

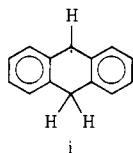
diradical **6** is, in fact, the species we have observed. It remains an open question whether or not dibenzobutalene also represents a potential minimum on this energy surface. The characterization of **6** strongly supports Bergman's evidence¹⁴ on the existence of 1,4-dehydrobenzene. The chemistry of 9,10-dehydroanthracene suggests that it may be an intermediate in the conversion of 1,5-didehydro-3,4-benz[10]annulene to anthracene.²²

A final point of interest deserves comment. The isosbestic points (280, 320 nm) observed in the ultraviolet spectra during photolysis of **5** and the absence of carbene intermediates (which should have been detected in the ultraviolet and ESR experiments)²³ suggests either that the loss of both molecules of carbon monoxide is operationally concerted or that the intermediate ketene-carbene is destroyed photochemically at a much faster rate than the bisketene.

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References and Notes

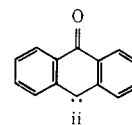
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- A referee has raised the question whether the species observed in the ultraviolet spectroscopic experiments might be the radical **i**. In an effort



to exclude **i** on a rigorous basis, we have irradiated ($\lambda > 200$ nm) 9,10-dihydroanthracene in 3-methylpentane at 77 K to generate **i** (see E. Migirdicyan and J. Bandet, *J. Am. Chem. Soc.*, **97**, 7400 (1975), for the technique). In this experiment anthracene and a reactive species believed to be the radical **i** are generated. The reactive species is converted to anthracene on warming to room temperature. The reactive intermediate has a sharp ultraviolet maximum at 352 nm (which corresponds to a minimum in the ultraviolet spectrum of 9,10-dehydroanthracene). The position of this band is in the wavelength range expected for the radical **i**. Diphenylmethyl radical, for example, is reported to have λ_{\max} 338 nm (H. T. J. Chilton and G. Porter, *Spectrochim. Acta*, **16**, 390 (1960)) and λ_{\max} 335 nm (G. Porter and M. W. Windsor, *Nature (London)*, **180**, 187 (1957)). Irradiation of diphenylmethane in our apparatus under the same conditions used for 9,10-dihydroanthracene gave diphenylmethyl radical (λ_{\max} 335 nm). The ESR spectrum of the radical **i** has been observed in the γ -irradiation of solid anthracene (L. A. Harrah and R. C. Hughes, *Mol. Cryst.*, **5**, 141 (1968); H. Blum, D. L. Mattern, and R. A. Arndt, *ibid.*, **3**, 269 (1967)).

- Significantly higher concentrations of carbon tetrachloride in the 3-methylpentane gave problems in generation of the intermediate.
- A weak $g = 2$ (radical) signal is observed. It is much narrower than the signal reported for **i** (see footnote 18). It is, in fact, not reasonable that **i** should be formed since no hydrogen donor is available in the argon matrix.
- Compare this result with the earlier observations of Jones and Bergman¹⁴ and Breslow, Napierski, and Clarke.¹⁵
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(23) We have, for example, observed 9-oxo-10-anthracenylidene (ii).



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A Novel Heterometallic Molecule Consisting of a New Triangular Tungsten Cluster Bridged by Oxochromium and Alkoxy Ligands

Sir:

Species resulting from the reactions of $W(CO)_6$ with carboxylic acids have escaped definitive characterization even though such reactions have been examined in several laboratories¹⁻³ as possible routes to the unknown dimers $W_2(O_2CR)_4$, isostructural with the well-known quadruply bonded dimers $Mo_2(O_2CR)_4$.⁴ We report here the characterization of a new tungsten cluster compound which resulted from efforts to prepare the heteronuclear dimetal carboxylate derivatives $WCr(O_2CR)_4$. Recent successes in preparation of the related heteronuclear analogues, $MoW(O_2CC(CH_3)_3)_4$ ⁵ and $MoCr(O_2CCH_3)_4$,⁶ provided impetus to attain this goal. However, as shown below, the presence of chromium in the reactions instead served to trap the trinuclear tungsten carboxylate, resulting from reaction of $W(CO)_6$ with carboxylic acids, in a readily isolated crystalline compound of fascinating architecture.

