

STEREOCHEMICALLY NONRIGID ORGANOMETALLIC MOLECULES XXX*. OBSERVATIONS ON SOME CYCLOPENTADIENYLMOLYB- DENUM COMPOUNDS

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SUMMARY

The PMR spectra of $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$ have been examined to temperatures as low as -120° . Neither compound shows any broadening of the resonance due to all ten protons. This result supports our previous views on the structural and dynamical nature of $(C_5H_5)_3Mo(NO)$. Tetracyclopentadienylmolybdenum has been prepared in pure form by the reaction of C_5H_5I with $(C_5H_5)_2MoI_2$. Its PMR spectrum implies the structure $(h^5-C_5H_5)_2(h^1-C_5H_5)_2Mo$, with the $h^1-C_5H_5$ rings fluxional at 25° .

We report here the results of studies which extend or correct some observations currently in the literature having to do with the fluxional cyclopentadienylmolybdenum compounds $(C_5H_5)_2Mo(NO)I$ (Ia), $(C_5H_5)_2Mo(NO)CH_3$ (Ib) and $(C_5H_5)_4Mo$.

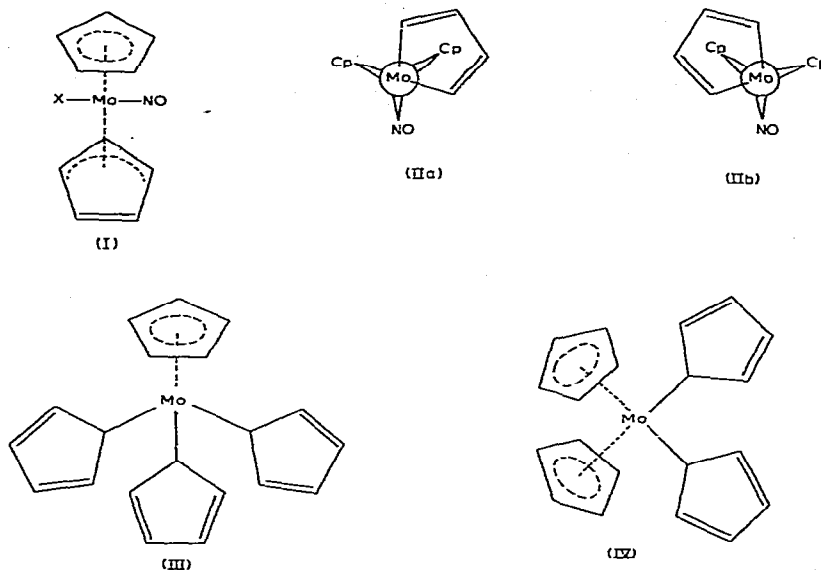
RESULTS AND DISCUSSION

$(C_5H_5)_2Mo(NO)X$ molecules

Compounds (Ia) and (Ib), the first of type $(C_5H_5)_2Mo(NO)X$, were reported by King², who proposed a structure of type (I) for them with the added postulate that rapid ring rotations and rapid ring interchange together caused all ten cyclopentadienyl protons to be PMR equivalent at room temperature. He also examined the PMR spectrum of (Ia) down to -55° observing no broadening of the single sharp resonance

Subsequent work^{3,4} in this Laboratory led to the preparation and characterization of the compound (Ic), $(C_5H_5)_3Mo(NO)$, in which the univalent ligand X in structure (I) would be $h^1-C_5H_5$. These studies showed that all 15 protons in (Ic) are PMR equivalent at room temperature but that as the temperature is lowered, the pattern characteristic of a *monohapto*-cyclopentadienyl ring first separates and then the other two rings begin to show separate singlet resonances. These observations are not inconsistent with structure (I). However, the X-ray crystallographic work failed to confirm structure (I). Instead, it showed that the two rings other than the $h^1-C_5H_5$

* For Part XXIX see ref. 1.



ring are equivalent to each other in their bonding relationship to the metal. The PMR difference observed between them at temperatures below $\sim -80^\circ$ was attributed to the very slow hindered rotation about the Mo-C bond to the h^1 -C₅H₅ ring such that this ring stays mainly in one of the positions shown as (IIa) and (IIb). The highly anisotropic π system of the h^1 -C₅H₅ group then causes the two otherwise equivalent C₅H₅ rings to experience different magnetic environments.

