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MECHANISTIC ASPECTS OF 1,2-DIALKYLDIMOLYBDENUM $(M \equiv M)$ CHEMISTRY

by

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The following three reactions are reported:

(1) $Mo_2Cl_2(NMe_2)_4 + 2\ LiCH_2CD_3 \longrightarrow Mo_2(CH_2CD_3)_2(NMe_2)_4 + 2\ LiCl$

(2) $Mo_2(CH_2CH_3)_2(NMe_2)_4 + CO_2$ (excess) $\longrightarrow Mo_2(O_2CNMe_2)_4 + CH_2{=}CD_2 + CH_2DCD_3$

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(3) $Mo_2(CH_2CD_3)_2(NMe_2)_4 + Bu^tOH \text{ (excess)} \longrightarrow Mo_2(C_2H_3D_2)(OBu^t)_5 + 4\ HNMe_2 + CH_2DCD_3$

The products of these reactions were characterized by ^1H and ^2H nmr spectroscopy. The elimination of ethylene and ethane in reaction (2) was found to be intramolecular. The mechanistic conclusions which can be extracted from these findings are noted.

Mechanistic Aspects of 1,2-Dialkyldimolybdenum (M≡M) Chemistry

Sir:

ALPHA

Both historically[1] and commercially[2] σ-alkyl complexes have played a prominent role in the development of mononuclear transition metal chemistry. The recent syntheses and characterizations of 1,2-dialkyl-dimolybdenum[3-4] and -ditungsten[5-7] compounds ~~(M≡M)~~ afford the opportunity of studying the reactivity patterns of σ-alkyl groups bonded to the simplest of metal clusters,[8] namely dimetal centers. We wish here to report the results of labelling studies using the σ-CH_2CD_3 ligand and furthermore to address ourselves to the mechanistic implications of these results.

The reaction between $Mo_2Cl_2(NMe_2)_4$ and $LiCH_2CD_3$ (2 equiv) proceeded smoothly to yield $Mo_2(CH_2CD_3)_2(NMe_2)_4$, according to eq. 1. The 1,2-diethyldimolybdenum compound was purified by

$$\underset{\sim}{1} \qquad Mo_2Cl_2(NMe_2)_4 + 2\,LiCH_2CD_3 \xrightarrow[-78\,°C]{\text{toluene}} Mo_2(CH_2CD_3)_2(NMe_2)_4 + 2\,LiCl$$

sublimation at 80°C, 10^{-6} cm Hg. The low temperature limiting ^1H nmr spectra of $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and $Mo_2(CH_2CH_3)_2(NMe_2)_4$ obtained at -60°C, 270 MHz in toluene-d_8 are shown in Figures 1a and 1b, respectively. Both compounds exist in a mixture of gauche and anti rotamers with the gauche being the predominant rotamer. The most striking difference is in the ethyl resonances. In the gauche rotamer, which lacks a plane of symmetry, the methylene protons are diastereotopic and at

270 MHz form part of an ABX_3 spectrum. It is therefore obvious from a comparison of the spectra in Figure 1 that the compound $Mo_2(CH_2CD_3)_2(NMe_2)_4$ retains its ^2H label in the methyl position. The methylene protons resemble an AB spin pattern since $^3J_{^1H-^2H}$ is very small compared to the geminal $J_{^1H-^1H}$.

Addition of CO_2 to a hydrocarbon solution of $Mo_2(Et)_2(NMe_2)_4$ leads to the formation of $Mo_2(O_2CNMe_2)_4$ ($M\equiv M$) and equimolar amounts of ethylene and ethane.[4] Reaction $\underset{\sim}{2}$ was carried out in an nmr tube. The fine yellow precipitate of $Mo_2(O_2CNMe_2)_4$ was centrifuged to the top of the nmr tube and the ^2H spectrum of the solution was recorded at 220 MHz. The spectrum is shown

$$\underset{\sim}{2} \qquad Mo_2(CH_2CD_3)_2(NMe_2)_4 + CO_2 \longrightarrow Mo_2(O_2CNMe_2)_4 + CH_2{=}CD_2 + CH_2DCD_3$$

in Figure 2a. The ^2H spectrum of $CH_2{=}CD_2$ agreed well with that which can be computed with a knowledge of all the $^1H-^1H$ couplings in ethylene[9] and the relative gyromagnetic ratios of ^1H and ^2H.[10]

In order to compare the ^2H spectrum of CH_2DCD_3 obtained in reaction $\underset{\sim}{2}$ with that of an authentic sample, we reacted a solid sample of $LiCH_2CD_3$ with D_2O in a vacuum manifold. The gases were condensed into an nmr tube using benzene as solvent and the ^2H spectrum was recorded. This is shown in Figure 2b. The ^2H spectrum of the ethane is identical with that in Figure 2a; furthermore, it is apparent that addition of D_2O to a solid sample of $LiCH_2CD_3$ also induces the formation of

CH_2=CD_2.

