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INDIANA UNIV AT BLOOMINGTON DEPT OF CHEMISTRY
INTRIGUING ASPECTS OF 1,2-DIALKYL-DIMOLYBDENUM AND -DITUNGSTEN --ETC(U)
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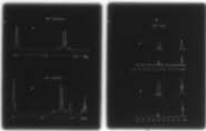
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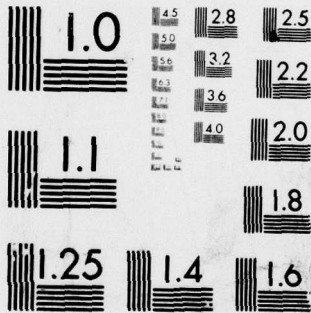
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⁹ TECHNICAL REPORT NO. ¹⁴ 79-4 *TR-*

⁶ INTRIGUING ASPECTS OF 1,2-DIALKYL-DIMOLYBDENUM AND
-DITUNGSTEN (M≡M) CHEMISTRY,

(M TRIPLE BOND M)

by

¹⁰ Malcolm H. Chisholm and Deborah A. Haitko

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Dimolybdenum Dialkyl, β-hydrogen elimination, reductive elimination.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → The preparation of a series of 1,2-dialkyl compounds of dimolybdenum and ditungsten (M≡M) having the general formula $M_2R_2(NMe_2)_4$ is reported for R = CH ₃ , CH ₂ CH ₃ , CH ₂ CD ₃ , CH ₂ CH ₂ CH ₂ CH ₃ , CH(CH ₃) ₂ , CH ₂ C(CH ₃) ₃ , CH ₂ Si(CH ₃) ₃ and C(CH ₃) ₃ . The isolation of the labelled compounds $M_2(CH_2CD_3)_2(NMe_2)_4$ and the isopropyl and tert-butyl derivatives implies that β-hydrogen elimination is either kinetically or thermodynamically not favorable. All of the → beta		

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20. ABSTRACT continued

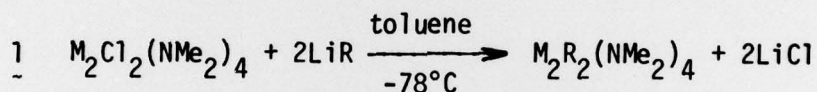
above react in hydrocarbon solutions with CO_2 . When R = a β -hydrogen elimination stabilized alkyl the products are $\text{M}_2\text{R}_2(\text{O}_2\text{CNMe}_2)_4$ ($\text{M}=\text{M}$) for both M = Mo and W. When R contains β -hydrogen atoms, the reaction proceeds differently for molybdenum and tungsten. For molybdenum $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4$ ($\text{M}=\text{M}$) is formed along with 1-alkenes and alkanes. Using the labelled compound $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ this reaction is shown to be intramolecular and to form specifically $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 , which is consistent with an irreversible β -hydrogen elimination followed by C-H/C-D reductive elimination. Addition of alcohols to $\text{M}_2\text{R}_2(\text{NMe}_2)_4$ lead to products which depend on the nature of (i) the alcohol, (ii) the alkyl group R and (iii) the metal, Mo or W. For example, the reaction between $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ and Bu^tOH is shown to give $\text{Mo}_2(\text{C}_2\text{H}_3\text{D}_2)(\text{OBu}^t)_5$ and CH_2DCD_3 .

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Intriguing Aspects of 1,2-Dialkyl-dimolybdenum and -ditungsten ($M \equiv M$) Chemistry

Sir:

Both historically¹ and commercially² σ -alkyl complexes have played a prominent role in the development of mononuclear organotransition metal chemistry. Our syntheses³ of anti-1,2-dichlorotetradimethylamido compounds, $M_2Cl_2(NMe_2)_4$ ($M \equiv M$, $M = Mo, W$) affords the opportunity of attempting to prepare 1,2-dialkyl-tetradimethylamido compounds by use of the general metathetic reaction shown in eq. 1. Compounds of the form $M_2R_2(NMe_2)_4$ allow an investigation of the



reactivity patterns of σ -alkyl groups bonded to the simplest of metal clusters, namely dimetal centers. We wish here to report our extended⁴ syntheses of compounds of the general formula $M_2R_2(NMe_2)_4$ and, in particular, to describe their reactivity patterns towards carbon dioxide and tert-butanol with special attention being given to the labelled compounds $M_2(CH_2CD_3)_2(NMe_2)_4$.

