Preliminary communication

THE MOLECULAR STRUCTURE AND DYNAMIC NMR SPECTRUM OF BIS[(η5-CYCLOPENTADIENYL)DICARBONYLMOLYBDENUM]-μ-ETHYNE(*Mo—Mo*)

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Summary

The title compound, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CH)$ has a molecular structure practically identical to that of its previously described analog containing $\mu\text{-}EtC{\equiv}CEt$. Its ^{13}C NMR at $-144°C$ has a broad doublet in the terminal CO region; this sharpens at $-118°C$ then again broadens ($-100°C$) and finally coalesces below $-58°C$ to a single resonance. The appearance of a semibridging CO (SBCO) ligand in the title compound and its EtC≡CEt analog, but not in a related compound with $\mu\text{-}H_2C{=}C{=}CH_2$ is attributed to internal crowding and it is suggested that these compounds may provide the most unambiguous examples of such an effect.

We recently reported [1] the molecular structure and the surprisingly complex ^{13}C NMR spectrum of I. The structure provided an explanation for the

Cp(CO)₂Mo ——— Mo(CO)₂Cp

(I) X = EtC≡CEt

(II) X = H₂C=C=CH₂

(III) X = CH≡CH
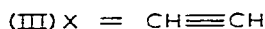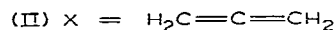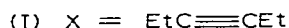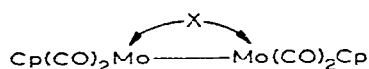
observation that the infrared spectrum contains a CO stretching bond at a frequency as low as 1830 cm⁻¹ by revealing the presence of a semibridging CO group, SBCO. The first explanation proposed [2a] for SBCO's by Cotton and Troup dealt with cases where they would help to equalize what would otherwise be a very unequal charge distribution. It is pertinent to emphasize that it has never been stated, nor implied, that this is the only context in which SBCO's may exist and a subsequent, more detailed discussion [2b] should also be consulted. But this only raises the question of why there is an SBCO, since structure a in which all CO groups are terminal or b in which

there are two symmetrical bridges, with, in each case a 2-electron bond between the metal atoms, provides 18-electron configurations to the metal atoms and conventional bonding and structural relationships to all other groups.

a   b
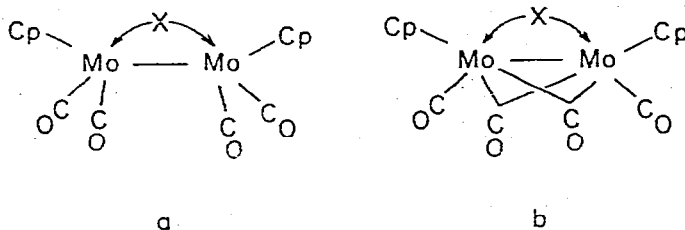
In the case of II, as we recently reported [3], a structure of type a was found.

In an effort to obtain further information on the electronic and stereodynamic behavior of this class of compound, we have now studied the simplest analog of I, namely, III. The compound was prepared by refluxing a toluene solution of $Cp_2Mo_2(CO)_6$ in an acetylene atmosphere for 12 h. After chromatography crystals were grown from methylcyclohexane solution by slow. cooling. Crystal data: Space group $P2_1/n$; $a = 10.376(2)$; $b = 17.188(6)$; $c = 8.646(2)$ Å; $\beta = 94.52(2)°$; $Z = 4$. Using 2560 reflections with $I > 3\sigma(I)$ the structure has been refined to $R_1 = 0.041$ and $R_2 = 0.064$.

Its molecular structure in the crystal, Fig. 1, is essentially identical to that of I in all respects. The Mo—Mo distances are 2.977(1) Å in I and 2.984(1) Å in III, and the long Mo—C distances for the semibridging CO groups are 2.826(6) Å in I and 2.911(4) Å in III. The difference of ca. 0.08 Å in the latter has a significant effect upon the infrared spectrum; the CO stretching frequencies are 1997s, 1938 (sh), 1930vs, 1852s cm^{-1} for I in hexane.

The carbon-13 NMR spectra of III at various temperatures, Fig. 2, are far less complicated than those of I. Since the structure found in the crystal has four non-equivalent CO ligands, it is evident that even at −144°C these have
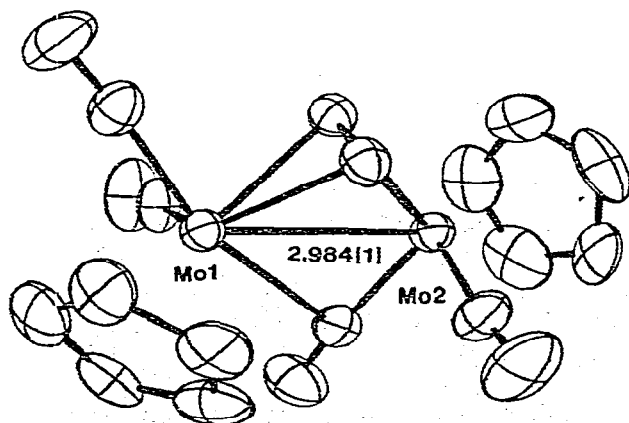

