*Journal of Organometallic Chemistry*, 316 (1986) C29–C34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

**Preliminary communication**

# STRUCTURE AND BONDING CHARACTERISTICS OF BIS(2,3-DICARBOMETHOXYNORBORNADIENE)DICARBONYLMOLYBDENUM AND RELATED COMPLEXES

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(Received July 12th, 1986)

## Summary

A crystal of bis(2,3-dicarbomethoxynorbornadiene)dicarbonylmolybdenum is in space group $P2_1/c$, with $a$ 11.0406(25), $b$ 14.7281(29), $c$ 15.3310(27), $\beta$ 110.38(2)° and $Z = 4$. Very large out-of-plane torsional angles (27–41°) for the vinylic carbomethoxy groups are observed. The bonding properties therefore are analyzed by comparison of spectroscopic data with those of related complexes, i.e. $L_2Mo(CO)_2$ where L = norbornadiene, 2-*p*-tosylnorbornadiene, and 2-carbomethoxynorbornadiene. Instead of $\sigma$-bonds, metal to C=C $\pi$-coordinations are believed to exist in these complexes. The presence of electron-withdrawing groups on the NBD ligands has increased their chelation strength, but at the same time has weakened the metal–CO bonds.

Dimerization of norbornadiene (NBD) may be accomplished stereospecifically for the formation of cyclooctaquinone upon thermolysis with hexacarbonylmolybdenum [1–3]. The reaction has been shown to proceed through a key intermediate $(NBD)_2Mo(CO)_2$ (I) [4]. Two other 7-substituted NBDs (II and III) seem to follow the same line of reactivity but with variable yields [5]. However, when one or more of the vinyl hydrogens are substituted by electron-withdrawing groups, dimerizations fail to occur. The properties of complexes IV–VII are significantly different from that of I, not only with regard to their reactivities of dimerization, but also to their geometries and bonding characters. In this report the spectroscopic data of IV–VII are systematically analyzed with the aid of X-ray crystallography so that structural changes induced by the presence of substituents can be rationalized.

Complexes IV, V and VI were similarly prepared from the corresponding NBD derivatives [6] by refluxing with $Mo(CO)_6$ in petroleum ether (100–140°C) for five days; complex VII, however, was made from $(NBD)Mo(CO)_4$ and 2,3-dicarbomethoxynorbornadiene. The purified yield of IV was 75%, which was much

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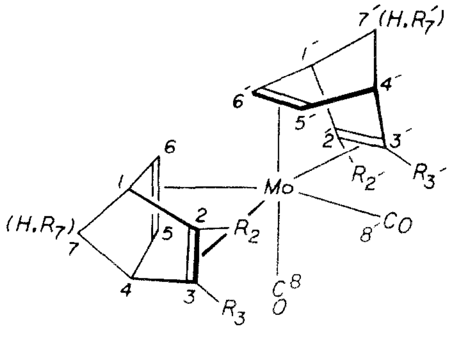


I $R(2) = R(3) = R(7) = R(2)' = R(3)' = R(7)' = H$

II $R(7) = R(7)' = OBu^t$; $R(2) = R(3) = R(2)' = R(3)' = H$

III $R(7) = R(7)' = OCOPh$; $R(2) = R(3) = R(2)' = R(3)' = H$

IV $R(2) = R(3) = R(2)' = R(3)' = COOCH_3$; $R(7) = R(7)' = H$

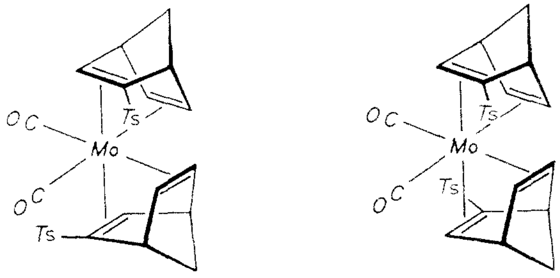
V $R(2)$ & $R(3) = R(2)'$ & $R(3)' = H$ & $COOCH_3$; $R(7) = R(7)' = H$

VI $R(2)$ & $R(3) = R(2)'$ & $R(3)' = H$ & p-tosyl; $R(7) = R(7)' = H$

VII $R(2) = R(3) = COOCH_3$; $R(2)' = R(3)' = R(7) = R(7)' = H$

higher than that of I. A better stability of IV was also noticed since it stayed intact for more than two weeks in chloroform at ambient temperature. The double bonds containing ester groups were found to be located *trans* to each other across the metal atom. This seemed to be a general phenomenon for all the products of IV to VII, since isomers with electron-deficient double bonds *trans* to carbonyls were not detected. This structural selectivity can be easily explained by the *trans*-effect of metal-carbonyl groups, their strong electron demand for back-donation preferring more electron-rich groups in *trans* positions.