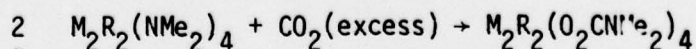
From reaction 1 we have obtained $M_2R_2(NMe_2)_4$ compounds for both $M = Mo$ and W where $R = CH_3, CH_2CH_3, CH_2CD_3, CH_2CH_2CH_2CH_3, CH(CH_3)_2, CH_2CMe_3, CH_2SiMe_3$ and CMe_3 .⁵ Purification of these compounds followed the following general procedure: (1) the reaction mixture was warmed slowly to room temperature whereupon the solvent was stripped; (2) hexane was added and the solution was filtered using a medium frit and standard Schlenk-techniques; (3) the hexane solvent was again stripped and the residue was purified by sublimation ($80-100^\circ C, 10^{-6}$ cm Hg) to give yellow-orange ($M=Mo$) or orange-red solids ($M=W$). When

R = n-butyl, the compounds were liquids at room temperature and were purified by vacuum distillation.

In all cases the ^1H nmr spectra of the $\text{M}_2\text{R}_2(\text{NMe}_2)_4$ compounds obtained in toluene- d_8 solution at -60°C (100 or 270 MHz) showed a mixture of anti- and -gauche 1,2-dialkyl rotamers. The gauche rotamer was always the predominant rotamer and rather interestingly as the bulk of the alkyl group increases $\text{CH}_3 \rightarrow \text{CH}_2\text{CMe}_3$ so the predominance of the gauche rotamer increases.⁶ At -60°C rotations about M-N bonds are restricted leading to proximal and distal N-methyl resonances.⁷ A mixture of anti- and -gauche $\text{M}_2\text{R}_2(\text{NMe}_2)_4$ should have a total of 3 proximal and 3 distal N-methyl resonances.⁸

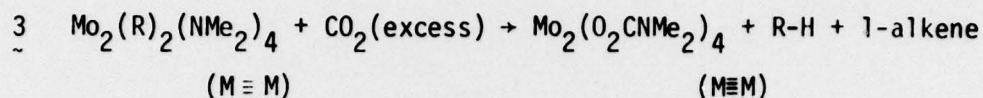
The thermal stability of these compounds is quite remarkable and the stability of the isopropyl and tert-butyl compounds⁹ with respect to isomerization to n-propyl and iso-butyl ligands, respectively, implies that β -hydrogen elimination is either kinetically or thermodynamically not favorable. This is also implied by our observation that when LiCH_2CD_3 ¹⁰ is used in reaction 1, the resultant 1,2-diethyl compounds retain their ^2H atoms exclusively in the β -position: $\text{M}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$. Figures 1a and 1b compare the ^1H nmr spectra of the labelled, CH_2CD_3 containing compound and the protio compound, respectively.

In hydrocarbon solutions all of the above compounds react with CO_2 to give selective insertion into the metal-nitrogen bond.¹¹ The β -elimination stabilized alkyls of both molybdenum and tungsten react according to eq. 2.



In this reaction the M-M triple bond is retained.¹² However, rather interestingly, the non- β -hydrogen elimination stabilized alkyl of dimolybdenum and

ditungsten react quite differently. The molybdenum compounds react according to eq. 3. Reaction of the labelled compound $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ with CO_2 in