Fig. 1. The molecular structure of $Mo_2Cp_2(CO)_4(\mu\text{-}C_2H_2)$. Atoms are represented by their ellipsoids of thermal vibration contoured to enclose 50% of their electron density. Hydrogen atoms were not located.

become (dynamically) equivalent in pairs. This could be accomplished by the c/d interconversion process, in which the carbonyl groups β and δ alternately occupy the semibridging position with concomitant equivalencing of α and γ. However, we see no immediately or uniquely obvious mechanism by which all CO groups become NMR equivalent, as shown in Fig. 2.
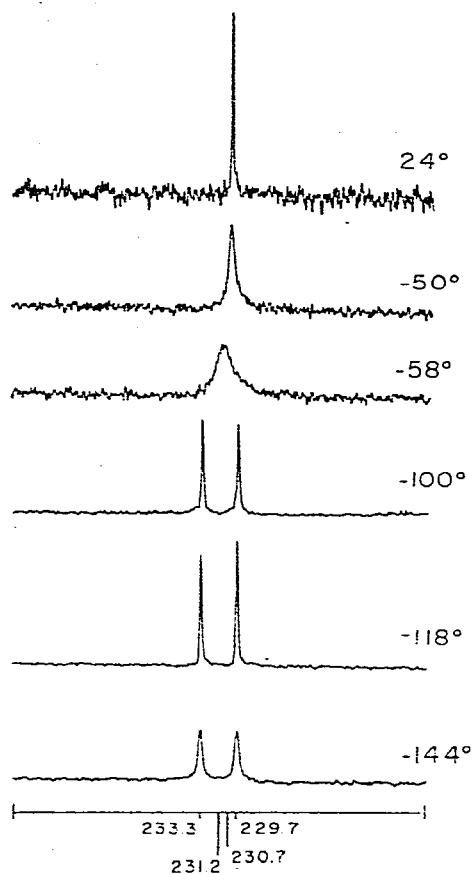

Fig. 2. Carbon-13 NMR spectra at various temperatures in the CO region. Chemical shifts are in ppm downfield from internal $Si(CH_3)_4$.

It is our tentative suggestion that the occurrence of the SBCO's in I and III may be attributed to internal crowding. In other words, structure a in which the space below the Mo—Mo bond (i.e., opposite the bridging group X) is vacant is unstable because too many atoms are then crowded into the upper and end regions; it collapses to the type of structure found for I and III. In short, the SBCO is present to solve a steric problem, not an electronic one. The non-occurrence of such a structure for II is understandable because the bridging moiety (X) is allene; this allows a longer Mo—Mo bond, 3.117(1) Å, and hence less crowding. Actually, in II there is perhaps incipient formation of the b type structure since the two CO ligands lying below the Mo—Mo bond are each slightly bent (171°, 164°) in directions corresponding to those

c   d
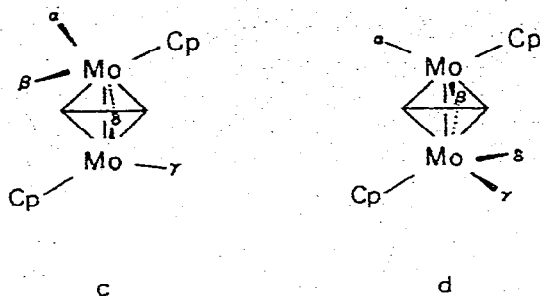
required for the formation of CO bridges. It is not obvious why I and III do not tend toward a structure of type b.

The internal crowding in I and III is evidently not much dependent on whether the R groups in RC≡CR are C_2H_5 or H. Thus, it is contacts between atoms all of which are bound directly to the metal atoms that seem to be crucial.

It is important to mention that this is not the first time a purely steric explanation for an SBCO has been proposed, since Vahrenkamp made such a proposal [4] for $Mn_2(CO)_6(C_5H_5)As(CH_3)_2$. We do not believe, however, that his case is as unambiguous as this one since that molecule is necessarily polar, to some extent.

Acknowledgements

References

1 W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson and J.R. Kolb, J. Organometal. Chem., 121 (1976) C23.
2 (a) F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 1233; (b) F.A. Cotton, Prog. Inorg. Chem., 21 (1976) 1.
3 M.H. Chisholm, L.A. Rankel, W.I. Bailey, Jr., F.A. Cotton and C.A. Murillo, J. Amer. Chem. Soc., 99 (1977) 1261.
4 H. Vahrenkamp, Ber., 107 (1974) 3867.

Erratum

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page 381, the 9th line of the Summary should read:

$a = 12.038(6)$ Å, $b = 12.900(12)$ Å, $c = 13.878(10)$ Å, $\alpha = 95.83(7)°$, $\beta = 103.47°$

page 384, the 6th line from the top should read:

with a unit cell of dimensions $a = 12.038(6)$ Å, $b = 12.900(12)$ Å, $c = 13.878(10)$ Å