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Preliminary communication

A REMARKABLE INTRAMOLECULAR DIFFERENCE IN LOCAL SCRAMBLING RATES FOR TWO $Mo(CO)_3$ GROUPS AND ABSENCE OF METAL-TO-METAL SCRAMBLING

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Summary

The carbon-13 NMR spectrum of guaiazulenedimolybdenum hexacarbonyl has been examined from −112 to +92°C. There is local scrambling of the three CO's on each Mo atom but at vastly disparate rates; resonances for one set coalesce below −112°, those of the other at about −30 °C. No scrambling of CO's from one metal atom to the other is observed.

In one of the earliest studies of carbonyl scrambling [1] it was shown that in $(\eta^5\text{-}C_5H_5)(CO)_3Mo{-}Mo(CO)_2(CNCH_3)(\eta^5\text{-}C_5H_5)$ the CH_3NC ligand moves rapidly over all six available positions, evidently through an intermediate or transition state with two bridging groups. Presumably similar scrambling of the CO groups occurs in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ itself. Very recently, there have been a number of studies [2] of the localized (i.e., CO ligands remaining on one metal atom) scrambling of the nonequivalent CO ligands in $M(CO)_3$ groups, especially $Fe(CO)_3$. The activation energies of such processes vary considerably depending on the ligand set making up the remainder of the coordination group of the metal atom.

As part of a continuing, systematic study of the fluxionality of metal carbonyls and their derivatives, we have examined a molecule in which the possibility of different rates of local scrambling as well as the possibility of internuclear scrambling exist, namely guaiazulenedimolybdenum hexacarbonyl.

The structure of this molecule [3] is shown in Fig. 1. It has one $Mo(CO)_3$ unit bound to a cyclopentadienyl unit and the other to a pentadienyl unit in the 7-membered ring. Within each $Mo(CO)_3$ portion of the $Mo_2(CO)_6$ unit, which has a "sawhorse" shape, there are two distinctly different types of CO ligand: two which are the legs of the sawhorse and one which is an extension of the crosspiece, approximately colinear with the Mo–Mo bond. The two legs on each molybdenum atom are not strictly equivalent because of the sub-

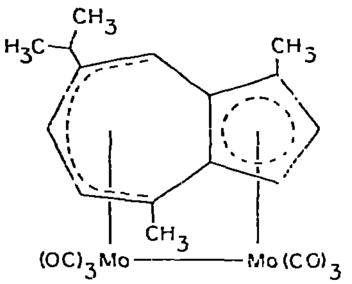

Fig.1 The molecular structure of guaiazulenedimolybdenum hexacarbonyl as reported by Churchill and Bird [3].

stituents on the guaiazulene, but it was anticipated that the resulting chemical shift differences might be at or below the level of resolution. They did, indeed, prove to be unresolvable.

The carbon-13 NMR spectra from −112 to +28 °C are shown in Fig. 2. Three important results are evident. (1) In one Mo(CO)$_3$ group scrambling is rapid enough to give a single sharp signal even at −80 °C. However, by −92 °C it had noticeably broadened and by −112 °C (see Fig. 2) it had nearly collapsed. Below −112 °C, the presence of solid in the tube was evident and thus no sure significance can be attached to results at lower temperatures, although further broadening at −125 °C was observed. (2) The scrambling in the other Mo(CO)$_3$ group becomes rapid enough to produce a single sharp line only at −10 °C. (3) Even at a temperature of +28 °C there is no evidence for the onset

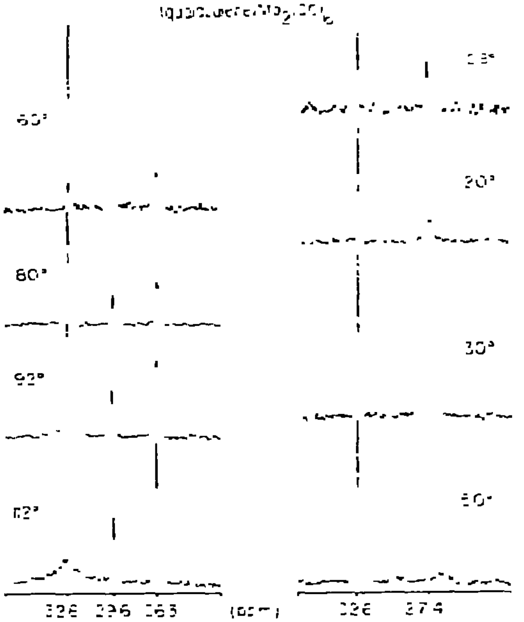

Fig.2. The carbon-13 NMR spectra from −112 to +28 °C. Chemical shifts are in ppm downfield from internal CS$_2$.

of internuclear scrambling; that is, the two sets of three CO groups give distinct, sharp resonances at the highest temperature of observation.*

Although different barriers to scrambling in the two different $Mo(CO)_3$ units would be expected, the difference actually observed is remarkably large. If it is assumed that the chemical shift difference for the two kinds of CO groups in the rapidly scrambling $Mo(CO)_3$ unit is the same as that in the slower one, the activation energies must differ by 4 to 5 kcal mol^{-1}. The only qualitative difference between the two is in the nature of the associated pentadienyl ligand, cyclic in one case and not in the other. The two $Mo(CO)_3$ groups per se, "have essentially equivalent stereochemistries [3]". However, this qualitative difference in the olefin—metal bonding must be the cause of the great difference in activation energies.

The obvious question, which cannot be resolved with the available data, is: which $Mo(CO)_3$ group is the faster one and which the slower? If a derivative in which one CO group is replaced by a different ligand, such as a phosphine or isocyanide can be prepared, it should be possible to resolve this ambiguity. An X-ray crystallographic study will be needed to determine the location of the substituent. An effort to conduct these experiments will be made, but in the meantime, it would be interesting to see if a correct theoretical prediction could be made.

The fact that CO groups do not easily, if at all, pass via bridges from one molybdenum atom to the other, in sharp contrast to the behavior of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$, despite the fact that the Mo—Mo distances in the present compound (3.267 Å) and in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$ [2] (3.230 Å) as well as $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ [4] (3.235 Å) are practically the same is noteworthy. It indicates that the M—M distance is not so important as the nature of the ligand system. Evidently, the fact that in the present case the two pentadienyl ligands are fused into a rigid coplanar system precludes the conformational changes necessary to permit the $(OC)_3Mo\text{—}Mo(CO)_3$ structure to rearrange into a $(OC)_2Mo(\mu\text{-}CO)_2Mo(CO)_2$ intermediate or transition state.

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**Note added in proof* Spectra have now been recorded at 62, 75° and 92°. At 62 and 75 the two carbonyl resonances are sharp and of almost identical widths (ca. 3 Hz). The spectrum recorded at 92° showed that sometime between raising the temperature from 75 to 92° and collecting 1000 pulses at 92° (a total time of about 25 min) complete decomposition had occurred. We conclude that no passage of CO ligands from one metal atom to the other occurs until at some temperature above 75° rapid decomposition terminates the experiment.