

## The thermolysis of homohypostrophene with hexacarbonylmolybdenum

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### Abstract

Thermolysis of homohypostrophene (HHS) with  $\text{Mo}(\text{CO})_6$  produces two major chelates  $(\text{HHS})\text{Mo}(\text{CO})_4$  and  $(\text{HHS})_2\text{Mo}(\text{CO})_2$ . Prolonged heating of the two complexes induces an intramolecular retrocyclization of HHS to give dicarbonylmono(dicyclopentadienylmethane)molybdenum. The spectroscopic character of the products is described and the mechanism of the reactions is discussed.

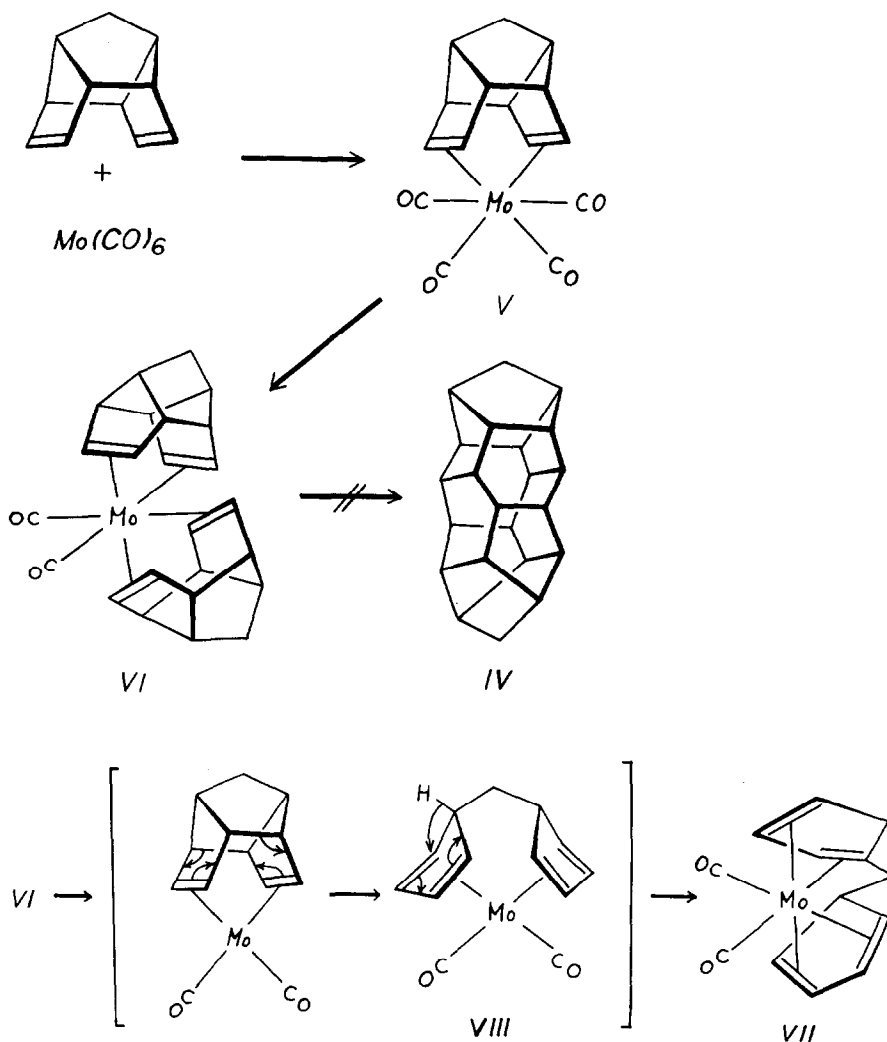
### Introduction

Dimerization of norbornadiene (NBD) for the formation of a cage cyclooctaquinane (heptacyclo[6.6.0.0.<sup>2,6</sup>0.<sup>3,13</sup>0.<sup>4,11</sup>0.<sup>5,9</sup>0.<sup>10,14</sup>]tetradecane, I) [1,2] was found to proceed regiospecifically by reaction with  $\text{Mo}(\text{CO})_6$ . Two key intermediates  $(\text{NBD})\text{Mo}(\text{CO})_4$  (II) and  $(\text{NBD})_2\text{Mo}(\text{CO})_2$  (III) were isolated and the reaction sequence was shown to go through  $\text{NBD} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \text{I}$  [3–5].