For monosubstituted NBDs, two types of isomers were isolated, which were best illustrated by examining the structure of VI. Two enantiomers of 2-*p*-tosylnorbornadiene were produced simultaneously from cyclizations of cyclopentadiene with



(VIA) (VIB)

Fig. 1. Stereoview of the isomers of VI. VIA has two enantiomeric NBD ligands. VIB has two identical NBD ligands.

TABLE 1

$^1$H NMR (δ, ppm) SIGNALS OF IV, V, VI AND VII [a]

| | Vinyls | Bridgeheads | C(7) and substituents |
|---|---|---|---|
| IV | 5.4, 4.6 (2m, 2H) | 3.9 (m, 2H) | 3.7, 3.5 (2s, 3H each), 1.4 (br, 2H) |
| V | 5.3, 4.45, 3.8 (3m, 3H) | 3.65 (m, 2H) | 3.5 (s, 3H), 1.2 (AB pattern, $J$ 9 Hz) |
| VI [b] | 5.8, 5.7, 3.4 (3m, 3H) | 3.7 (m, 2H) | 7.7, 7.3 (2m, 4H), 2.4 (s, 3H), 1.2 (AB pattern, $J$ 9 Hz, 2H) |
| VI [c] | 5.8, 5.6, 5.4, 5.2 3.4, 3.3 (6m, 6H) | 3.8 (m, 4H) | 7.6–7.9, 7.1–7.3 (2m, 8H), 2.4 (br, 6H), 1.1, 1.2 (AB patterns, $J$ 9 Hz, 4H) |
| VII | 5.6, 5.3, 5.1, 4.4 3.3, 2.3 (6m, 6H) | 3.9, 3.6, 3.5 (3m, 2H each) | 3.6, 3.5 (2s, 6H), 1.3 (m, 2H), 1.2 (m, 2H) |

[a] Spectra were taken in $CDCl_3$, using tetramethylsilane as internal standard. [b] VIB. [c] VIA.

*p*-tosylacetylene. When used in the synthesis of VI, the situation became even more complex since the metal atom itself was another chiral center. Theoretically three pairs of enantiomeric complexes should exist: one pair consisting of two enantiomeric NBD ligands (as shown in Fig. 1 VIA), and two pairs consisting of two identical NBD ligands (as shown in Fig. 1, VIB). In our experiment, only one of the two pairs of VIB was observed due to the ready flexibility of the orientation of the ligands in these complexes which prevented formation of disfavoured structures. Complexes of VIA and VIB could be separated by chromatography on a silica gel column and were easily distinguished by their respective $^1$H NMR spectra (Table 1). The two NBD units in VIB were chemically equivalent, interchangeable through the $c_2$ axis, and therefore gave only one set of NBD signals, while the two NBD units in VIA were unequivalent and produced two separate sets of NBD signals.

The presence of an electron-withdrawing substituent on C(2) and/or C(3) of

TABLE 2

COMPARISON OF SELECTED BOND DISTANCES (Å) OF IV AND I

| Bond distance | IV | (Average) | I | (Average) |
|---|---|---|---|---|
| C(2′)=C(3′) | 1.438(4) | | | |
| C(2)=C(3) | 1.433(4) | (1.436) | 1.392(3) | |
| Mo–C(2′) | 2.225(3) | | | |
| Mo–C(3′) | 2.261(3) | | | |
| Mo–C(2) | 2.226(3) | | 2.251(2) | |
| Mo–C(3) | 2.243(3) | (2.239) | 2.301(2) | (2.276) |
| C(5′)=C(6′) | 1.366(4) | | | |
| C(5)=C(6) | 1.368(4) | (1.367) | 1.348(3) | |
| Mo–C(5′) | 2.461(3) | | | |
| Mo–C(6′) | 2.440(3) | | | |
| Mo–C(5) | 2.483(3) | | 2.492(2) | |
| Mo–C(6) | 2.482(3) | (2.467) | 2.457(2) | (2.475) |
| C(8′)≡O(8′) | 1.137(3) | | | |
| C(8)≡O(8) | 1.133(3) | (1.135) | 1.148(3) | |
| Mo–C(8′) | 2.002(3) | | | |
| Mo–C(8) | 2.003(3) | (2.003) | 1.968(2) | |