The reaction was performed by refluxing a solution of $W(CO)_6$, $Cr(CO)_6$, and pivalic acid, in the mole ratio 1:1:2, in *o*-dichlorobenzene until CO evolution ceased. Removal of solvent from the green-black solution by very slow vacuum distillation at 25 °C provided well-formed crystals of the dark green product. The mass spectrum showed a set of lines for the molecular ion centered around 2055 amu, having relative intensities in good agreement with those calculated for the composition $W_3Cr_3O_{28}C_{65}H_{119}$. Subsequent x-ray diffraction structure determination⁷ showed the compound is best formulated as $W_3(OCH_2C(CH_3)_3)_3O_3Cr_3(O_2CC(CH_3)_3)_{12} \cdot 2C_6H_4Cl_2$. Both the analytical data and structure determination indicated, however, that full occupancy of the two sites for the solvent molecules is not achieved, resulting in the inclusion of about 1.5 mol of solvent per mole of compound.⁸ The molecular structure of $W_3(OCH_2C(CH_3)_3)_3O_3Cr_3(O_2CC(CH_3)_3)_{12}$ is depicted in Figure 1. At the center of this beautifully interwoven, multiply connected molecule is the important new triangular tungsten cluster with bridging "oxo" oxygen atoms over the edges and the "alkoxo" oxygen of $OCH_2C(CH_3)_3$ triply bridging over the opposite face as shown in Figure 2. In addition to the bridging oxo and alkoxo O atoms each tungsten is bound to three carboxylate O atoms, one from each of three different carboxylate groups. As shown in Figure 2, the Cr atoms are bound to the bridging oxo O atoms to form W_2CrO triangular arrays reminiscent of the Cr_3O units found previously in $Cr_3O(O_2CCH_3)_6(H_2O)_3^+$.⁹

The coordination sphere about both W and Cr includes six O atoms in deformed octahedral arrangement. Each W atom also is bonded to the two adjacent W atoms to form the equilateral triangle, $d(W-W) = 2.608(1), 2.608(1), 2.614(1)$ Å. The nearest neighbor W-Cr distances, average 3.528(4) Å, attest to the absence of W-Cr bonding. There are no important differences in the bonding about the individual metal atoms

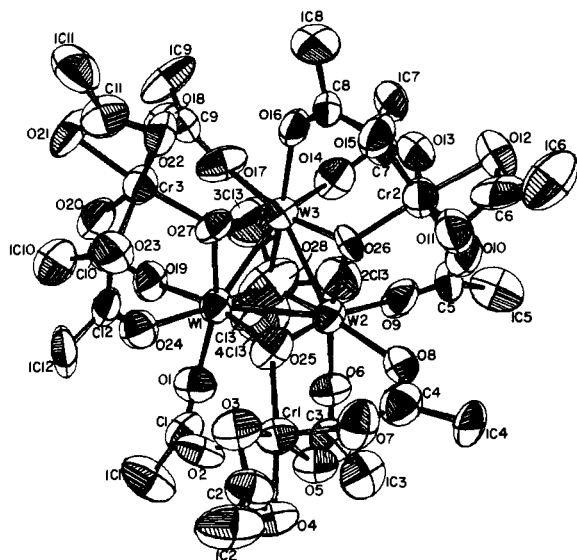


Figure 1. Structure and labeling scheme for the molecular unit $W_3(OCH_2C(CH_3)_3)_3O_3Cr_3(O_2CC(CH_3)_3)_{12}$, with all C(methyl) atoms of the carboxylate ligands omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