In this report we describe the reaction of  $\text{Mo}(\text{CO})_6$  with a diene homologue, tetracyclo[6.3.0.0.<sup>4,11</sup>0.<sup>5,9</sup>]undeca-2,6-diene (homohypostrophene, HHS) [6]. Homohypostrophene possesses a pair of double bonds similar to those of NBD. Dimerization of HHS in an *endo-cis-endo* fashion, if successful, should have produced a very unusual cage molecule (IV). Two metal carbonyl complexes,  $(\text{HHS})\text{Mo}(\text{CO})_4$  (V) and  $(\text{HHS})_2\text{Mo}(\text{CO})_2$  (VI) were successfully isolated. Subsequent thermolysis of VI at elevated temperature resulted in its transformation to a novel product, dicarbonylmono(dicyclopentadienylmethane)molybdenum (VII). The target compound IV was not observed.

### Results and discussion

The geometry of diene HHS shares many features with that of NBD. In both structures the double bonds are in parallel and can act as a bidentate ligand toward



metals. The major ring portion of HHS may be viewed as a bent cycloocta-1,5-diene (COD), and COD itself has long been recognized as a chelate which is as effective as NBD [7,8]. The distance across the double bonds in HHS (carbon to carbon) is 2.8 Å [9], slightly longer than that in NBD 2.4 Å. Despite all the similarities, a major difference does exist between these two dienes; the 'bite angle' formed by the  $\pi$  orbitals in HHS is 130° [10], while it is only 73° in NBD [3] (Fig. 1). In a standard octahedral complex, a bite angle of 90° is optimal for a bidentate ligand. This difference seems to have rendered HHS inferior to NBD as a metal ligand.

A mixture of HHS and  $\text{Mo(CO)}_6$  in petroleum ether (110–140°C) solution, heated under reflux for several days, yielded complexes V and VI in sequence. Light-yellow products crystallized pure after isolation by silica gel chromatography. The  $^1\text{H}$  NMR of V shows a triplet at  $\delta$  5.1 ppm for the vinyl protons, which is shifted 0.8 ppm upfield from the parent HHS signal ( $\delta$  5.9 ppm). This shift is smaller than the 2.0 ppm shift upfield of the  $(\text{NBD})\text{Mo(CO)}_4$  signal (4.7 ppm) from

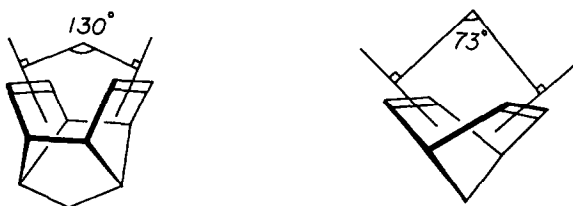


Fig. 1. The 'bite angles' of HHS and NBD when they act as bidentates.

the NBD signal (6.7 ppm), but is comparable to the 0.9 ppm shift upfield of  $(\text{COD})\text{Mo}(\text{CO})_4$  signal (4.7 ppm) from COD (5.6). Signals of the vinyl protons of VI are scattered over a wide range:  $\delta$  2.4, 3.6, 5.4 and 6.3 ppm. This is similar to the spectrum of  $(\text{NBD})_2\text{Mo}(\text{CO})_2$  which shows four widely-spaced signals at  $\delta$  2.2, 3.4, 5.1, and 5.6 ppm [3]. The signal at  $\delta$  6.3 ppm is interesting since it is rather unusual to observe a downfield shift for a vinyl proton when it is bonded to molybdenum. Some properties of the  $\pi$  coordination of  $-\text{CH}=\text{CH}-$  to Mo can be understood by examining their  $^{13}\text{C}$  NMR spectra (Table 1). The  $^{13}\text{C}-^1\text{H}$  coupling constants of the vinyl carbons are within the range 166–174 Hz, which indicates the persistence of  $sp^2$  hybridizations.