In order to test further the correctness of this proposal two additional studies have been undertaken. First, the crystal structure of (C₅H₅)₂Mo(NO)CH₃ has been investigated; this will be reported later. Second, the PMR spectra of (C₅H₅)₂Mo(NO)-CH₃ and (C₅H₅)₂Mo(NO)I have been examined at low temperatures, and those results are reported here. We consider it reasonable to suppose that if (C₅H₅)₂Mo(NO)(h^1 -C₅H₅) were actually to have a structure of type (I) in solution, with the appearance of separate resonances for the two rings other than (h^1 -C₅H₅) being due to a slowing of their interchange, then either or both of the molecules (Ia) and (Ib) would be expected to behave similarly. Since King had examined (Ia) only down to -55° , where (Ic) had not yet shown a broadening of the resonance in question, and had observed the PMR spectrum of (Ib) only at room temperature, we have extended the range of the observations into what should be the significant region by studying the PMR spectra of both (Ia) and (Ib) to temperatures as low as -120° . Even at this low a temperature, neither of these compounds shows any broadening of the resonance due to the ten C₅H₅ protons, whereas, in compound (Ic), a splitting into two separate, sharp peaks had already been consummated at -100° . This does not, of course prove, but we think it strongly supports, the view that the splitting observed in compound (Ic) is for the reason previously proposed⁴ and not because this, or any of the three (C₅H₅)₂Mo(NO)X compounds have a structure of type (I) in solution.

(C₅H₅)₄Mo

The preparation of this substance was reported by Fischer and Hristidu⁵. They

described it as an *extremely* air-sensitive compound with a PMR spectrum which required, "with certainty", the formulation (III). We considered that structure (IV), which gives an 18-electron configuration to the molybdenum atom, would be *a priori* the expected one, whereas the "certain" structure, (III), which gives only a 14-electron configuration seemed rather difficult to understand. Indeed, even empiricism of the crudest sort would seem to favor (IV) since a number of ($h^5\text{-C}_5\text{H}_5$)₂MoX₂ (X = a univalent group) molecules are well known. It also seemed a little surprising that (IV) would be *extremely* air sensitive, unless, of course, one wished to take this very fact as evidence against structure (IV). Finally, we could not understand why the $h^1\text{-C}_5\text{H}_5$ rings in (III) would not be fluxional, giving a sharp line at room temperature in contrast to the broad, complex resonance reported⁵ for it.

Because we deemed it important to know whether our understanding of cyclopentadienyl-metal bonding was or was not capable of providing a correct prediction of the structure of such a compound, we decided to reinvestigate this substance.

Several attempts to repeat the original work, using cyclopentadienylsodium, led to markedly impure products which were *extremely* air sensitive. These materials invariably had PMR spectra having one sharp peak and one broad, structured absorbance, in about the places reported⁵ for the $h^5\text{-C}_5\text{H}_5$ and olefinic $h^1\text{-C}_5\text{H}_5$ resonances. However, the relative intensities varied from sample to sample and batch to batch. We became convinced that such spectra were meaningless and that it was owing to sheer chance that a 12/5 intensity ratio had previously been observed.

By using TiC_5H_5 , pure (C_5H_5)₄Mo has been prepared. The compound is air sensitive, though not pyrophoric as previously reported, and it has a PMR spectrum in excellent accord with structure (IV), assuming the two $h^1\text{-C}_5\text{H}_5$ rings are fluxional, as one would expect them to be.

EXPERIMENTAL

General

All experiments were carried out in an atmosphere of purified argon. All solvents were purified by standard methods, and freed from oxygen prior to use. Microanalyses for C and H were performed in our Department by Mrs. N. Alvord under the supervision of Dr. J. S. Fleming. The proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with a variable temperature probe. Chemical shifts were obtained by internal referencing with TMS.

Dicyclopentadienylnitrosylmolybdenum iodide and dicyclopentadienylnitrosylmethylmolybdenum

These compounds were prepared according to the method of King². Proton magnetic resonance spectra were recorded in either carbon disulfide or a mixture (3/1) of carbon disulfide and Freon 11 as solvents. Temperatures down to -120° were obtained before precipitation occurred.

Tetracyclopentadienylmolybdenum

A mixture of 2.40 g (5 mmoles) of (C_5H_5)₂MoI₂, prepared by a published procedure⁶, 4.03 g (15 mmoles) of cyclopentadienylthallium and 150 ml of tetrahydrofuran was stirred for 72 h under argon at room temperature. After about 12 h

a yellow precipitate of thallium(I) iodide had formed and the color of the solution changed from green to red. After an additional 60 h, during which the color of the solution became violet, the solvent was removed in vacuum at 25° (10⁻² mm) and the dry residue was extracted with 200 ml of toluene. The solution was filtered and the filtrate cooled to -10° for 12 h. The resulting violet crystals were filtered and dried to give 1.4 g (78% yield) of pure (C₅H₅)₄Mo. (Found: C, 67.3; H, 5.42. C₂₀H₂₀Mo calcd.: C, 67.41; H, 5.65%.)

Tetracyclopentadienylmolybdenum is very air sensitive as a solid, though not pyrophoric as previously reported, and extremely so when in solution. Solutions other than those in toluene decomposed very rapidly.

The PMR spectrum (toluene-*d*₈) consisted of two very sharp singlets at τ 6.17 and τ 6.06, with equal intensities.

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