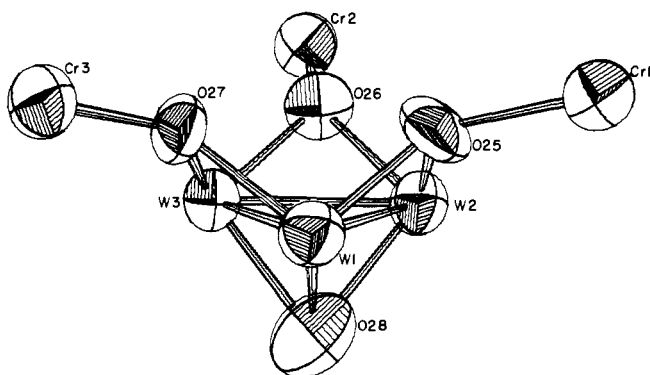


Figure 2. A view of the W_3 cluster showing the triply bridging alkoxo (O28) and doubly bridging oxo O atoms, and the nonplanarity of the three oxo O atoms with the metals to which they are bonded.

within either the W or Cr set; the average bond distances are $d(W-O) = 2.07$ (1) and $d(Cr-O) = 1.97$ (2) Å. The small range of the Cr-O distances, e.g., 1.92–2.00 Å about Cr1, clearly indicates Cr(III), rather than Cr(II) which would be expected to show a much larger range because of Jahn-Teller distortion.¹⁰ Another perspective of the structure is gained by viewing the cluster of W atoms and their bonded O atoms as a W_3O_{13} unit. The bonded O atoms form two closest packed layers, six atoms in one and seven in the other, between which the W atoms occupy adjacent octahedral sites. This structure then is analogous to the triangular clusters found in $Zn_2Mo_3O_8$ ¹¹ and Nb_3Cl_8 ,¹² but represents the first molecular example of this type.

Assessment of oxidation state as 3+ for chromium is confirmed by the magnetic susceptibility. Over the range 77–300 K the temperature independent molecular moment of $6.44 \mu_B$ indicates the paramagnetism arises entirely from Cr(III), i.e., $6.44 (3^{-1/2}) = 3.72 \mu_B$ per Cr atom, and that all electrons in the tungsten cluster are paired. Thus, by deduction the average oxidation state of W is 3.33+, and a total of four electron pairs are involved in the W-W interactions of the cluster. According to Cotton's MO results for clusters of this type¹³ six electrons clearly occupy the bonding orbitals $a_1^{(1)}$ and $e^{(1)}$. The next two electrons must reside in an $a_1^{(2)}$ orbital, but the bonding character is uncertain. A comparison of average metal-metal bond distances, 2.610 (1) Å in this compound vs. 2.53 (1) Å in $Zn_2Mo_3O_8$ ¹¹ and 2.52 Å in $W_3O_4F_9^{5-}$,¹⁴ each with six

electrons, strongly suggests the last two electrons have anti-bonding character.

In previous studies of the reaction between $W(CO)_6$ and acetic acid amorphous trimeric products were obtained and variously formulated as $W_3O(O_2CCH_3)_9$ ² or $W_3O(O_2CCH_3)_8(OH) \cdot H_2O$,¹ each with W in the average oxidation state 3.67+. If these products are diamagnetic as reported, then their identification as derivatives of W (3.67+) cannot be correct. Yet it is clear that oxygen is indeed abstracted from the carboxylic acid in these reactions, for not only the abstracted O atoms but also an alkoxy radical formed thereby is trapped and incorporated in the molecule reported here. This is an important feature because the enhanced ability of W to abstract O atoms may prevent formation of the quadruply bonded $W_2(O_2CR)_4$, in marked contrast to the ready formation of $Mo_2(O_2CR)_4$ in the related reactions of $Mo(CO)_6$.

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Disproportionation of Lithium Salts of Radical Anions of Planar Aromatic Hydrocarbons in Diethyl Ether. Its Large Magnitude and Correlation with the Cation-Anion Coulomb Energy

Sir:

Radical anions may disproportionate into dianions in a reaction described by the equation $2A^{\cdot-} \rightleftharpoons A + A^{2-}$. In this process the two electrons moving in two separated orbitals, each associated with a molecular entity independent of the