Prolonged heating of VI in petroleum ether did not yield the anticipated cage molecule IV. The reason may be partly attributed to the high geometrical strain that must be overcome to form a cage [11]. In the hope that the reaction might proceed at a higher temperature, n-nonane (b.p.  $151^\circ\text{C}$ ) was chosen as an alternative solvent. In n-nonane, the rates of  $\text{HHS} \rightarrow (\text{HHS})\text{Mo}(\text{CO})_4 \rightarrow (\text{HHS})_2\text{Mo}(\text{CO})_2$  were accelerated significantly. After 72 h the concentrations of both V and VI diminished to zero, and a new product was detected. The product which was isolated gave a very interesting  $^1\text{H}$  NMR spectrum with twelve well-separated peaks (Fig. 2). The two strong IR absorptions at 1885 and  $1940\text{ cm}^{-1}$  indicate the presence of coordinated carbonyls, and the fragmentations on mass spectrum indicate its formula as  $(\text{C}_{11}\text{H}_{12})\text{Mo}(\text{CO})_2$ .

To fulfill the 18-electron rule around Mo, 8  $\pi$ -electrons are required on the  $\text{C}_{11}\text{H}_{12}$  ligand and would count as 4 double bonds. A retro-cyclization of HHS to dicyclopentadienylmethane produces the "logical" structure, VIII. This symmetry-disfavored process may have been catalyzed by the metal. However, after careful

Table 1

$^{13}\text{C}$  NMR chemical shifts and  $^{13}\text{C}-^1\text{H}$  coupling constants for V and VI <sup>a</sup>

	Vinyls	Bridgeheads	Methylene bridge	Metal-CO
V	96.62(d, $J$ 170 Hz, 4C)	53.71(d, $J$ 132 Hz, 4C) 68.25(d, $J$ 147 Hz, 2C)	39.16(t, $J$ 131 Hz, 1C)	217.1(s, 1C) 219.1(s, 1C)
VI	71.75(d, $J$ 166 Hz, 2C) 80.16(d, $J$ 166 Hz, 2C) 105.14(d, $J$ 174 Hz, 2C) 106.93(d, $J$ 172 Hz, 2C)	51.40(d, $J$ 139 Hz, 2C) 52.97(d, $J$ 144 Hz, 2C) 57.35(d, $J$ 135 Hz, 4C) 66.36(d, $J$ 136 Hz, 2C) 67.71(d, $J$ 139 Hz, 2C)	39.23(t, $J$ 130 Hz, 2C)	231.1(s, 2C)

<sup>a</sup> Spectra were taken in  $\text{CDCl}_3$  and the center peak at  $\delta$  76.90 of solvent's triplet used as internal standard.

