AD-A117 606 INDIANA UNIV AT BLOOMINGTON DEPT OF CHEMISTRY F/G 7/2
1,2-DIBENZYLTETRADIMETHYLAMIDO-DIMOLYBDENUM AND -DITUNGSTEN (M=--ETC(U)
JUL 82 M J CHETCUTI, M H CHISHOLM, K FOLTING N00014-79-C-0044
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Contract No. N00014-79-C-0044

Task No. NR 056-703

TECHNICAL REPORT NO. INDU/DC/TR-82/1-MC

1,2-DIBENZYLTETRADIMETHYLAMIDO-DIMOLYBDENUM AND -DITUNGSTEN (M≡M) COMPOUNDS AND THEIR REACTIONS WITH CARBON DIOXIDE AND 1,3-DIARYLTRIAZINES. A RADICAL DIFFERENCE.

by

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Prepared for Publication

in

Journal of the American Chemical Society

Department of Chemistry
Indiana University
Bloomington, IN 47405

July 7, 1982

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER INDU/DC/TR-82/1-MC	2. GOVT ACCESSION NO. AD-A117866	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 1,2-Dibenzyltetradimethylamido-dimolybdenum and -ditungsten (M≡M) Compounds and Their Reactions with Carbon Dioxide and 1,3-Diaryltriazines. A Radical Difference.		5. TYPE OF REPORT & PERIOD COVERED Technical Report 1982
		6. PERFORMING ORG. REPORT NUMBER INDU/DC/TR-82/1-MC
7. AUTHOR(s) M.J. Chetcuti, M.H. Chisholm, K. Folting, J.C. Huffman and J. Janos		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0044
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Indiana University Bloomington, IN 47405		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE July 7, 1982
		13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

dimolybdenum, ditungsten, metal-metal triple bonds, reductive elimination, metal-carbon bond homolysis

M triple bond M

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The preparation of 1,2-$M_2(benzyl)_2(NMe_2)_4$ (M≡M) compounds (M = Mo and W) and their reactions with each of CO_2 and 1,3-diaryltriazines are described. The molybdenum and tungsten dibenzyl compounds differ in their reactivity quite markedly. For tungsten, the M≡M bond is preserved in the formation of $W_2(benzyl)_2(NMe_2)_2(ArN_3Ar)_2$ and $W_2(benzyl)_2(O_2CNMe_2)_4$ compounds, while molybdenum favors reductive elimination and formation of M-M quadruply bonded compounds $Mo_2(O_2CNMe_2)_4$ and $Mo_2(ArN_3Ar)_2$, where Ar = phenyl and p-tolyl. Reductive elimination is shown to proceed via a radical pathway.

1,2-Dibenzyltetradimethylamido-dimolybdenum and -Ditungsten (M≡M) Compounds and Their Reactions with Carbon Dioxide and 1,3-Diaryltriazines. A Radical Difference.

Sir:

Both molybdenum and tungsten have a rich dinuclear chemistry which in many ways, but by no means all ways, is very similar.[1] The search and ultimate discovery of a successful route to a tungsten $M_2(O_2CR)_4$ (M≣M) compound is an interesting story[2] and reveals what is now generally accepted: the $(W≣W)^{4+}$ unit is notably more reactive toward oxidative-addition reactions than the $(Mo≣Mo)^{4+}$ unit. McCarley's[3] spectacular success in preparing pure $MoW(O_2CBu^t)_4$ (M≣M) used this principle. We wish here to report an intriguing difference between reactions involving $(M\equiv M)^{6+}$ units (M = Mo and W)[4] which reveals the complementary fact: reductive elimination occurs for molybdenum, $(M\equiv M)^{6+} \rightarrow (M≣M)^{4+}$, but not for tungsten under comparable conditions.

As part of a continuing study of the properties and reactions of $1,2\text{-}M_2R_2(NMe_2)_4$ (M≡M) compounds,[5] we have prepared $1,2\text{-}M_2(\text{benzyl})_2(NMe_2)_4$ compounds (M = Mo, W) from reactions involving $1,2\text{-}M_2Cl_2(NMe_2)_4$ compounds[6] and benzyl-lithium or -Grignard reagents.[7] The new benzyl compounds are diamagnetic, air-sensitive, hydrocarbon soluble, yellow-orange crystalline solids. A gauche-$Mo_2(CH_2Ph)_2(NMe_2)_4$ molecule has been structurally characterized[8] and a view of the molecule is shown in Figure 1. The benzyl ligands are σ bonded and as a result of forming a Mo≡Mo bond, three Mo-L σ bonds and two Me_2N-to-Mo π bonds, each metal atom attains a 16 valence shell of electrons. The benzyl compounds are thus directly analogous to 1,2-$M_2R_2(NMe_2)_4$ compounds recently reported[5] for M = Mo and W and R = Me, Et, n-, and i-Pr and n-, s- and t-Bu, and in solution they exist in both anti and gauche rotamers.

The molybdenum and tungsten compounds differ in their reactions[9] with CO_2 and 1,3-diaryltriazines as shown in reactions **1**-**4**.

