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Preliminary communication

UNEXPECTEDLY COMPLEX STRUCTURE AND DYNAMIC BEHAVIOR OF BIS[(η^5-CYCLOPENTADIENYL)DICARBONYL MOLYBDENUM]-μ-PENT-3-YNE (*Mo—Mo*)

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Summary

The title compound, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}EtC{\equiv}CEt)$ in its crystalline form, has a molecular structure that lacks symmetry. Two $(\eta^5\text{-}C_5H_5)$Mo groups are connected by an Mo—Mo bond 2.977(1) Å in length with the usual sort of crosswise acetylene bridge. There are two terminal CO groups on Mo(1) and one on Mo(2). The fourth CO group is in a semi-bridging posture with Mo(2)—C = 1.936(6) and Mo(1)—C = 2.826(6). The ^{13}CO NMR spectrum at −126°C has six lines, indicative of the presence of two isomers, in each of which two CO's are either statically or dynamically equivalent. Complex changes occur in the spectrum as the temperature is increased so that at −40°C there is only a single line. A detailed interpretation of these spectra is not yet available.

Compounds containing quasi-tetrahedral C_2M_2 cores of which the C_2 portion is derived from the central carbon atoms of an acetylene, RC≡CR, have long been known [1]. Compounds of the earliest group to be characterized structurally [2, 3], $(\mu\text{-}RC_2R)[Co(CO)_3]_2$, have virtual C_{2v} symmetry and a single bond between the metal atoms. Subsequently, there have been several reported examples in which there are M=M double bonds [3—5], some with a single μ-RCCR group and some with two such bridges.

Methods of preparing such compounds are numerous. For those of Group VI metals a recent innovation [6] is the reaction of the triply-bonded dimers, $[(\eta^5\text{-}C_5H_5)M(CO)_2]_2$, with an acetylene to afford $[(\eta^5\text{-}C_5H_5)M(CO)_2]_2(\mu\text{-}RCCR)$ products. Actually, compounds of this sort containing Mo have been known since the work of Nakamura [7], who prepared them in several ways, including the reaction of RCCR with $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$, a procedure that might well involve the transient presence of the $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ intermediate.

Our interest was aroused by Nakamura and Hagihara's report [7a] that the PhCCPh compound had CO frequencies of 1980, 1928(sh), 1918 and 1860 cm^{-1}, since the last of these seemed inconsistent with the presence of only terminal CO ligands. We therefore prepared several of these compounds, and upon confirming the occurrence of a low-frequency IR band, we determined the crystal structure of the EtCCEt derivative.

The compound crystallizes in space group $P2_1/n$ with $a = 9.262(2)$, $b = 13.765(4)$, $c = 15.554(3)$ Å, $\beta = 105.45(2)°$, $V = 1911(1)$ Å^3 and $Z = 4$. The structure was solved by direct methods and refined anisotropically to $R_1 = 0.036$ and $R_2 = 0.057$. Fig. 1 shows the molecule and gives the Mo—Mo distance. The semibridging CO group can be seen lying approximately opposite to the μ-EtCCEt group across the Mo—Mo bond.

It is the semibridging CO group which must be responsible for the low-frequency IR band, which occurs at 1830 cm^{-1}, along with bands at 1977 and 1905 cm^{-1}, for the EtCCEt compound measured in toluene. It is known [8] that CO stretching frequencies drop very fast as CO groups move from terminal towards bridging positions.

It is noteworthy that the Mo—Mo bond, which we take to be essentially single, is very short when compared with Mo—Mo single bonds in other organodimolybdenum polycarbonyl type compounds. In $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ Mo—Mo = 3.27 Å [10].

An even more remarkable observation on this compound is its ^{13}C NMR spectrum in the CO region at various temperatures. At −126°C, it consists of 6 signals which eventually, after several stages of coalescence, are combined into one signal, as shown in Fig. 2. It seems likely that these spectra are explainable, in part, by the existence of two isomers, each having a 2:1:1 pattern at low temperature. Further work is in progress to elucidate the dynamical behavior in detail.

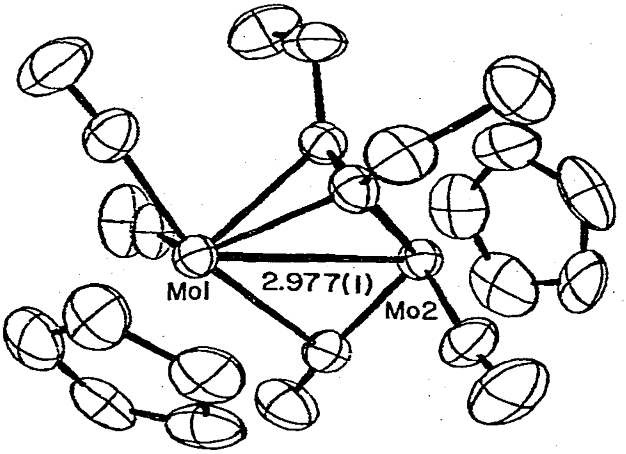

Fig. 1. An ORTEP drawing of the molecule $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-EtCCEt})$.