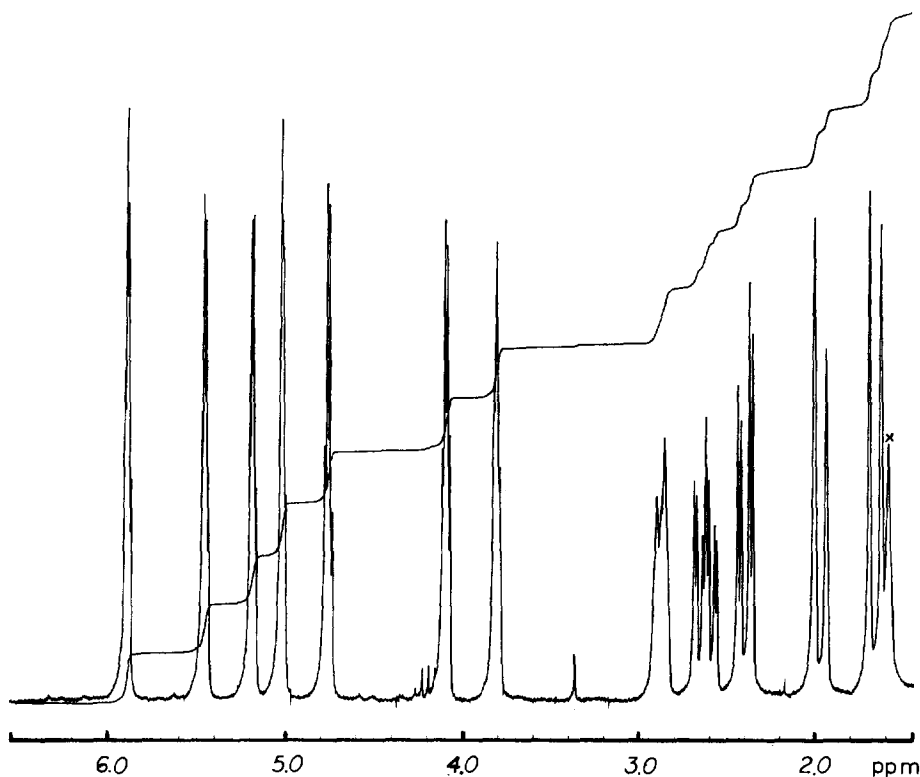


Fig. 2.  $^1\text{H}$  NMR spectrum of VII taken in  $\text{CDCl}_3$  using tetramethylsilane as an internal standard. The mark x in the spectrum indicates an impurity in the solvent.

examination of the molecular model, the stability of VIII became questionable. The four double bonds, if located at the 2(2') and 4(4') positions of cyclopentadienes as the drawing shows, cannot form a stable octahedral around the metal with two carbonyl groups. Hydrogen migration must have occurred immediately after ring opening to give VII. The coordination in VII gives a better regular-octahedral fit. The hydrogen shift on the cyclopentadienyl moiety from VIII to VII should happen with ease. The driving force of the conversion  $\text{VI} \rightarrow \text{VIII} \rightarrow \text{VII}$  seems to come from enhancement of the  $d-p$  orbital overlap. Complex VII can be readily distinguished from VIII by examining its  $^{13}\text{C}$  off-resonance spectrum.

The off-resonance  $^{13}\text{C}$  NMR spectrum of VII shows eleven groups of peaks corresponding to the  $\text{C}_{11}\text{H}_{12}$  moiety. There are two triplets, eight doublets and one singlet indicating the presence of two secondary, eight tertiary and one quaternary carbon atoms. For structure VIII, the spectrum would have consisted of only one triplet in addition to ten doublets.

Heterolytic coupling between HHS and NBD has also been considered. The reaction was tested without success. In another experiment COD was used instead of HHS under the same reaction conditions; only the monochelated complex  $(\text{COD})\text{Mo}(\text{CO})_4$  was observed. The absence of the bischelated analogue  $(\text{COD})_2\text{Mo}(\text{CO})_2$  was probably due to the large ring size of COD which caused too much steric hindrance for two rings to attach to one metal atom.

## Experimental

Melting points were determined on a Yamato model MP-21 melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Proton and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 200 MHz MSL-200 FT spectrometer. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane standard in  $\delta$  units and coupling constants are in hertz (Hz). Elemental analyses were obtained on a Perkin-Elmer 240 EA instrument. Mass spectra were carried out on a JEOL JMS-D300 mass spectrometer.

Homohypostrophene was synthesized as reported in the literature [6]. Hexacarbonylmolybdenum, petroleum ether (100–140 °C) and n-nonane were purchased from Merck and used as received. All procedures where heating was necessary were conducted under nitrogen.

### *Mono(homohypostrophene)tetracarbonylmolybdenum (V) and bis(homohypostrophene)dicarbonylmolybdenum (VI)*

Petroleum ether (25 ml) was degassed in a round-bottom flask by bubbling dry nitrogen gas through the liquid while it was irradiated with ultrasound. Homohypostrophene (570 mg, 4.0 mmol) and hexacarbonylmolybdenum (530 mg, 2.0 mmol) were then dissolved in the liquid. A refluxing condenser was fitted to the top of the flask and the solution was heated in an oil bath under reflux. After 10 h the presence of complex V was clearly shown by TLC, and after 16 h the spot corresponding to VI also started to appear. Heating was terminated after 120 h. The solution was cooled and filtered. The precipitates were extracted three times with n-hexane. All the liquid portions were combined and solvent was evaporated on a rotary evaporator. Complexes V (60 mg, 0.17 mmol, 8.6%) and VI (34 mg, 0.078 mmol, 3.9%) were isolated from the residue by chromatography on silica gel with n-hexane as eluent, and were recrystallized from n-hexane. The yields were rather low, partially due to continuous decomposition of the complexes during purification processes. No evidence for the formation of IV was detected.

