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Preliminary communication

THE ISOLATION AND CHARACTERIZATION OF BIS(7-t-BUTOXYNORBORNADIENE)DICARBONYLMOLYBDENUM ISOMERS AS THE INTERMEDIATES OF METAL-MEDIATED DIMERIZATION OF 7-t-BUTOXYNORBORNADIENE

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Summary

The mechanism for stereospecific dimerization of 7-t-butoxynorbornadiene catalysed by molybdenum is explained by the isolation and characterization of bis(7-t-butoxynorbornadiene)dicarbonylmolybdenum isomers as the key intermediates. A ligand-exchange process is proposed and verified by experiments for the conversion of an *exo*-chelated ligand to the *endo—endo*-coupled dimer.

Recently we have found that dimerization of norbornadiene (NBD) catalysed by molybdenum carbonyl complexes produces stereospecifically the cage molecule heptacyclo$[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0.^{5,9}0.^{10,14}]$tetradecane (cyclooctaquinane) [1—3]. The key intermediate $(NBD)_2Mo(CO)_2$ for dimerization of NBD was isolated and shown to have both NBD ligands chelating to the metal through their *endo* faces. It is noteworthy that a similar reaction with 7-butoxynorbornadiene (BNBD) also gave exclusively a cage compound di-t-butoxycyclooctaquinane without the formation of any noticeable amount of *exo*-coupled dimers [4]. The oxygen atom on C(7) of BNBD was known to have the possibility to promote *exo*-chelation to metals [5], so yield enhancement of *exo*-coupled dimers could be expected [6].

We now describe our investigations on the mechanism of this reaction, and the successful isolation of two major groups of intermediates. The intermediates are identified as stereoisomers of formula $(BNBD)_2Mo(CO)_2$. The BNBD ligands are found to chelate the metal either at the *endo* or *exo* faces (compounds I and II). It is very interesting indeed to have observed that upon heating both isomers I and II yield the same cage dimer. A ligand-exchange mechanism is proposed for the conversion of II to cyclooctaquinane which is verified by experiments.

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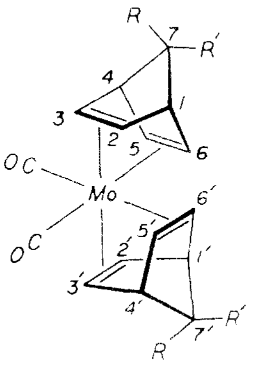
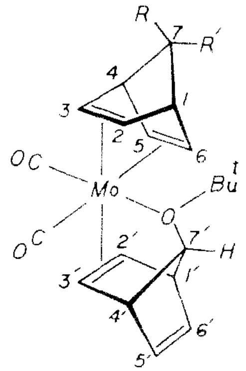


(Ia R = H, R' = O-t-Bu,
Ib R = O-t-Bu, R' = H)



(IIa R = H, R' = O-t-Bu;
IIb R = O-t-Bu, R' = H)

Refluxing a solution of BNBD (2.2 equiv.) and $Mo(CO)_6$ (1 equiv.) in petroleum ether (b.p. 110–140°C) for 24 h produced a mixture which gave the major groups of spots on a silica gel TLC plate eluted with benzene. The products were isolated by passing through a silica gel column using n-hexane/ethyl acetate (9/1) as eluent. Two isomers were found in each groups of spots. All isomers were recrystallized from n-hexane to form pale yellow needles with sharp melting points [7] (the combined yield ca. 60%, ratio of I/II 3/1). Their ^1H NMR, IR, and mass spectra as well as their microanalyses were consistent with the assigned structures.

The ^1H NMR spectra for the two isomers of I are identical to those for the known complexes $(NBD)_2M(CO)_2$ (M = Mo, W) [8]. The two organic ligands are chemically equivalent to each other. The more polar isomer shows two vinylic absorptions at δ 5.4 and 4.9 ppm, which are assigned to the double bond *trans* to a carbonyl (C(5)=C(6)), and two absorptions at δ 3.3 and 2.2 ppm, which are assigned to the double bond *trans* to the other NBD (C(2)=C(3)). The corresponding vinylic protons on the less polar isomer show small shifts at 5.6, 5.0, and 3.2, 2.0 ppm. The definite identities for polarity and Ia/Ib could not be determined at the present stage. Single crystals suitable for X-ray crystallography were grown and analysed. The relative abundance for Ia and Ib is approximately equal, which seems to signify that the t-butoxy group has little influence on the stereoselectivity of *endo*-complexation.

