Journal of Organometallic Chemistry, 281 (1985) C33—C37
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE SYNTHESIS AND CHARACTERIZATION OF BIS(NORBORNADIENE)DICARBONYLMOLYBDENUM. AN INTERMEDIATE OF THE METAL-ASSISTED DIMERIZATION OF NORBORNADIENE

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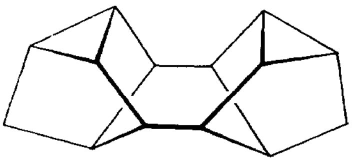
(Received October 15th, 1984)

Summary

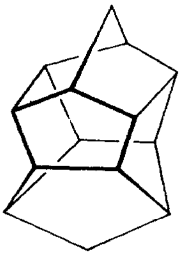
Bis(norbornadiene)dicarbonylmolybdenum was isolated in a good yield during molybdenum-mediated dimerization of norbornadiene for the formation of heptacyclo[5.5.1.$1^{4,10}$.$0^{2,6}$.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tetradecane. The carbon-to-metal bondings of the complex were examined by ^{1}H and ^{13}C NMR, and it was found that the chemical shifts of one double bond on each norbornadiene ligand are located significantly upfield from the other. The structure was analyzed by single crystal X-ray crystallography and an approximate 0.2 Å difference in the metal—carbon bond distances was observed.

Metal-catalyzed dimerizations of norbornadiene (NBD) have been studied quite well [1]. Among the dimers, Binor-S (I) [2] and the cage compound heptacyclo[5.5.1.$1^{4,10}$.$0^{2,6}$.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tetradecane (II) [3,4], for which *endo-cis-endo* coupling has occurred with a high efficiency, are of special interest. Dimerization of both compounds has to be initiated by metals capable of holding two NBD ligands facing each other with their *endo* sides. Intermediates with such a geometry have frequently been proposed but have never been isolated. We report our preliminary findings on the characterization of bis(norbornadiene)dicarbonylmolybdenum (IV), which has been isolated for the first time as a mononuclear complex formed during the formation of II. The geometry of the complex shows that the two NBD ligands bind to the metal in a tilted fashion, i.e. one double bond lies closer to the metal than the other. The two ligands are also oriented 90° with respect to each other, which logically explains why the cage molecule II is formed in preference to the still-unknown structure heptacyclo[7.4.1.$0^{2,8}$.$0^{3,7}$.$0^{4,12}$.$0^{6,11}$.$0^{10,13}$]tetradecane (III).

The synthesis of IV was accomplished by refluxing a solution of molybdenum



(I)



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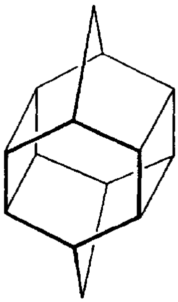
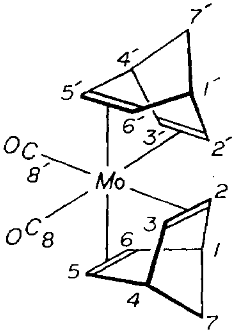
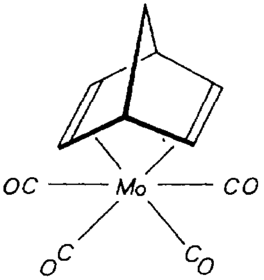


(III)



(IV)



(V)

hexacarbonyl (1 equiv.) and norbornadiene (3 equiv.) in petroleum ether (110—140°C) for 40 h. The dark brown solution was decanted and the oily precipitates were extracted several times with n-hexane. The two liquid parts were combined and concentrated in vacuo. It was then eluted with n-hexane through a silica gel liquid chromatography column. The first component leaving the column was a white solid, identified as the cage compound II [5]. Complex IV was collected next. It solidified upon evaporation of the solvent and was recrystallized from methanol to give light yellow needles (m.p. 85°C, yield 45%). The compound is stable in pure form under nitrogen but decomposes slowly in solution when exposed to air.

It was found that the above reaction proceeds clearly through four separable stages. At each stage the major product could be isolated. The complete sequence was easily monitored by periodically eluting a silica gel TLC plate with n-hexane. The formation of mono(norbornadiene)tetracarbonylmolybdenum (V) was observed first and it reached its optimal yield (55% isolated) at ca. 20 h,

