III) N,N-dialkylcarbamato, -monothiocarbamato, and -dithiocarbamato compounds, respectively. The N,N-dialkylcarbamato compounds are diamagnetic yellow crystalline solids and are dimeric in benzene. In the mass spectrum they show parent ions $W_2L_5NR_2^+$ corresponding to loss of one CO_2 from W_2L_6 ($L = O_2CNR_2$). From a comparison of vibrational spectra of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O_2$ labeled $W_2(O_2CNMe_2)_6$ and other N,N-dimethylcarbamato compounds of known structure,[11] we believe the ditungsten compound contains two types of bidentate $^-O_2CNMe_2$ ligands. Consistent with this suggestion are the observations that $W_2(O_2CNMe_2)_6$ and $W_2(O_2CNMeEt)_6$ show only one N-methyl resonance in their respective ^{1}H NMR spectra at room temperature and above but at lower temperatures these appear as doublets in the integral ratio 2:1. These carbamato compounds are all extremely labile toward CO_2 exchange as represented by eq 1[12]

$$W_2L_6 + {}^*CO_2 \rightarrow W_2L_6{}^* + CO_2 \qquad (1)$$

where $L = O_2{}^{12}CNMe_2$, $L^* = O_2{}^{13}CNMe_2$. In contrast to the diamagnetic nature of $W_2(O_2CNR_2)_6$, the N,N-dialkyldithiocarbamates $W(S_2CNR_2)_3$ are paramagnetic green crystalline substances (cf.[13] $Mo(S_2CNR_2)_3$).

We conclude that (i) there is probably an extensive chemistry surrounding tungsten in its trivalent state, (ii) $W_2(NR_2)_6$ provide good starting materials for an exploration of this chemistry, (iii)[14] M–M multiple bond formation is greatly favored for W(III) relative[15] to Cr(III), and (iv) many of the above new tungsten(III) compounds pose intriguing structural questions and are worthy of detailed structural investigations.

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(quartet) and 1.02 ppm (triplet); $T = -80°$, δ (N*Me*) 4.28 (singlet), δ (NCH_2CH_3) 2.38 (quartet) and 0.95 ppm (triplet). Cf. $W_2(NEt_2)_6$, $T = +75°$, 3.65 (quartet), 1.11 ppm (triplet); $T = -60°$, 4.87 and 2.37 ppm (quartets) and 1.30 and 0.97 ppm (triplets). δ in parts per million relative to Me_6Si_2O.

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(8) Analysis for $W(NEt_2)_2Cl$ calcd (found): C, 26.43 (26.52); H, 5.55 (5.57); N, 7.71 (7.60); Cl, 9.75 (9.41). $W_2(NEt_2)_4Cl_2$ reacts with $2LiNEt_2$ to give $W_2(NEt_2)_6$.

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Electron Density Distribution in Cumulenes. A Low Temperature X-Ray Study of Tetraphenylbutatriene

Sir:

In recent years accurate X-ray (and neutron) diffraction measurements at low temperatures, together with the development of various computational techniques,[1] have led to significant progress in determining the electron density distribution in a chemical bond.

As part of a study on the correlation between the alignment of π electrons in crystalline ethylenes and their photoreactivity[2] we have mapped the bonding densities in a butatriene[3] chain confirming that the π densities of adjacent C=C bonds lie in mutually perpendicular planes. The molecular difference density was derived from low temperature X-ray data with the aid of a charge deformation model as developed by Hirshfeld.[1b] In this method, the charge displacement is expanded in a basis of localized deformation functions centered on the several atoms, and the coefficients of these functions are determined by least squares from the X-ray intensities.

