The Nature of the Product from the Reaction between Hexacarbonylmolybdenum and 8,9-Dihydroindene

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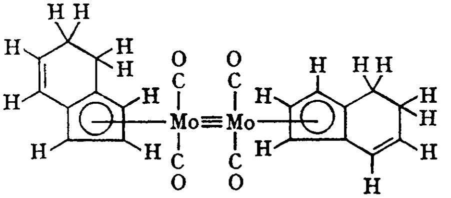
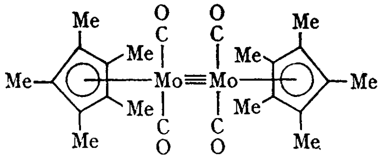
IN 1960 the reaction between $Mo(CO)_6$ and 8,9-dihydroindene was reported[1] to give cyclononatetranetricarbonylmolybdenum, $C_9H_{10}Mo(CO)_3$; further evidence is clearly inconsistent with its formulation as a cyclononatetraene complex, and suggests the formulation $[C_9H_9Mo(CO)_2]_2$ with the probable structure (I). This compound appears to contain a metal–metal triple bond and to be closely related to the recently reported[2] π-pentamethylcyclopentadienyl derivative, $[Me_5C_5Mo(CO)_2]_2$ (II).



(I)



(II)

The mass spectrum of the product of the reaction between $Mo(CO)_6$ and 8,9-dihydroindene† exhibits only barely detectable concentrations of the ions $C_9H_{10}M(CO)_n^+$ (n = 1,2,3, and 4). The highest *m/e* ion observed in the mass spectrum corresponds to the ion $(C_9H_9)_2Mo_2(CO)_4^+$. Other ions are observed corresponding to its decarbonylation products $(C_9H_9)_2Mo_2(CO)_n^+$ (n = 1, 2, and 3). However, once all carbonyl groups are lost, dehydrogenation becomes a much favoured process.‡ No $(C_9H_2)_2Mo_2^+$ can be detected. Instead the ion $(C_9H_7)_2Mo_2^+$ is observed in far greater concentration than any other molybdenum-containing ion. Important further fragments include $(C_9H_7)_2Mo_2^{2+}$, $C_9H_7Mo^+$, $C_9H_8^+$, and $C_9H_7^+$.

The mass spectrum thus clearly indicates the formula $[C_9H_9Mo(CO)_2]_2$ for this complex. This formula is also supported by analytical data on recently prepared material.§ Furthermore, once the possibility of a C_9H_9 ligand rather than a C_9H_{10} ligand is realized, the previously incomprehensible ^1H n.m.r. spectrum[1] in C_6F_5Br solution¶ at 55° becomes clearly explicable with the structure (I). On the basis of their relative intensities, the resonance at τ 4·05 can be assigned to the two olefinic protons of the six-membered ring, the resonance at τ 5·0 to the unique proton of the five-membered ring, the resonance at τ 5·22 to the pair of almost equivalent protons of the five-membered ring, and the resonances of τ 7·57 and τ 8·2—8·3 to the two different types of methylene protons of the six-membered ring.

Recent studies by Davison and Rode[3] make very doubtful the reasoning based on the presence of two or four ν(CO) frequencies[4] ** used originally[2] to infer the presence of a molybdenum–molybdenum multiple bond in $[Me_5C_5Mo(CO)_2]_2$. However, on the basis of the relative amounts of mono- and dimetallic ions, the mass spectra suggest the strength of metal–metal bonds in related bimetallic compounds to increase in the sequence $[C_5H_5Cr(CO)_3]_2$ (weakest) $<$ $[C_5H_5Mo(CO)_3]_2$ $<$ $[Me_5C_5Mo(CO)_2]_2$ $\sim$ $[C_9H_9Mo(CO)_2]_2$ (strongest). Especially noticeable is the near absence of monometallic ions in the mass spectra of $[Me_5C_5Mo(CO)_2]_2$ and $[C_9H_9Mo(CO)_2]_2$ (as compared with the amounts of dimetallic ions). The unusual strength of the molybdenum–molybdenum bonds in $[C_9H_9Mo(CO)_2]_2$ and $[Me_5C_5Mo(CO)_2]_2$ and the requirements for the molybdenum atoms to attain the favoured rare-gas configuration make reasonable the postulation of metal–metal triple bonds in these compounds.

