Polyhedron Vol. 3, No. 6, pp. 759–760, 1984
Printed in Great Britain.

0277-5387/84 $3.00 + .00
Pergamon Press Ltd.

COMMUNICATION

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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(*Received* 14 *November* 1983; *accepted* 6 *December* 1983)

Abstract—A general high yield synthesis for $W_2(O_2CR)_4$ compounds is proposed based on eqn (1), wherein a W–W triple bond is converted to a quadruple bond, and this has been established for R=Me, Et and *t*-Bu.

$$W_2Et_2(NMe_2)_4 + 4RCOOCOR \rightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_4 + C_2H_6 \quad (1)$$

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 $W_2Cl_6(THF)_4$ with 2 equivalents of sodium amalgam in THF at −20°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, $W_2(O_2CPh)_4.2THF$, from Na/Hg reduction of WCl_4 in THF followed by treatment with sodium benzoate. We wish to report a general high yield synthesis for $W_2(O_2CR)_4$ (M≡M) compounds based on reductive elimination (alkyl group disproportionation) from W≡W containing compounds.

Hydrocarbon solutions of 1,2-$W_2Et_2(NMe_2)_4$[5] react quickly at room temperature with acid anhydrides RCOOCOR, where R=Me, Et and *t*-Bu, according to eqn (1). These reactions appear quantitative when they are carried out in sealed NMR tubes and followed by ^1H NMR spectroscopy and, by crystallization, have given yields in the range

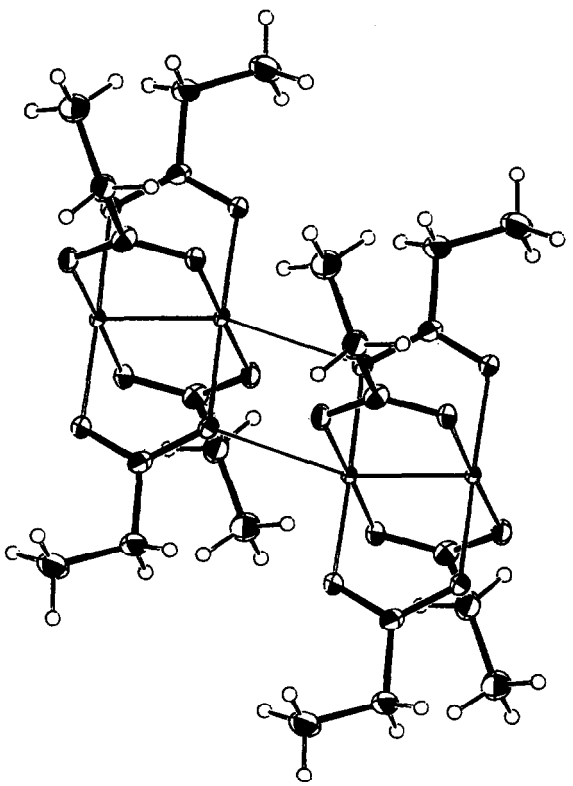

Fig. 1. An ORTEP view of the centrosymmetric $W_2(O_2CEt)_4$ molecule showing the connectivity in the infinite chain $[W_2(O_2CEt)_4]_n$. Pertinent distances (Å) and angles (°) (averaged where appropriate), are W–W = 2.189(1), W–O = 2.08(2), W—O = 2.665(4), W–W–O = 91(1), W–W—O = 161.6(1).

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40–65%. 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 Fig. 1, or as the $RCONMe_2$ adduct $W_2(O_2C\text{-}t\text{-}Bu)_4.2t\text{-}BuCONMe_2$, by crystallization from benzene or hexane. These new bright-yellow, crystalline, volatile, air-sensitive compounds appear analogous to the two previously reported related compounds. An extension of eqn (1) to include other R groups seems obvious.

$$W_2Et_2(NMe_2)_4 + 4RCOOCOR \rightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_6 + C_2H_4. \quad (1)$$

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.[7] This is the first observation of this transformation.

Acknowledgement—We thank the Office of Naval Research and the Wrubel Computing Center for support.

†Full details of this structure analysis including all relevant tables have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic co-ordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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6. Crystal data for $W_2(O_2CEt)_4$ at $-160°C$: $a = 9.377(2)$ Å, $b = 8.271(2)$ Å, $c = 5.527(1)$ Å, $\alpha = 102.49°$; $\beta = 84.61(1)°$; $\gamma = 89.45(2)$, $Z = 1$, $d_{calc} = 2.631$ gcm^{-3} and space group $P\bar{1}$. Data collection was performed using standard moving crystal-moving detector techniques (Mo$K\alpha$ $6° < 2\theta < 50°$. 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/Å^3, located near the W position. Final residuals are $R(F) = 0.016$ and $R_w(F) = 0.015$.†
7. Reactions between $W_2Et_2(NMe_2)_4$ and each of CO_2 and ArNNNHAr do not appear to parallel reactions wherein Mo–Mo triple bonds are converted to Mo–Mo quadruple bonds. These reactions are under continuing investigation: M. J. Chetcuti, M. H. Chisholm, K. Folting, D. A. Haitko and J. C. Huffman, *J. Am. Chem. Soc.* 1982, **104**, 2138.