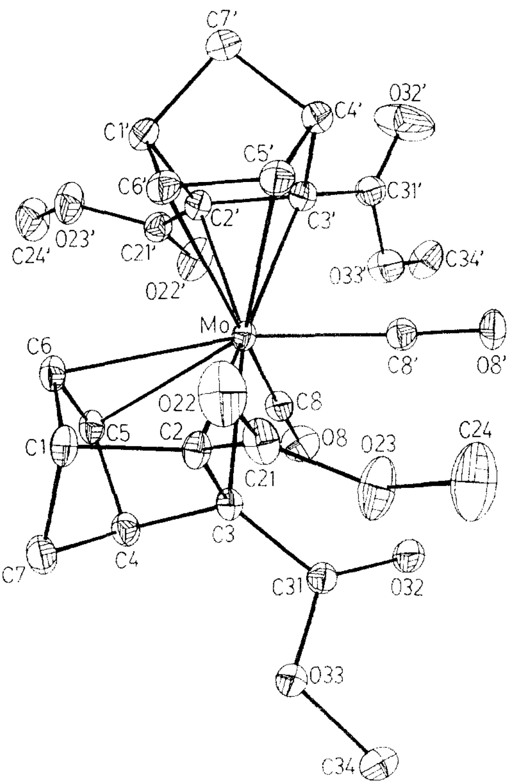


Fig. 2. ORTEP drawing of complex IV.

NBD significantly enhances its coordinating strength toward metal. The most direct evidence would be a comparison of bond distances between C=C and the metal. The average distance of C(2,3)–Mo for IV (2.239 Å) is 0.037 Å shorter than that for I (2.276 Å) (Table 2) [7]. When this distance becomes shorter, more electron density will flow into the $\pi^*$ orbital due to increased back-donation from the metal. A lengthening of the C=C bond should be observed and at the extreme two metal–carbon $\sigma$ bonds would result [8]. In the case of IV, the length of C(2)=C(3) is 1.436 Å, which is in between a typical double bond (1.34 Å) and a typical single bond (1.54 Å). A large torsional angle of C(31) (or R(3)) from the plane of C(2)–C(3)–C(4) is clearly shown in its ORTEP structure (Fig. 2). The averaged dihedral angle for distorsions of the four ester groups is 33° (Table 3), which again is about half that of a standard bond angle of an $sp^3$ carbon. The question of how much $\sigma$ character should be assigned to these Mo–C bonds then arises?

Previously we have successfully used $J(^1H-^{13}C)$ as a criterion for hybridizations of the vinyl carbons of I. This method can not be applied for IV since no such protons exist. However a look on $J(^1H-^{13}C(3))$ of V should reveal more. Variation of coupling constants should be noticeable from I to V if there is a trend of changing hybridization from I through V to IV. The $^{13}C$ signal of I, IV and V along with their coupling constants are listed in Table 4. Surprisingly it was found that $J(^1H-^{13}C(3))$ (172 Hz) of V is not very different from the corresponding value of I

TABLE 3

SELECTED OUT-OF-PLANE TORSIONAL ANGLES FOR THE ESTER GROUPS OF IV

| Plane 1 | Plane 2 | Dihedral angle |
|---|---|---|
| C(1)–C(2)–C(3)–C(4) | C(21)–C(2)–C(3) | 29° |
| C(1)–C(2)–C(3)–C(4) | C(31)–C(3)–C(2) | 41° |
| C(1′)–C(2′)–C(3′)–C(4′) | C(21′)–C(2′)–C(3′) | 27° |
| C(1′)–C(2′)–C(3′)–C(4′) | C(31′)–C(3′)–C(2′) | 37° |

(176 Hz). Though the geometry of the NBD ligands of IV is apparently different from that of the unbonded NBD, the C=C to Mo bonds in IV can be described as $\pi$-coordinations rather than as $\sigma$-bonds.