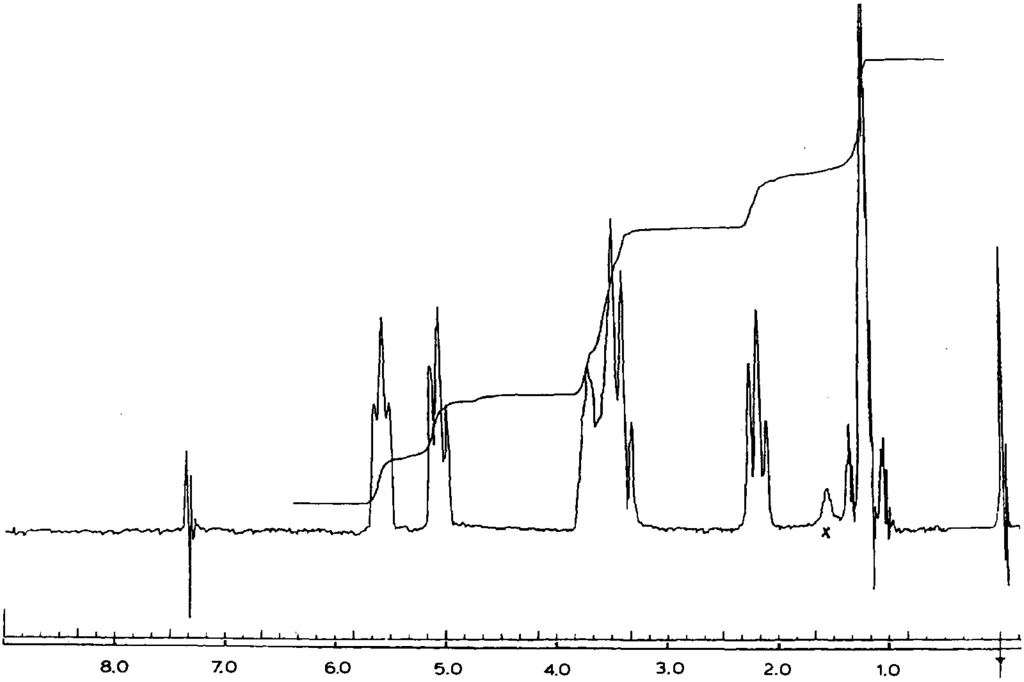


Fig. 1. ^{1}H NMR spectrum of IV taken in $CDCl_3$ with tetramethylsilane as the internal standard. The mark X in the figure indicates a contamination in the solvent.

then it gradually transformed to IV until it completely disappeared. Continuous refluxing for 110 h destroyed IV to give II as the only major product in a yield of 26%. This is the highest yield ever reported for II. The well-defined reaction sequence of NBD → V → IV → II is uniquely different from analogous reactions which generally produce several isomeric dimers simultaneously.

The ^{1}H NMR spectrum of IV (Fig. 1) shows two groups of vinylic protons at δ 5.07 and 5.60 ppm, which agree well with the corresponding vinylic hydrogens of V [6]. However, unlike V, the protons on the second double bond move significantly upfield as two triplets at δ 2.20 and 3.40 ppm due to the effect of weaker deshielding. Both the results of elemental analysis and mass spectrometry confirm that the molecular formula is $(C_{14}H_{16})Mo(CO)_2$ [7]. In the IR spectrum the molybdenum carbonyl stretchings show two very strong absorptions at 1930 and 1890 cm^{-1}. The proton decoupled ^{13}C NMR spectrum gives eight distinct lines (Table 1). All these pieces of information when taken together lead to a structure consisting of two equivalent but unevenly bonded NBD ligands in addition to the carbonyls.

TABLE 1

^{13}C NMR (δ, ppm) SIGNALS OF IV[a]

C(1,4)	C(5,6)	C(2,3)	C(7)	C(8)
48.8(d); 48.9(d)	44.2(d); 51.6(d)	79.0(d); 82.5(d)	60.9(t)	229
(J 149 Hz)	(J 178 Hz)	(J 176 Hz)	(J 133 Hz)	

[a] Spectrum taken in $CDCl_3$, using tetramethylsilane as the internal standard.

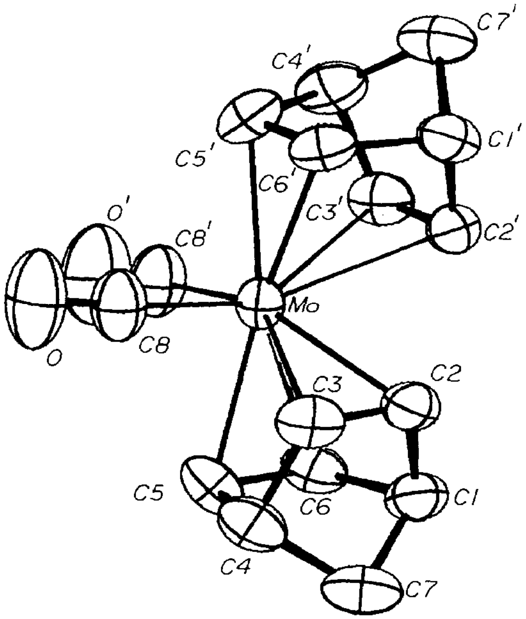


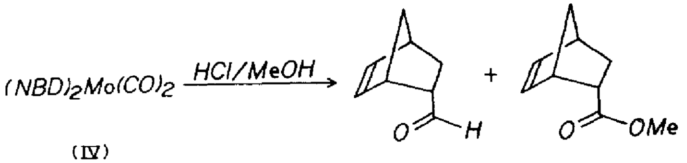
Fig. 2. ORTEP drawing of $(C_7H_8)_2Mo(CO)_2$ (IV) with atomic numbering scheme. The atoms marked with a prime ′ were generated by the crystallographic 2-fold axis bisecting C(8)—Mo—C(8′).