benzene in a sealed nmr tube led to the specific formation of $\text{CD}_2=\text{CH}_2$ and CH_2DCD_3 as determined by ^2H nmr. See Figure 2a. The ^2H spectrum of the ethylene, $\text{CD}_2=\text{CH}_2$, showed the predicted splitting based on the reported ^1H - ^1H couplings reported for ethylene and the known magnetudes of the gyromagnetic ratios of ^1H and ^2H .¹⁴ As a further check, we purchased $^{15}\text{CD}_2=\text{CH}_2$, trans- $\text{CHD}=\text{CHD}$ and cis- $\text{CHD}=\text{CHD}$ and recorded their ^2H spectrum in benzene: the observed splittings agreed well with the predicted¹⁴ and thus confirmed unequivocally the formation of exclusively $^{16}\text{CD}_2=\text{CH}_2$ in reaction 3 for $\text{R} = \text{CH}_2\text{CD}_3$. In order to check the ^2H spectrum of CH_2DCD_3 in benzene, we prepared a sample by the addition of D_2O to a solid sample of LiCH_2CD_3 using a vacuum manifold followed by condensation into an nmr tube. The ^2H spectrum of the gaseous products showed the same pattern for CH_2DCD_3 and, moreover, revealed that some ethylene, specifically $\text{CD}_2=\text{CH}_2$, is formed when D_2O is added to anhydrous LiCH_2CD_3 in a vacuum manifold.¹⁷

In a separate experiment, a mixture of $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ and $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ in benzene was reacted with CO_2 in a sealed nmr tube. The ^2H nmr spectrum was identical to that shown in Figure 2a. Thus within the limits of nmr detection, CH_2DCD_3 was the only deuterated ethane present.¹⁶

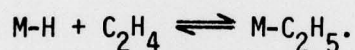
When CO_2 is added to a hydrocarbon solution of $\text{W}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ a green-blue tungsten containing precipitate is formed and only ethane is evolved.

Using the labelled $W_2(CH_2CD_3)_2(NMe_2)_4$, the ethane appears by 2H nmr spectroscopy to be predominantly CH_3CD_3 . The fate of the ethylene and the nature of tungsten compounds are presently unknown.

Reactions of these $M_2R_2(NMe_2)_4$ compounds with alcohols are dependent on the nature of (i) the alkyl group R, (ii) the alcohol and (iii) the metal, Mo or W. For example, $M_2(CH_3)_2(NMe_2)_2$ compounds ($M = Mo, W$) both react with tert-butanol to give $M_2(CH_3)_2(OBu^t)_4$ compounds. However, addition of Pr^iOH to $Mo_2(CH_3)_2(NMe_2)_4$ yields $Mo_2(OPr^i)_6$ ($M \equiv M$) and CH_4 (2 equiv.). The analogous reaction involving $W_2(CH_3)_2(NMe_2)_4$ has not yet been carried out but it is known that attempts to prepare $W_2(OPr^i)_6$ have led to $W_4(\mu-H)_2(OPr^i)_{14}$.¹⁸ The reaction of $Mo_2(C_2H_5)_2(NMe_2)_4$ with Bu^tOH yielded $Mo_2Et(OBu^t)_5$ and ethane.^{4b} Using the labelled compound $Mo_2(CH_2CD_3)_2(NMe_2)_4$, we find that addition of Bu^tOH causes the exclusive¹⁶ elimination of CH_2DCD_3 . The resulting ethyl ligand in $Mo_2(C_2H_3D_2)(OBu^t)_5$ contains a statistical distribution of deuteriums on the α and β carbons, namely integration indicates $\alpha:\beta = 2:3$.

The purpose of this communication is to draw attention to the intriguing chemistry associated with alkyl groups coordinated to the dimolybdenum or ditungsten ($M \equiv M$) centers. (1) In $M_2R_2(NMe_2)_4$ compounds, β -hydrogen elimination is either kinetically or thermodynamically not favorable. (2) Addition of CO_2 to $Mo_2(CH_2CH_3)_2(NMe_2)_4$ ($M \equiv M$) leads to formation of $Mo_2(O_2CNMe_2)_4$ ($M \equiv M$) by an intramolecular mechanism. It seems likely that this involves an initial irreversible β -hydrogen elimination which is then followed by C-H reductive elimination. However, it is not known at what step during CO_2 insertion that this process occurs, nor is it known whether C-H reductive elimination occurs across the M-M triple bond, $H-M \equiv M-Et \rightarrow M \equiv M + Et-H$ or via an oxidative addition-