There are other interesting features of the structures of IV. The averaged bond distance of C(5,6)–Mo (2.467 Å) is also shorter than that in I (2.475 Å). Since the *trans*-located carbonyl group is a much stronger $\pi$ acid than C=C, the shortening of this bond, which transfers extra $\pi$ electron densities to the metal should cause a strengthening of the Mo–C(O) bonding due to enhanced back-donation. Therefore, shortening of the Mo–C(O) bond along with bond lengthening of C≡O would be expected. Yet the structural data in Table 2 show just the opposite. The reason for this abnormality is obviously a result of competing electron demand by the four ester groups which deplete more electron density from Mo than that supplied by the shortening of C(5,6)–Mo. The stability of the NBD-chelations seem to increase at the expense of weakening the C≡O coordinations. The increase of C≡O bond order also emerges in their IR stretching frequencies (Table 5). The increase in C≡O frequencies is proportional to the number of ester groups present in the complexes, i.e. in the order of I < V = VII (two ester groups) < IV (four ester groups). The increase of electron density of the ester groups also polarizes their own C=O bonds, which accounts for a ca. 50 $\text{cm}^{-1}$ bathochromic shift compared to that of the free ligands (Table 5).

Prolonged heating of IV–VI does not produce cage-dimers as was hoped, the reason for this is still not clear. Increasing the refluxing temperature resulted only in the decomposition of the complexes. For instance, two adducts were identified as trimethyl 1,2,4-benzenetricarboxylate and trimethyl 1,3,5-benzenetricarboxylate,

TABLE 4

$^{13}$C NMR ($\delta$, ppm) SIGNALS OF I, IV AND V (numbers in the parentheses are $^{1}$H–$^{13}$C coupling constants in Hz) [a]

| | C(1,4) | C(2,3) | C(5,6) | C(7) | R(2,3) |
|---|---|---|---|---|---|
| I [b] | 48.8 (d, 149) | 79.0 (d, 175) | 44.2 (d, 177) | 60.9 (t, 133) | |
| | 48.9 (d, 149) | 82.5 (d, 177) | 51.6 (d, 179) | | |
| IV | 51.2 (d, 155) | 53.6 (s) | 82.7 (d, 181) | 57.2 (t, 135) | 51.2 (q, 147) |
| | 53.1 (d, 160) | 61.0 (s) | 84.6 (d, 181) | | 52.1 (q, 147) |
| | | | | | 171.1 (s) |
| V [c] | 48.0 (d, 151) | 51.4 (s) | 79.7 (d, 181) | 57.9 (t, 135) | 50.4 (q, 146) |
| | 48.5 (d, 151) | 51.7 (d, 172) | 85.4 (d, 184) | | 172.3 (s) |

[a] Spectra were taken in $CDCl_3$, using tetramethylsilane as internal standard. [b] Data taken from ref. 1. [c] The isomer with two identical NBD ligands.

TABLE 5

SELECTED CARBONYL STRETCHING FREQUENCIES ($cm^{-1}$) (numbers in parentheses are stretching frequencies of free ligands)

| | I | IV | V | VII |
|---|---|---|---|---|
| Metal–CO | 1930 | 2000 | 1980 | 1980 |
| | 1890 | 1980 | 1940 | 1930 |
| NBD–$COOCH_3$ | | 1685 | 1675 | 1675 |
| | | (1730) | (1720) | (1730) |

these are trimers of methyl propiolate, which is a by-product of thermo-decomposition of IV.

**Acknowledgement**. This work was partially supported by the National Science Council of The Republic of China.

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7 Complex IV crystallizes in space group $P2_1/c$ with $a$ 11.0406(25), $b$ 14.7281(29), $c$ 15.3310(27), $\beta$ 110.38(2)° and $Z = 4$. X-ray diffraction data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. A total of 6340 independent reflections with $0° < 2\theta < 56°$ were collected by using $\theta - 2\theta$ scan technique. 4445 reflections with $I > 2.5\sigma(I)$ were used in the least-squares refinement. The structure was solved by the heavy-atom method using the NRCC SDP program library (E.J. Gabe and F.L. Lee, Acta. Cryst. A, 37 (1981) 5399.). The final values of the agreement indices were $R$ 3.42% and $R_w$ 3.22% with 317 variables.

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