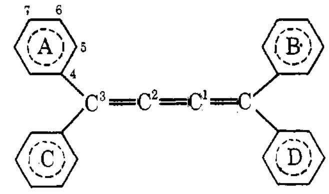
X-Ray diffraction data of tetraphenylbutatriene[4] were collected at ~100°K on a computer-controlled Nonius CAD-3 diffractometer[5] with graphite-monochromatized Mo Kα radiation. A total of 22241 reflections were measured up to $\theta = 40°$, yielding 8325 independent reflections. The structure was refined by full-matrix least-squares adjustment of 341 parameters; these included 92 electron-density deformation coefficients, 144 positional, and 104 thermal parameters. A thermal-motion rigid-body constraint[6] was applied to each of the phenyl rings.

Final reliability indices were $R = 0.07$ and

$$r = [\Sigma w(F_o^2 - K^2F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.08$$

The quality of the structure determination[7] is reflected in the low estimated variances of the mean bond lengths of chemical equivalent bonds shown in Table I.

Table I. Mean Bond Lengths (A), Their Estimated Variances[a] and Their Estimated Net "Bonding" Charge (electrons)



Bonds	Mean bond length	Net charge
C_1–C_2	1.2596	0.30
C_2–C_3	1.3479 (6)	0.22
C_3–C_4	1.4775 (5)	0.11
C_4–C_5	1.4063 (10)	0.20
C_5–C_6	1.3936 (8)	0.20
C_6–C_7	1.3986 (15)	0.20

[a] $\sigma^2(\bar{l}) = \Sigma(l_i - \bar{l})^2/n(n-1)$, where $\bar{l}$ is the mean and n is the number of chemically equivalent bonds.

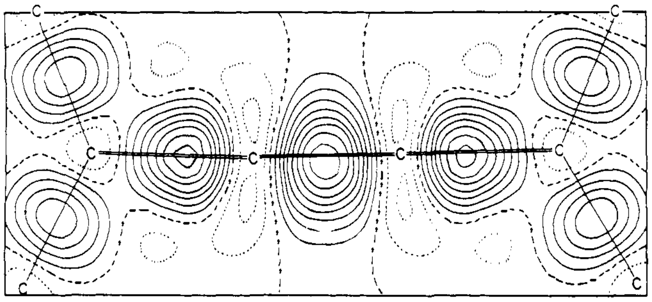


Figure 1. Deformation density in the butatriene plane (>C=C=C=C<). Contour interval 0.1 eÅ^{-3}: zero contour broken, negative contours dotted.

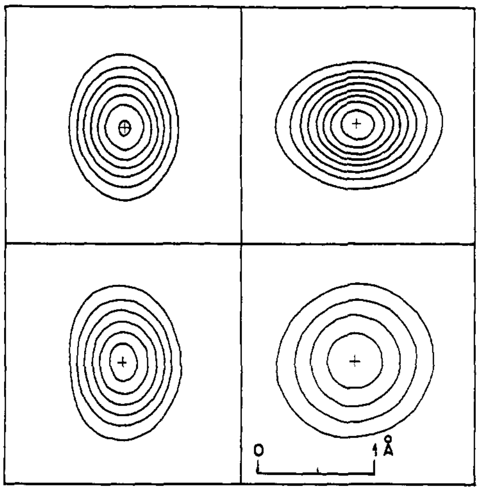


Figure 2. Deformation density sections perpendicular to the various C-C bonds through their centers: (top left, a) the outer $C^2{=}C^3$ bond, (top right, b) the inner $C^1{=}C^2$ bond, (bottom left, c) an aromatic bond, (bottom right, d) the exocyclic C^3-C^4 bond. The vertical direction is perpendicular to the butatriene plane for (a) and (b) and to the phenyl plane for (c) and (d). Contours as in Figure 1. The center of the bond is marked +.

The deformation densities showed accumulation of charge between bonded atoms, with the carbon atoms lying in shallow troughs of negative difference density. In the butatriene chain the peak heights at the bond centers (Figure 1) are 0.9 (±0.05) and 0.75 (±0.05) e/Å^3 for the inner and outer C=C bonds. The density sections perpendicular to these two bonds through their centers (Figure 2a, b) are eliptic, with their long axes mutually perpendicular, the charge in the outer C=C bond is elongated along the normal to the butatriene plane while that in the inner C=C bond is elongated in the plane.