Complex V: yellow solid decomposes at 125 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.45 (d,  $J$  1.5 Hz, 2H), 2.87 (m, 4H), 3.12 (m, 2H), 5.05 (t, 4H,  $J$  1.3 Hz); IR (KBr): (CO) 1880(s) and 1950(s)  $\text{cm}^{-1}$ ; MS:  $m/z$  354 ( $M^+$  for Mo = 98), 326 ( $M^+ - \text{CO}$ ), 298 ( $M^+ - 2\text{CO}$ ), 270 ( $M^+ - 3\text{CO}$ ), 242 ( $M^+ - 4\text{CO}$ ); Anal. Found: C 51.33; H 3.64.  $\text{C}_{15}\text{H}_{12}\text{O}_4\text{Mo}$  calc: C 51.16; H 3.43%. Complex VI: pale-yellow crystals which decompose at 143 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.40 (s, 4H), 2.40 (dd, 2H,  $J$  5.3 and 7.8 Hz), 2.68 (m, 2H), 2.79 (m, 2H), 2.90 (m, 4H), 3.00 (m, 2H), 3.15 (m, 2H), 3.58 (dd, 2H,  $J$  5.3 and 7.8 Hz), 5.37 (t, 2H,  $J$  5.8 Hz), 6.31 (t, 2H,  $J$  5.8 Hz); IR (KBr):  $\nu(\text{CO})$  1890(s) and 1950(s)  $\text{cm}^{-1}$ ; MS:  $m/z$  442 ( $M^+$  for Mo = 98), 414 ( $M^+ - \text{CO}$ ), 386 ( $M^+ - 2\text{CO}$ ); Anal. Found: C, 65.62; H, 5.56.  $\text{C}_{24}\text{H}_{24}\text{O}_2\text{Mo}$  calc: C, 65.46; H, 5.49%.

### *Dicarbonylmono(dicyclopentadienylmethane)molybdenum (VII)*

A solution of homohypostrophene (720 mg, 5.0 mmol) and  $\text{Mo}(\text{CO})_6$  (660 mg, 2.5 mmol) in 20 ml degassed n-nonane was poured into a round-bottom flask fitted with a condenser and heated under reflux for 72 h, and then cooled. During this complex V appeared after ca 3 h and complex VI appeared after 5 h. Both V and VI

had disappeared after the 72 h and complex VII became the only major product. It was extracted four times with hot n-hexane and purified by passage through a column packed with silica gel followed by recrystallization from n-hexane. It forms light-yellow solid which decomposes at 86 °C (50 mg, 0.17 mmol, 4.0%). The stability of VII is low in solution. An analytically pure sample could not be obtained.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.66 (d,  $J$  13 Hz), 1.97 (d,  $J$  13 Hz), 2.40 (dd,  $J$  13 and 4 Hz), 2.62 (t of m,  $J$  13 Hz), 2.87 (m), 3.80 (m), 4.09 (m), 4.76 (m), 5.02 (m), 5.19 (m), 5.45 (m), 5.89 (m);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  34.00 (t), 38.11 (t), 53.49(d), 56.58(d), 72.23(d), 81.95(d), 83.75(d), 87.75(d), 91.72(d), 100.35(d), 123.65(s), 238.8 (s), 239.12(s); IR (KBr):  $\nu(\text{CO})$  1890(s), 1950(s)  $\text{cm}^{-1}$ ; MS:  $m/z$  298 ( $M^+$ , for  $\text{Mo} = 98$ ), 270 ( $M^+ - \text{CO}$ ), 242 ( $M^+ - 2\text{CO}$ ).

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