A more careful analysis of the mass spectrum of $[Me_5C_5Mo(CO)_2]_2$ [$= C_{20}H_{30}Mo_2(CO)_4$] has been made including particularly a detailed inspection of the complex cluster of peaks for each ion arising from various combinations of the several molybdenum isotopes. This shows that in $[Me_5C_5Mo(CO)_2]_2$, as in $[C_9H_9Mo(CO)_2]_2$, dehydrogenation of

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† In this work the red crystalline product was obtained by the reaction between $Mo(CO)_6$ and 8,9-dihydroindene in boiling cyclo-octane. The similarity of the ^1H n.m.r. spectra in CS_2 solution indicates that the compound studied in this work is identical to that prepared previously (*cf.*, ref. 1.)

‡ A similar phenomenon has been noted in the mass spectrum of the π-allyl derivative $C_3H_5Mo(CO)_2C_5H_5$ (R. B. King, results submitted for publication). Here the highest *m/e* ions are $C_3H_5Mo(CO)_2C_5H_5^+$, $C_3H_5MoCOC_5H_5^+$, and $C_3H_3MoC_5H_5^+$. The latter ion appears to be a π-cyclopropenyl derivative. Thus in $C_3H_5Mo(CO)_2C_5H_5$ as in the compounds discussed in this Communication, dehydrogenation appears to accompany the loss of the last carbonyl group.

§ Analytical data for carbon and hydrogen alone are insufficient to distinguish unequivocally between the formulations $C_9H_{10}Mo(CO)_3$ and $[C_9H_9Mo(CO)_2]_2$. In the previous work[2] a direct oxygen analysis was not performed. The analysis for molybdenum was based on the weight of the ash remaining after the combustion for the carbon and hydrogen determinations. This procedure has since been found to be unreliable in some cases. The instability of this material in solution could account for the previously found molecular weight (ref. 1) of 302 ± 17 now known to be incorrect.

¶ The tendency for $[C_9H_9Mo(CO)_2]_2$ to decompose in solution made the quality of the observed n.m.r. spectra too poor to permit unequivocal identification of the fine structure. Bromopentafluorobenzene was found to be the best solvent for this purpose.

** The infrared spectra of $[C_9H_9Mo(CO)_2]_2$ and $[Me_5C_5Mo(CO)_2]_2$ appear to be different in the ν(CO) region. Unfortunately, the instability of $[C_9H_9Mo(CO)_2]_2$ in solution makes observation of solution spectra difficult. In compounds of this type possibilities for isomerism exist which depend on the relative orientations of the π-bonded rings in the two halves of the molecules; this could account for the observed spectral differences.

the hydrocarbon ligand accompanies decarbonylation. Predominant ions in the mass spectrum of $[Me_5C_5Mo(CO)_2]_2$ are $C_{20}H_{30}Mo_2(CO)_4^+$ (the parent ion), $C_{20}H_{30}Mo_2(CO)_3^+$, $C_{20}H_{28}Mo_2(CO)_2^+$, $C_{20}H_{28}Mo_2CO^+$ and $C_{20}H_{26}Mo_2^+$. Thus it appears possible that dehydrogenation accompanying decarbonylation may be a general feature of the this type of compound with molybdenum–molybdenum triple bonds.

The formulation of the product from the reaction between $Mo(CO)_6$ and 8,9-dihydroindene as $[C_9H_9Mo(CO)_2]_2$ rather than $C_9H_{10}Mo(CO)_3$ finally provides an explanation of its relatively low volatility (sublimes 140°/0·1 mm.) as compared with what would have been similar compounds such as the 1,3,5-cyclo-octatriene complex, $C_8H_{10}Mo(CO)_3$ (sublimes 100°/0·25 mm.).[5] It also now appears unlikely that any authentic metal complexes of cyclononatetraene have yet been synthesized.

I am indebted to the National Science Foundation for partial support of this work.

(*Received, July 24th,* 1967; *Com.* 764.)

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[1] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 4557.

[2] R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1967, **8**, 287.

[3] A. Davison and W. C. Rode, to be published; private communication of June, 1967.

[4] R. B. King, *Inorg. Chem.*, 1966, **5**, 2242.

[5] E. O. Fischer, C. Palm, and H. P. Fritz, *Chem. Ber.*, 1959, **92**, 2645.