reductive elimination process at one metal center, $M^{II} \equiv M^{IV}(H)(Et) \rightarrow M^{II} \equiv M^{II} + Et-H$. (3) That $W_2(C_2H_5)_2(NMe_2)_4$ should react so differently with CO_2 is also fascinating, and once again points to the elusive nature of $W_2(O_2CX)_4$ (MEM) compounds.¹⁹ (4) Addition of Bu^tOH to $Mo_2(CH_2CD_3)_2(NMe_2)_4$ which leads to $Mo_2(C_2H_3D_2)(OBu^t)_5$ and CH_2DCD_3 implies that alcoholysis, as with CO_2 insertion (2 above), once again facilitates an irreversible β -hydrogen process which is then followed by C-D reductive elimination. This further implies that formation of the σ -ethyl ligand arises from $CH_2=CD_2$ and Bu^tO-H . The statistical distribution of H/D atoms over the α - and β -carbons in σ -ethyl ligand thus formed is consistent with a then reversible β -hydrogen elimination process favoring the coordinated ethyl ligand:



While all these observations raise intriguing mechanistic questions which cannot be answered at this time, we do note that our observations have at least one parallel with mononuclear transition metal alkyl chemistry: reductive elimination involving C-H bond formation is more facile than reductive elimination involving C-C bond formation.²⁰

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References and Footnotes

1. (a) G. Wilkinson, *Science*, 185, 109 (1974).
(b) M. F. Lappert, P. J. Davidson and R. Pearce, *Acc. Chem. Res.*, 7, 209 (1974).
(c) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 76, 243 (1976).
2. J. K. Kochi in "Organometallic Mechanisms and Catalysis", Academic Press, 1978.
3. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine and C. A. Murillo, *Inorg. Chem.*, 16, 2407 (1977).
4. (a) The preparation and structure of $\text{Mo}_2(\text{CH}_3)_2(\text{NMe}_2)_4$ has been reported: M. H. Chisholm, F. A. Cotton, M. W. Extine and C. A. Murillo, *Inorg. Chem.*, 17, 2338 (1978).
(b) The preparation and reactivity of $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ was previously reported: M. H. Chisholm, D. A. Haitko and C. A. Murillo, *J. Am. Chem. Soc.*, 100, 6262 (1978).
5. Satisfactory analytical data have been obtained. All compounds showed molecular ions in the mass spectrometer, $\text{M}_2\text{R}_2(\text{NMe}_2)_4^+$, and we thank Professor D. C. Bradley and Mr. Peter Cook at Queen Mary College for kindly obtaining these valuable spectra for us. This collaboration was promoted by a NATO grant to DCB and MHC.
6. We have no rationale for this observation; our intuition would have suggested the opposite trend.
7. For an assignment of proximal and distal N-Me resonances, see M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4469 (1976).
8. For a detailed discussion, see the variable temperature ^{13}C nmr studies carried out on $\text{W}_2(\text{CH}_3)_2(\text{NEt}_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar and B. R. Stults, *Inorg. Chem.*, 15, 2244 (1976).
9. Tert-butyl transition metal complexes (and to a lesser extent iso-propyl complexes) are relatively rare. See ref. 2. The reversible β -H-elimination from an alkyl metal complex without attendant reductive elimination of alkane was elegantly studied in alkyl gold(III) chemistry. The isomerization of trans-tert-butyldimethyl(triphenylphosphine) gold(III) proceeds spontaneously at 25°C in etherial solution to produce the trans-iso-butyldimethyl(triphenylphosphine) gold(III) complex in quantitative yield. See A. Tamaki and J. K. Kochi, *J.C.S. Chem. Commun.* (1973) 423.