A question to be answered is the cause of the unusual upfield shifts of the NMR signals for one of the two double bonds. It has been shown recently that molybdenum is capable of forming stable σ-bonded metallocycles with ethylenes [8]. The metal of IV might have formed a σ-bonded molybdenocyclopropane with one of the double bonds of NBD while maintaining π-coordination with the other. The simplest way to verify such a postulate is to measure the corresponding bond distances by examining its crystal structure. Therefore we carried out an X-ray crystallographic study of IV [9]; an ORTEP drawing is shown in Fig. 2. The bond distances measured between C(5) and C(6) (1.392(3) Å) as well as between C(2) and C(3) (1.348(3) Å) are within the range of typical double bonds, with a small elongation for the former (Table 2). The distance between the metal and C(5) and C(6) (average 2.28(2) Å) is 0.2 Å shorter than that between the metal and C(2) and C(3) (average 2.47(2) Å). The decrease of the metal—carbon bond length indicates a greater orbital overlap and an increase of the bond strength. The back donation of electrons from the *d* orbitals of the metal to the $\pi^\star$ orbital of C(5) and C(6) tends to reduce the bond order of C(5)=C(6). These changes therefore altered the diamagnetic environment of the protons and were responsible for the upfield shift of the NMR signals.

TABLE 2

SELECTED BOND DISTANCES (Å) FOR IV

Mo—C(2)	2.457(2)	C(1)—C(2)	1.534(3)
Mo—C(3)	2.492(2)	C(1)—C(6)	1.525(3)
Mo—C(5)	2.301(2)	C(1)—C(7)	1.542(3)
Mo—C(6)	2.251(2)	C(4)—C(3)	1.530(3)
C(2)—C(3)	1.348(3)	C(4)—C(5)	1.533(3)
C(5)—C(6)	1.392(3)	C(4)—C(7)	1.531(3)



(IV)

(VI) (VII)

An acid-catalyzed rearrangement of IV was carried out in methanol by bubbling gaseous HCl through the solution. The color of the solution changed slowly from light yellow to green, then to dark brown. Norbornene was originally expected since the carbons σ-bonded to the metal should become saturated upon protonation [8]. But the two major products identified by GC-MS were 5-norbornene-2-carboxaldehyde (VI) and methyl 5-norbornene-2-carboxylate (VII) (in approximately 1/2 ratio), by comparison with authentic samples (eq. 1) [10]. Carbonyl migration from molybdenum to carbon occurred with high efficiency. Norbornene was not observed as a product of this reaction.

Supplementary material available. Lists of crystal data are available upon request.

Acknowledgement. This work was supported by a grant (NSC73-0201-M001-05) from the National Science Council of The Republic of China.

References and notes

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5 Compound II shows a high intensity molecular ion in the mass spectrum (M^+ = 184, base peak), and has two signals in the ^{1}H NMR spectrum at δ 2.34 (s,6H) and 1.71 (s,2H) ppm. The absorption in the IR spectrum are also consistent with the reported values.

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7 Elemental anal. Found: C, 57.51; H, 4.76. $C_{16}H_{16}MoO_2$ calcd.: C, 57.10; H, 4.76%. Mass spec. m/e 340 (M^+ for Mo = 100), 312 ($M^+ - CO$), 280,256, 243, 230, 216, 205, 190, 164.

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9 The crystal was found to be in the monoclinic space group $C2/c$ with $Z = 4$ and cell dimensions a 16.097(1), b 7.234(1), c 11.930(1) Å, β 103.16(1)°. Intensity data up to $2\theta \leqslant 70°$ were collected using a Nonius-CAD4 automated diffractometer equipped with monochromated Mo-K_α radiation employing the ω-2θ scan method. The data were corrected for Lorentz polarization and absorption effects. The structure was solved by the heavy atom and Fourier methods and refined with a weighted least-squares routine. All hydrogen atoms were found in a difference map at anisotropic convergence. Final refinements with non-hydrogen atoms anisotropically and hydrogen atoms isotropically resulted in R = 0.028 and R_ω = 0.021 for 2σ data and counting statistical weights.

10 Compound VI was purchased from Aldrich Chemical Co. and VII was synthesized by mixing cyclopentadiene with methyl acrylate following the procedure described by: M. Mellor and C.F. Webb, J. Chem. Soc., Perkin Trans. 2, (1974) 17.