A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES
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A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES.
PREPARATION OF W-W QUADRUPLE BONDS BY REDUCTIVE-ELIMINATION
(ALKYL GROUP DISPROPORTIONATION) FROM 1,2-DIETHYL COMPOUNDS
WITH W-W TRIPLE BONDS.

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A General Synthesis for Ditungsten Tetracarboxylates. Preparation of W–W Quadruple Bonds by Reductive-Elimination (Alkyl Group Disproportionation) from 1,2-Diethyl Compounds with W–W Triple Bonds

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A general high yield synthesis for \(\text{W}_2(\text{O}_2\text{CR})_4\) compounds is proposed based on eq. 1, wherein a W–W triple bond is converted to a quadruple bond, and this has been established for \(R = \text{Me}, \text{Et}\) and \(\text{t-Bu}\).

\[
\text{W}_2\text{Et}_2(\text{NMe}_2)_4 + 4\text{RCOOCOR} \rightarrow \text{W}_2(\text{O}_2\text{CR})_4 + 4\text{RCONMe}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6
\]
A General Synthesis for Ditungsten Tetracarboxylates.

Preparation of W-W Quadruple Bonds by Reductive-Elimination (Alkyl Group Disproportionation) from 1,2-Diethyl Compounds with W-W Triple Bonds.

The search for compounds containing W-W quadruple bonds, particularly ditungsten tetracarboxylates, is one of the fascinating stories in the development of the chemistry of compounds containing multiple bonds between metal atoms.\(^1\)\(^2\) At this time there are two reports of the preparation and characterization of \(W_2(O_2CR)_4\) compounds. Sattelberger and McLaughlin\(^3\) reported in 1981 that reduction of \(W_2C_6(THF)_4\) with 2 equivalents of sodium amalgam in THF at \(-20^\circ\) C, followed by addition of sodium trifluoroacetate (4 equiv) gave, upon work up, \(W_2(O_2CCF_3)_4\) in 20% yield based on tungsten. More recently Cotton and Wang\(^4\) reported a higher yield synthesis (ca. 55% based on W) for the benzoate, \(W_2(O_2CPh)_4\cdot2THF\), from Na/Hg reduction of WC\(_4\) in THF followed by treatment with sodium benzoate. We wish here to report a general high yield synthesis for \(W_2(O_2CR)_4\) (M\(_2\)H) compounds based on reductive elimination (alkyl group disproportionation) from W\(_2\)W containing compounds.

Hydrocarbon solutions of 1,2-W\(_2\)Et\(_2\)(NMe\(_2\))\(_4\)\(^5\) react quickly at room temperature with acid anhydrides RCOOCOR, where R = Me, Et and t-Bu, according to equation 1. These reactions appear quantitative when they are carried out in sealed nmr tubes and followed by \(^1\)H nmr spectroscopy. In the absence of oxygen donor solvents, the tetracarboxylates are isolated either as weakly ligated polymers \([W_2(O_2CR)_4]_n\), where R = Me or Et\(^6\), as shown in Figure 1, or as the RCONMe\(_2\) adduct \(W_2(O_2C-t-Bu)_4\cdot2t-BuCONMe\(_2\), by crystallization from benzene or hexane. These
new compounds are bright yellow, crystalline, volatile, air-sensitive compounds and appear analogous to the two previously reported related compounds. An extension of eq. 1 to include other R groups seems obvious.

\[ W_2Et_2(NMe_2)_4 + 4RCOOCOR \rightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_6 + C_2H_4 \]

The present finding is of interest and worthy of note because it reveals that by appropriate synthetic strategy W-W triple bonds can be converted to W-W quadruple bonds. This is the first observation of this transformation.
Acknowledgement We thank the Office of Naval Research and the Wrubel Computing Center for support.


6. Crystal data for $\text{W}_2(\text{O}_2\text{CEt})_4$ at $-160^\circ$ C: $a = 9.377(2)\text{Å}$, $b = 8.271(2)\text{Å}$, $c = 5.527(1)\text{Å}$, $\alpha = 102.49\text{Å}$, $\beta = 84.61(1)\text{Å}$, $\gamma = 89.45(2)$, $Z = 1$, $d_{\text{calc}} = 2.631\text{gcm}^{-3}$ and space group P1. Data collection was performed using standard moving crystal-moving detector techniques (MoKα $6^\circ < 2\theta < 50^\circ$). Of 1477 unique intensities, 1464 having $F>2.33\sigma (F)$ were used in the refinement. The W atom position was located in a Patterson and all remaining atoms, including H atoms, were located in the Fourier synthesis. A final difference Fourier was featureless, the largest peak being $0.83e/\text{Å}^3$, located near the W position. Final residuals are $R(F) = 0.016$ and $R_w(F) = 0.015$.

7. Reactions between $\text{W}_2\text{Et}_2(\text{NMe}_2)_4$ and each of CO$_2$ and ArNNNHAr do not appear to parallel reactions wherein Mo-Mo triple bonds are converted to Mo-Mo quaduple bonds. These reactions are under continuing investigation: Chetcuti, J.J.; Chisholm, M.H.; Folting, K., Haitko, D.A., Huffman, J.C. J. Am. Soc. 1982, 104, 2138.
Caption to Figure 1

An ORTEP view of the centrosymmetric $W_2(O_2CEt)_4$ molecule showing the connectivity in the infinite chain $[W_2(O_2CEt)_4]_n$. Pertinent distances (Å) and angles (°) (averaged where appropriate), are $W-W = 2.189(1)$, $W-O = 2.08(2)$, $W---O = 2.665(4)$, $W-W-O = 91(1)$, $W-W---O = 161.6(1)$°.