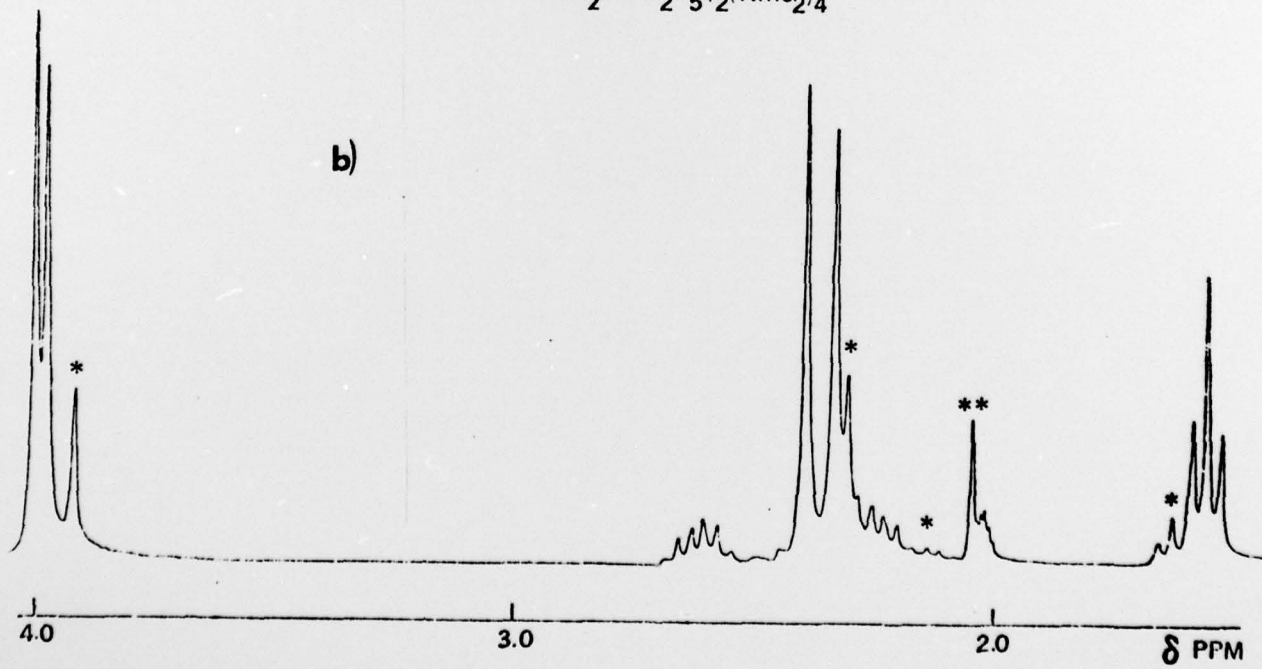
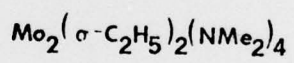
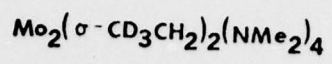
10. Prepared from the reaction between $\text{CD}_3\text{CD}_2\text{Br}$ and Li shot in hexane; purified by sublimation 65°C , 10^{-6} cm Hg. $\text{CD}_3\text{CH}_2\text{Br}$ was obtained from Merck, Sharp and Dohme.
11. The mechanism of this insertion has been shown to proceed via an amine catalyzed sequence: M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 99, 792 (1977).
12. All these compounds show molecular ions in the mass spectrometer and are believed to be directly analogous to the structurally characterized diethylcarbamato analogue $\text{W}_2(\text{CH}_3)_2(\text{O}_2\text{CNEt}_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine and B. R. Stults, *Inorg. Chem.*, 16, 603 (1977).
13. $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4$ is formed as a fine yellow precipitate in this reaction. It shows a strong molecular ion $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4^+$ and a doubly charged molecular ion $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4^{2+}$. In all respects it appears like $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds for which scores have been structurally characterized and all of which contain a Mo-Mo quadruple bond.
14. From R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. A.*, 269, 1385 (1965): for ethylene $J_{\text{cis}}^{\text{H-H}} = +11.7$ Hz, $J_{\text{trans}}^{\text{H-H}} = 19.1$ Hz and $J_{\text{gem}}^{\text{H-H}} = +2.5$ Hz; $\gamma_{\text{H}} = 2.675 \times 10^4$ radians/sec. gauss, $\gamma_{2\text{H}} = 4.107 \times 10^3$ radians/sec. Using this data it was possible to calculate the splittings of $\text{CD}_2=\text{CH}_2$, trans $\text{CHD}=\text{CHD}$ and cis $\text{CHD}=\text{CHD}$. The calculated splittings were obtained by utilizing the program entitled NMRCAL, a part of the Nicolet-80 system. For each of the isomeric dideuteroethylenes a centered three-line pattern was observed with the only apparent distinguishing characteristic being the separation between the outer lines. The calculated versus (observed) splittings in Hertz for each dideuteroethylene are as follows: 1,1-dideuteroethylene 4.8 (4.8); 1,2-cis-dideuteroethylene 3.3 (3.3) and trans 1,2-dideuteroethylene 2.2 (2.2).
15. From Merck, Sharp and Dohme.
16. By exclusively, we mean within the limits of nmr detection which is at least 95%.
17. Alkyl lithium and alkyl aluminum compounds are well known to undergo β -H-elimination under thermolysis (ref. 2) but we are not aware of anyone reporting the formation of ethylene upon the addition of water. It quite possibly is formed under our conditions because LiCH_2CD_3 is present in excess as D_2O is added and therefore thermolysis is a competitive reaction due to local heating effects which accompany hydrolysis. See also B. J. Wakefield in "The Chemistry of Organolithium Compounds", Pergamon Press publisher, 1974, Ch. 15.
18. M. Akiyama, D. Little, M. H. Chisholm, D. A. Haitko, F. A. Cotton and M. W. Extine, *J. Am. Chem. Soc.*, 101, 2504 (1979).