Acknowledgements

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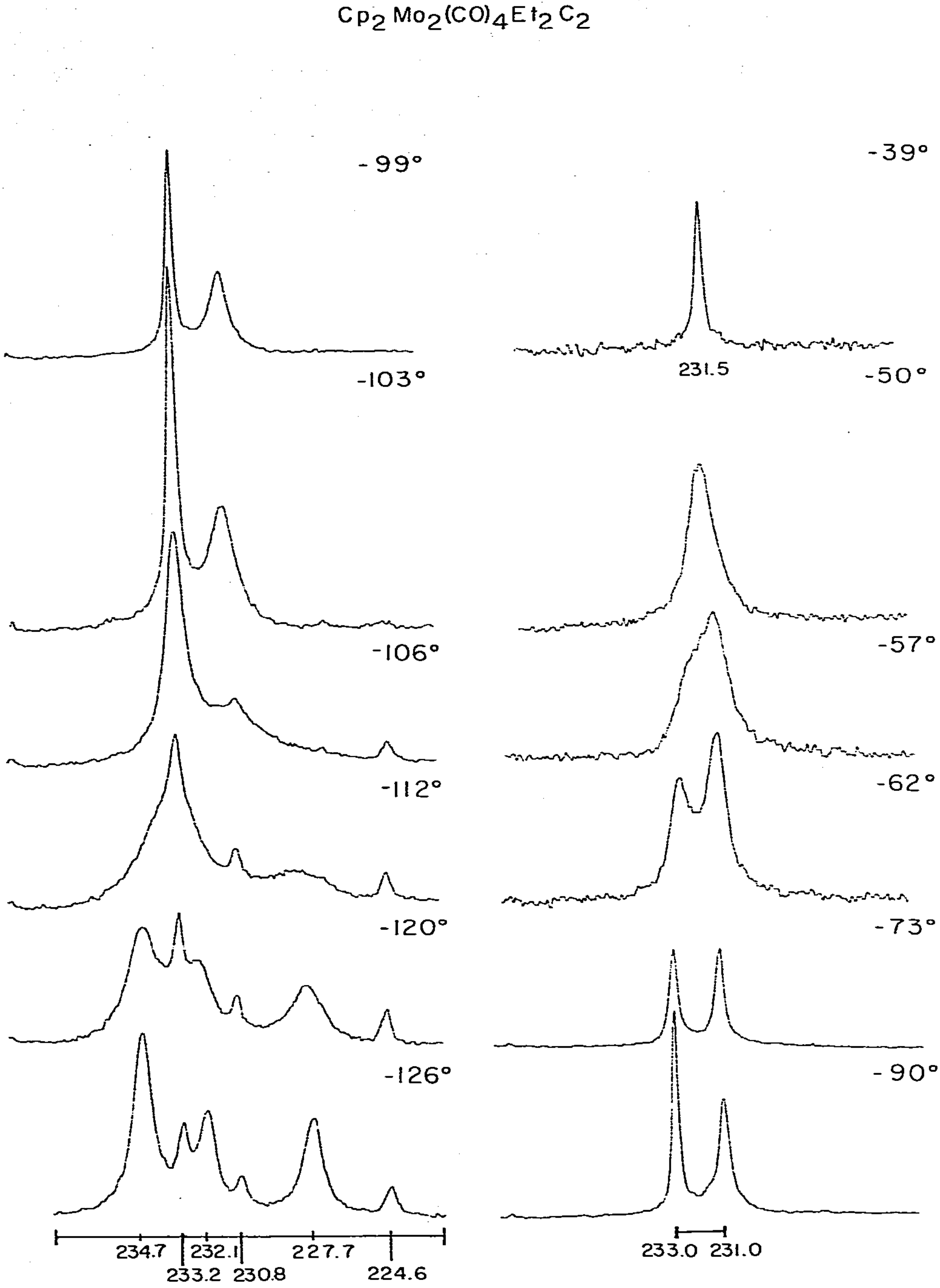

Fig. 2. ^{13}C spectra in the CO region for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-EtCCEt})$ at various temperatures.

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