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Preliminary communication

BINDING AND ACTIVATION OF ENZYMIC SUBSTRATES BY METAL COMPLEXES

III*. REACTIONS OF $Mo(CO)_2[S_2CN(C_2H_5)_2]_2$

JOHN W. McDONALD*, W.E. NEWTON, C.T.C. CREEDY and JAMES L. CORBIN
*Charles F. Kettering Research Laboratory***, Yellow Springs, Ohio 45387 (U.S.A.)*
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Summary

The complex $Mo(CO)_2L_2$ [$L = S_2CNEt_2$] reacts with acetylenes to yield both $Mo(CO)(RC_2R')L_2$ and $Mo(RC_2R')_2L_2$, with diazenes giving $Mo(RN_2R')L_2$ and $Mo(RN_2R')_2L_2$, and with CO and PPh_3 to form $Mo(CO)_3L_2$ and $Mo(CO)_2(PPh_3)L_2$.

We recently reported [1] the reactions of *cis*-$Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$ with a variety of unsaturated organic compounds and indicated the possible relevance of this reactivity to that displayed by the nitrogenase enzyme. In an attempt to extend and enhance such reactivity we began a study of the binding of similar substrates to $Mo(CO)_2(S_2CNEt_2)_2$. Our findings, which may give insight into the interaction of small molecules with molybdoenzymes, are described herein.

Previous reports [2] concerning $Mo(CO)_2(S_2CNEt_2)_2$ (I) described it as readily losing CO in solution and consequently the solution properties of I were not investigated. We find, however, that no CO is evolved from anerobic solutions of I and must conclude that proper measures for excluding oxygen were not employed previously. The observation that I is indeed stable in solution has allowed us to measure its visible spectrum which exhibits bands at 521 and 710 nm, neither of which obeys Beer's Law (Table 1). We attribute this deviation to a monomer—dimer equilibrium, the monomer increasing in relative concentration as the solution is diluted. Such reasoning is substantiated by the fact that at high dilution the spectrum seems to be approaching that of the monomeric [1] *cis*-$Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$ [λ_{max} 468 (ϵ 480), λ_{max} 688 (ϵ 900)]. We have been unable as yet to obtain molecular weight data for I due to its low solubility in suitable solvents.

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[*] For part II see ref. 1. The present paper was reported in part at the International Symposium on Nitrogen Fixation, Pullman, Wash., June, 1974.
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TABLE 1

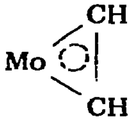
VISIBLE SPECTRUM OF $Mo(CO)_2(S_2CNEt_2)_2$ AS A FUNCTION OF CONCENTRATION

$10^3[Mo(CO)_2L_2]$	ϵ_{710}	ϵ_{521}
1.36	482	1118
0.92	589	1063
0.46	690	823
0.20	612 [a]	468 [a]

[a] Values obtained at very low absorbance and thus are accurate only to ~ 15%.

Although I generally interacts with small molecules in a similar manner to *cis*-$Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$, some striking differences in reactivity exist (see later). Complex I reacts reversibly with CO in solution* to form $Mo(CO)_3L_2$, and with PPh_3 to yield $Mo(CO)_2(PPh_3)L_2$. In CH_2Cl_2, I reacts with one mole of $EtO_2CN{=}NCO_2Et$ to yield $Mo(EtO_2CN_2CO_2Et)L_2$ (II) and with excess diazene giving $Mo(EtO_2CN_2CO_2Et)_2L_2$ (III). Both II and III hydrolyze to yield $EtO_2CNHNHCO_2Et$ as well as $OMoL_2$ and O_2MoL_2 respectively. These hydrolysis reactions resemble those previously reported [3] for $OMoL_2(EtO_2CN_2CO_2Et)$.

At room temperature I reacts with acetylene gas yielding $Mo(CO)(C_2H_2)L_2$ (IV). The spectral characteristics of IV (IR: ν(CO) 1960 cm^{-1}, absence of observable carbon—carbon stretch. NMR: resonance at 12.3 ppm downfield from TMS assigned to acetylenic protons) confirm that the $Mo—C_2H_2$ bonding in IV is very similar to that described [1] for $Mo(CO)(C_2H_2)[S_2P(i\text{-}Pr)_2]_2$, where a delocalized 2π aromatic system A



(A)

was postulated. Thus acetylene might be considered** as an effective four-electron donor to the 14-electron species $Mo(CO)L_2$ forming a stable 18-electron configuration. Reactions of substituted acetylenes ($PhC{\equiv}CPh$, $PhC{\equiv}CH$, $CH_3C{\equiv}CH$, $CH_3C{\equiv}CPh$, $CH_3O_2CC{\equiv}CCO_2CH_3$, $HC{\equiv}CCO_2CH_3$) with I under similar conditions yield compounds analogous to IV as determined by their IR and NMR spectra.

Reaction of I with excess $PhC{\equiv}CH$ in refluxing CH_2Cl_2 for 18 h yields the 2/1 adduct $Mo(HC{\equiv}CPh)_2L_2$ (V). No absorption assignable to carbon—carbon stretching is observed in the IR spectrum of V and its NMR spectrum ($CDCl_3$) contains a resonance (2 protons) 10.45 ppm downfield from TMS. While these acetylenic protons are not as deshielded as in the 1/1 adduct, $Mo(CO)(HC{\equiv}CPh)L_2$ (12.6 ppm), they are nevertheless much more deshielded than those of $(C_5H_5)_2Mo(C_2H_2)$ (7.68 ppm) [5].

This intermediate chemical shift suggests that each PhC_2H in V is effectively donating three electrons to the MoL_2 core to again give a stable 18-electron system. The substituted acetylenes $PhC{\equiv}CPh$, $CH_3C{\equiv}CPh$,

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*Previously only the reaction of CH_3OH-moistened I with CO was reported [2].

**Similar reasoning has been advanced to explain the existence of some substituted acetylene complexes of tungsten [4].

$CH_3O_2CC{\equiv}CCO_2CH_3$, and $HC{\equiv}CCO_2CH_3$ also react with I in refluxing CH_2Cl_2 to yield compounds analogous to V. The compound $Mo(C_2H_2)_2L_2$ was not prepared in a pure state, but NMR evidence (resonance at 10.15 ppm) indicated its formation from reactions utilizing higher temperatures and pressures of C_2H_2.

The formation of these 2/1 adducts is unique to the dithiocarbamate system as only the 1/1 series $Mo(CO)(RC_2R')L_2$ could be prepared for L = $S_2P(i\text{-}Pr)_2$. The ability of I to bind two acetylene molecules and the apparent tendency of I to dimerize (see above) may be related. Both characteristics could be attributed to either the capability of the molybdenum dithiocarbamate moiety to accommodate more electron density or to greater steric hindrance at molybdenum in the dithiophosphinate complex.

Addition of CF_3CO_2H to solutions of IV results in partial conversion of the coordinated acetylene to free ethylene. The yield of C_2H_4 from IV was only ~2% (GLC), a significantly smaller amount than was formed from the dithiophosphinate system [1] (~20% conversion). The fate of the acetylene in these reactions is being further investigated and is particularly important as nitrogenase is known [6] to catalyze the reduction of acetylene to ethylene.

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