19. A. Bino, F. A. Cotton, Z. Dosi, S. Koch, H. Kuepers, M. Millar and J. C. Sekutowski, *Inorg. Chem.*, 17, 3245 (1978).
20. J. R. Norton, *Acc. Chem. Res.*, 12, 139 (1979) and references therein.

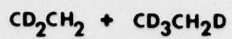
Captions to Figures

Figure 1. Proton NMR spectra recorded at 270 MHz, -61°C in toluene- d_8 of
a) *-anti and gauche - $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ and b) *-anti and
gauche - $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$. c) ** represents residual
protonated toluene.

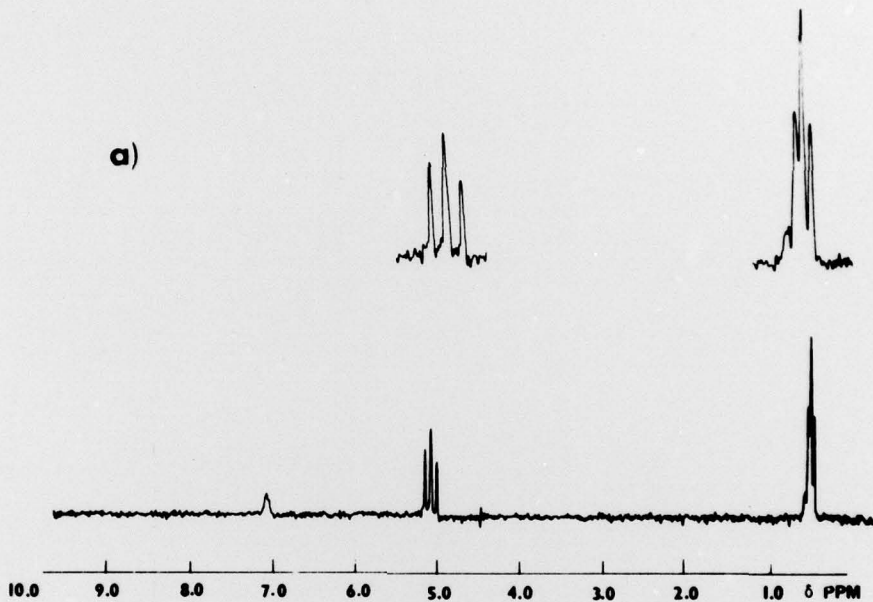
Figure 2. Deuterium NMR spectra recorded at 16°C and 33.77 MHz of the gases
formed in the reactions of a) CO_2 with $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ and
b) D_2O with LiCH_2CD_3 . Both spectra were recorded in benzene.
The scale expansions shown in a) and b) are not the same.



^2H



a)



b)