The spectra for the two isomers of II are a little more complicated than those for complexes I, but nevertheless are very indicative for elucidation of the structures. The spectrum for the less polar is shown in Fig. 1. The peak at δ 6.2 ppm (2H) is due to the protons on the free double bond (C(5')=C(6')), and the peaks at δ 5.1, 4.2 ppm (1H each) to protons on the C(5)=C(6) bond, which is *trans* to a carbonyl. The more upfield signals at δ 2.9 (2H, C(2')=C(3')), and 3.2, 2.4 ppm (1H each for C(2)=C(3)) represent two double bonds *trans* to each other. Thus the oxygen ligand is located *trans* to the second carbonyl. The more polar isomer of II shows a very similar pattern in the ^1H NMR spectrum except for the vinyl protons shift, which is a little downfield to δ 5.3 and 4.3 ppm (C(2)=C(3)). The definite orientations of the O-t-Bu groups in IIa and IIb can not yet be determined.

The isolation of complexes II thus provides solid evidence for the feasibility

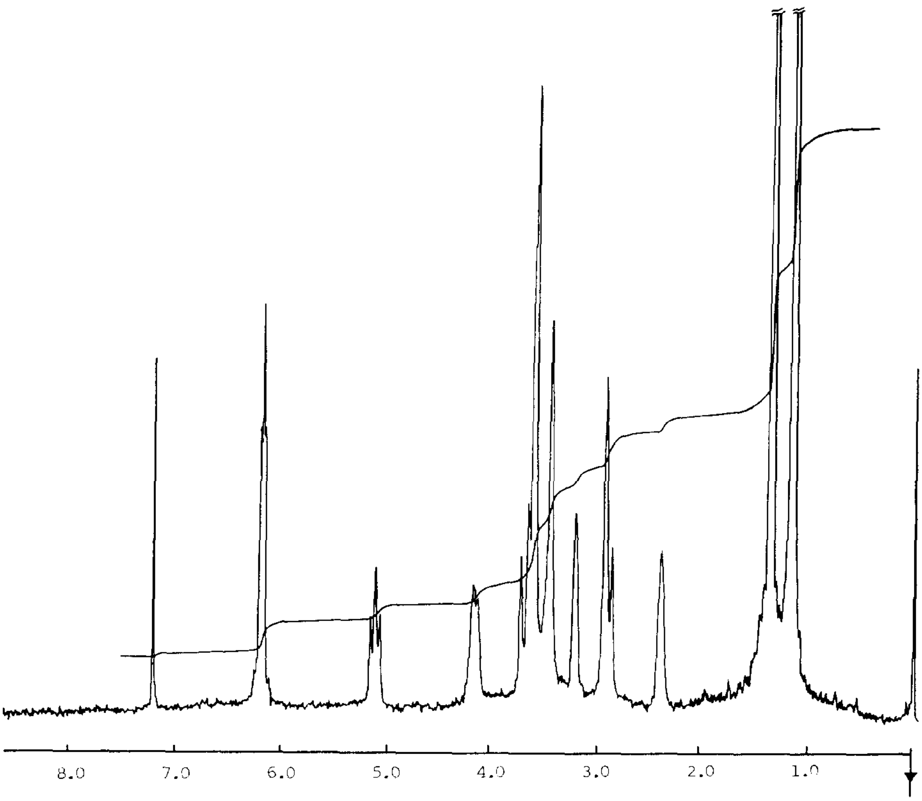


Fig. 1. ^{1}H NMR spectrum for the nonpolar isomer of complex II (in $CDCl_3$, tetramethylsilane as the internal standard.

of *exo*-complexation between molybdenum(0) and BNBD. This observation only intensifies the paradox for the lack of *exo-endo*-coupled dimers. We have noticed for some time that both the BNBD and NBD ligands on molybdenum are not rigidly bonded since in ^{1}H NMR spectra the vinyl signals frequently drift up- and down-field according to the operation conditions (i.e. solvents, etc.). Ligand-exchange should proceed readily. We also noticed by periodically examining TLC plates, that the spots of complexes II appeared prior to those of complexes I during the reaction. It seems that *exo*-complexation is kinetically more favoured, but later may be replaced via ligand-exchange to form the more stable *endo* product. The lacking of *exo*-coupled dimers directly derived from complexes II should be attributed to the steric blockade of the *exo* side by the bulky O-t-butoxy group.

In order to prove our proposed reaction scheme for II→I→cyclooctaquinane, an amount of pure II was heated with one equivalent BNBD in petroleum ether, and the reaction was followed by TLC. Indeed we observed the appearance of I after a few hours, and its concentration increased steadily with decrease of II. The presence of II was confirmed by its isolation from the reaction mixtures. Heating was terminated after ca. 60 h when most of the metal complexes had disintegrated, and cyclooctaquinane was isolated in over 50% yield. For comparison we also applied this reaction to pure I. Cyclooctaquinane was collected at the end of the reaction, but the conversion I→II was not observed.

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7 The less polar isomer of I has m.p. 130—131°C, and the more polar one 122—124°C. The less polar isomer of II has m.p. 112—113°C, and the more polar one 123—126°C. All complexes show satisfactory H and C element analyses for $C_{24}H_{32}O_4Mo$, as well as mass spectra $M^+ = 484$ for Mo = 100.
8 T.J. Chow and Y.-S. Chao, unpublished results for $(NBD)_2W$ and $(CO)_2$.