1 $$Mo_2(CH_2Ph)_2(NMe_2)_4 + CO_2 \text{ (excess)} \longrightarrow Mo_2(O_2CNMe_2)_4 + PhCH_2CH_2Ph$$

2 $$Mo_2(CH_2Ph)_2(NMe_2)_4 + PhNNNHPh \text{ (excess)} \longrightarrow Mo_2(PhN_3Ph)_4 + PhCH_2CH_2Ph + 4HNMe_2$$

3 $$W_2(CH_2Ph)_2(NMe_2)_4 + CO_2 \text{ (excess)} \longrightarrow W_2(CH_2Ph)_2(O_2CNMe_2)_4$$

4 $$W_2(CH_2Ph)_2(NMe_2)_4 + PhNNNHPh \text{ (excess)} \longrightarrow W_2(CH_2Ph)_2(NMe_2)_2(PhN_3Ph)_2 + 2HNMe_2$$

The tungsten compounds $W_2(CH_2Ph)_2(O_2CNMe_2)_4$ and $W_2(CH_2Ph)_2(NMe_2)_2(PhN_3Ph)_2$ are spectroscopically analogous to compounds which have been characterized by single crystal X-ray studies: $W_2Me_2(O_2CNMe_2)_4$ (M≡M)[10] and $Mo_2Me_2(NMe_2)_2(PhN_3Ph)_2$ (M≡M).[11] There can be little, if any, doubt that the $(W{\equiv}W)^{6+}$ unit is retained in the benzyl derivatives formed in reactions **3** and **4**. The existence of the (Mo≣Mo)$^{4+}$ unit in the compounds $Mo_2(O_2CNMe_2)_4$ and $Mo_2(ArN_3Ar)_4$ is similarly certain and has been established by single crystal X-ray studies for Ar = phenyl[12] and p-tolyl.[13]

The transformation of the $(M{\equiv}M)^{6+}$ unit to $(M{≣}M)^{4+}$ which occurs for molybdenum, but not for tungsten, has a parallel in the reactions of 1,2-$M_2R_2(NMe_2)_4$ compounds with each of CO_2 and 1,3-diaryltriazines, where R = Et, Pr and Bu.[13,14] See eq. 5.

$$Mo_2R_2(NMe_2)_4 + CO_2\ (\text{excess}) \longrightarrow Mo_2(O_2CNMe_2)_4 + \text{alkene} + \text{alkane} \tag{5}$$

In reaction 5, alkyl group disproportionation is intramolecular and involves the transference of a β-hydrogen of one alkyl ligand to the α-carbon of the other: $M_2(CH_2CD_3)_2 \rightarrow M_2 + CH_2{=}CD_2 + CH_2DCD_3$. When R = CH_3 and CH_2SiMe_3, no reductive elimination occurs and $Mo_2R_2(O_2CNMe_2)_4$ compounds are obtained.[13]

A number of observations suggest that the formation of dibenzyl in eq. 1 occurs by a radical pathway. (1) Reactions involving 1:1 mixtures of $Mo_2(CH_2Ph)_2(NMe_2)_4$ and $Mo_2(CH_2\text{-}p\text{-tolyl})_2(NMe_2)_4$ with CO_2 in hexane or benzene give a statistical mixture of coupled products: $PhCH_2CH_2Ph$, $PhCH_2CH_2$-p-tolyl, and p-tolyl-CH_2CH_2-p-tolyl which were characterized by g.c.,[15] g.c.–m.s. and high field ^1H nmr spectroscopy. (2) In addition to dibenzyl, some toluene (or xylene) was always formed and when reaction 1 was carried out in the presence of 1,4-cyclohexadiene, toluene (or xylene) was produced with concommitant suppression of dibenzyl (or p-tolyl-CH_2CH_2-p-tolyl). (3) Attempts to trap benzyl radicals during the course of 1 using nitrosodurene as a radical trap were thwarted by the fact that, in hexane, nitrosodurene and $Mo_2(CH_2Ph)_2(NMe_2)_4$ react, yielding the characteristic esr signal of the trapped benzyl radical and as yet uncharacterized molybdenum containing products.[16]

If one accepts the above as evidence for a radical elimination pathway, then tungsten by favoring the higher oxidation state should be less willing (than molybdenum) to undergo metal-carbon (alkyl) bond homolysis which would result in an oxidation state change from 3 to 2.[17] Analogous reasoning has been used in cobalt-carbon chemistry where it has been shown that ligand basicity affects $D_{(Co-R)}$. The more basic the ligand, the larger the value of $D_{(Co-R)}$ which is attributed to the stabilizing effect on the higher oxidation state, Co(III) relative to Co(II), the latter being formed upon homolysis of the Co-alkyl bond.[18] In view of the similar values obtained[19] for $D_{(Co-R)}$ in organocobalt Schiff base compounds [py(saloph)Co-R], where py = pyridine and saloph = N,N'-bis(salicylidene)-o-phenylenediamine and R = alkyl (n- and i-Pr) and benzyl, it is possible and even quite probable that a radical mechanism could be involved in 5. Alkyl group disproportionation could occur by β-hydrogen abstraction within the solvent cage of the geminate dimolybdenum-alkyl radical pair formed upon homolysis of one of the Mo-C (alkyl) bonds. Further studies aimed at extracting mechanistic information are planned.[20]