In a third experiment a mixture of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2(CH_2CD_3)_2(NMe_2)_4$ was reacted with CO_2 in a sealed nmr tube and the ^2H spectrum was recorded: this was identical to that shown in Figure 2a.

The ^1H spectra of all of the above were also recorded. The ^1H nmr spectrum of CH_2=CD_2 is a complex (AA'XX') but symmetrical spectrum since each proton is coupled to cis and trans ^2H nuclei, I = 1, and also to its geminal proton: gem-$\underline{J}_{^1H-^1H}$ in ethylene is +2.5 Hz.[9] Significantly, however, the ^1H nmr spectrum of the ethylene obtained from the addition of CO_2 to a mixture of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2(CH_2CD_3)_2(NMe_2)_4$ was merely the superimposition of a single line slightly downfield from the central portion of spectrum obtained for CH_2=CD_2.[11]

Previously we noted[4] that $Mo_2Me_2(NMe_2)_4$ and $Mo_2(Et)_2(NMe_2)_4$ react with tert-butanol to give $Mo_2Me_2(OBu^t)_4$ and $Mo_2Et(OBu^t)_5$, respectively. In both reactions the replacement of NMe_2 by OBu^t groups with the formation of $HNMe_2$ is expected,[12] but in the latter reaction the additional substitution of one ethyl group by OBu^t and the liberation of one equivalent of ethane was puzzling to us. Consequently we carried out the reaction of $Mo_2(CH_2CD_3)_2(NMe_2)_4$ with excess Bu^tOH in a sealed nmr tube and recorded the ^2H spectrum of the products. The reaction proceeds according to equation $\underset{\sim}{3}$. The ethane is CH_2DCD_3 while

$$\underset{\sim}{3} \qquad Mo_2(CH_2CD_3)_2(NMe_2)_4 + Bu^tOH \longrightarrow Mo_2(C_2H_3D_2)(OBu^t)_5 + CH_2DCD_3$$

the σ-ethyl group has a statistical distribution of deuteriums on the α and β carbons. The ^2H spectrum of the σ-ethyl group consists of two broad featureless signals at $\delta = 2.96$ and 1.72 ppm in the integral ratio 2:3.

These observations allow the following conclusions. (1) In $Mo_2(CH_2CH_3)_2(NMe_2)_4$ 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≡M) leads to the formation $Mo_2(O_2CNMe_2)_4$ (M$\equiv$M) by an intramolecular C-H reductive elimination reaction which is preceded by an irreversible β-hydrogen elimination reaction. (3) Addition of Bu^tOH to $Mo_2(CH_2CH_3)_2(NMe_2)_4$ causes the elimination of ethane by a C-H reductive elimination which is also promoted by an irreversible β-hydrogen elimination reaction. The σ-ethyl group subsequently formed in reaction 3 is formed from $CH_2{=}CD_2$ and a hydroxyl hydrogen atom from Bu^tOH (or possibly, but less likely the amine hydrogen of $HNMe_2$). β-hydrogen elimination from the σ-ethyl ligand is then a reversible process with the equilibrium favoring the σ-ethyl group.

These results raise many interesting mechanistic questions concerning factors favoring β-hydrogen elimination and reductive elimination reactions in dinuclear chemistry. We resist the temptation to speculate at this time but do note that our observations have one parallel with mononuclear transition metal chemistry. Reductive elimination involving C-H bond formation is more facile than reductive elimination involving

C-C bond formation.

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9. From R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. A, 269, 1385 (1962). For ethylene J_{cis} $^1H-^1H$ = +11.7 Hz, J_{trans} $^1H-^1H$ =+19.1, and J_{gem} $^1H-^1H$ =+2.5 Hz.

10. γ_H = 2.675 X 10^4 radians/sec. gauss.

    γ_D = 4.107 X 10^3 radians/sec. gauss.

11. This isotope influence on the chemical shift of the ethylenic protons is really only apparent in nmr spectra obtained at high field, 220 MHz in this instance.