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7. All reactions were carried out using dry and oxygen-free solvents and atmospheres. Satisfactory analytical data were obtained.
8. Crystal data at -165°C: $a = 17.595(7)$ Å, $b = 16.038(6)$ Å, $c = 10.542(4)$ Å, $\beta = 122.11(2)^\circ$, $Z = 4$ and $d_{calcd} = 1.451$ g cm^{-3} in the space group $P2_1/a$. Of the 5121 reflections collected, the 3916 having $F >$

2.33σ(F) were used in the full matrix refinement. Final residuals are R(F) = 0.036 and Rw(F) = 0.037.

9. Reactions were carried out in hexane or benzene at room temperature in a manner previously described: ref. 13.
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15. We thank Dr. Kevin Gilbert for assistance in obtaining g.c. analytical data.
16. We thank Dr. Willie Lau for assistance in obtaining esr results.
17. An alternate, but essentially similar argument can be made on the observed general trends for $\overline{D}$(M-L) in homoleptic transition metal complexes. "In general the mean bond enthalpy, $\overline{D}$(M-L) decreases in the order of L = F > OR > Cl > NR$_2$ > CH$_2$R and the values increase monotonically from one transition series to another in the order M(3d) < M(4d) < M(5d)... The mean bond enthalpy D(M-CH$_2$R) increases with increasing atomic number in any one group whereas in the main group (s, p-block) metals the mean bond enthalpy decreases in the same sense." Connor, J.A. Topics in Current Chemistry 1977, 71, pp. 83-84.

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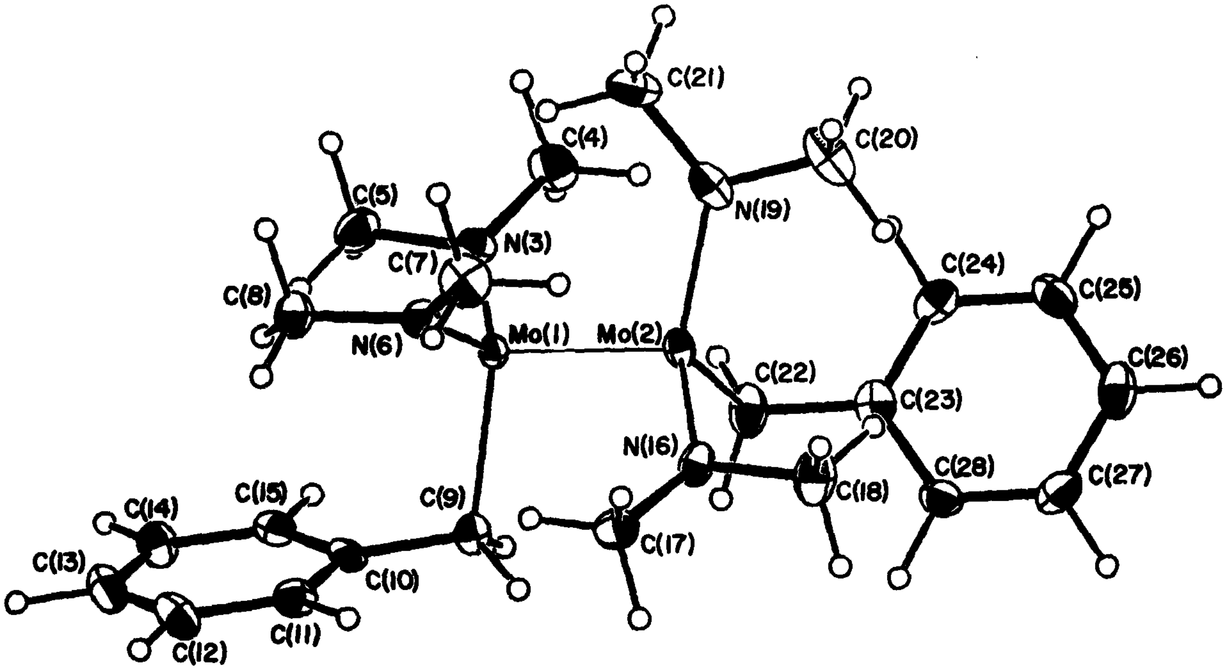
20. We thank the Office of Naval Research and the Petroleum Research Fund administered by the American Chemical Society for support.

Supplementary Material Available. Fractional coordinates and isotropic thermal parameters. Ordering information is given on any current masthead page.

Caption to Figure

An ORTEP view of the gauche-1,2-$Mo_2(benzyl)_2(NMe_2)_4$ molecule. Some pertinent bond distances (Å) and bond angles (degrees) (averaged where appropriate) are Mo-Mo = 2.200(1), Mo-N = 1.950(5), Mo-C = 2.19(1), Mo-Mo-N = $104(1)^{\circ}$, Mo-Mo-C = $100.0(4)^{\circ}$. The Mo-to-orthocarbon distances are essentially all the same at 3.7 Å.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