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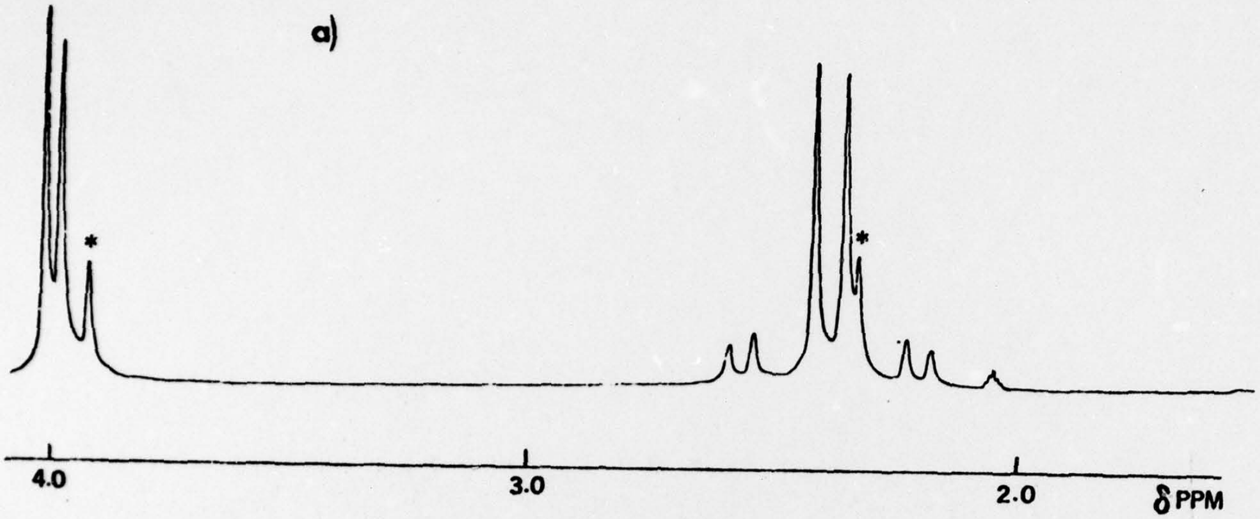
Captions to Figures

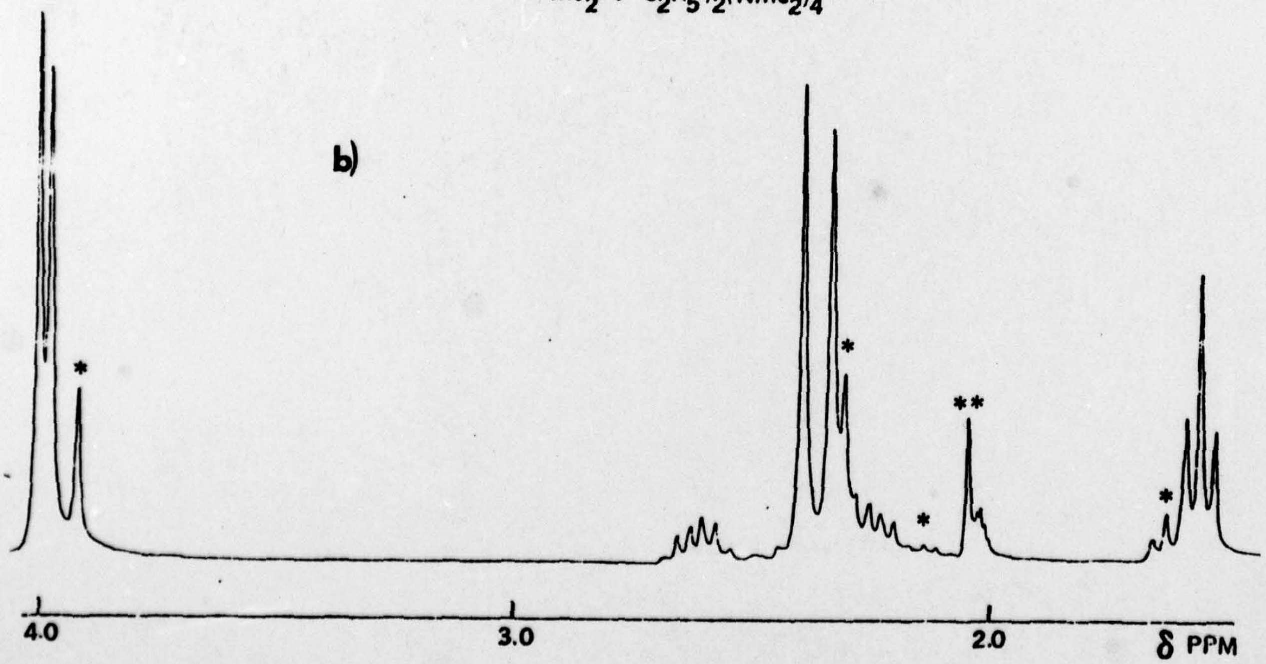
Figure 1. Proton NMR spectra recorded at 270 MHz, -61°C in toluene-d_8 of a) *-anti and gauche - $Mo_2(CH_2CD_3)_2$-$(NMe_2)_4$ and b) *-anti and gauche - $Mo_2(CH_2CH_3)_2$-$(NMe_2)_4$. c) ** represents residual protonated toluene.

Figure 2. Deuterium NMR spectra recorded at 16°C and 220 MHz of the gases formed in the reactions of a) CO_2 with $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and b) D_2O with $LiCH_2CD_3$. Both spectra were recorded in benzene.

$Mo_2(\sigma\text{-}CD_3CH_2)_2(NMe_2)_4$



$Mo_2(\sigma\text{-}C_2H_5)_2(NMe_2)_4$



^{2}H

CD_2CH_2 + CD_3CH_2D