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The reaction of 2-trimethylsilylnorbornadiene with hexacarbonylmolybdenum

Tahsin J. Chow *,* and Chien-Chung Cheng

Institute of Chemistry, Academia Sinica, Taipei, Taiwan (Republic of China)

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Abstract

Thermolysis of 2-trimethylsilylnorbornadiene (ID) with hexacarbonylmolybdenum produces two types of stable complexes, viz., $Mo(CO)_4(ID)$ and $Mo(CO)_2(ID)_2$. Their structures have been confirmed by spectroscopic studies. Photolysis of $Mo(CO)_2(ID)_2$ under UV light induces a geometrical isomerization. Diastereotopic selectivity for the formation of these complexes is observed.

Introduction

Thermolysis of norbornadiene (NBD) with hexacarbonylmolybdenum produces the cage molecule heptacyclo[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0.^{5,9}0.^{10,14}]tetradecane (HCTD) [1] in a regiospecific manner [2]. A few 7-substituted NBD derivatives have been shown to have similar reactivities but are obtained in variable yields [3]. For example, the yields of HCTD for 7-t-butoxy-NBD, NBD, and 7-benzyloxy-NBD are found to be 45%, 27%, and $< 5\%$, respectively [4]. When electron-withdrawing groups are substituted at the double bonds, dimerizations fail to occur [5]. It was thought that this change in reactivity could be ascribed to the change in electron density in the double bonds, i.e. electron-withdrawing substituents retard dimerization, and electron-accepting groups would tend to enhance it. To verify this postulation, several 2-substituted NBD derivatives with groups of electron-releasing properties have been synthesized, and their reaction with hexacarbonylmolybdenum are described.

Results and discussion

2-Methyl-NBD (IA) [6], 2-phenyl-NBD (IB) [7], 2-trimethylsilyloxy-NBD (ID) [8], and 2-trimethylsilyl-NBD (ID) [9] were prepared by published procedures.

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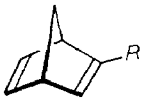
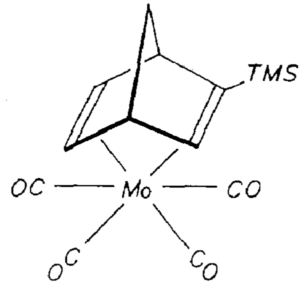
* Currently a visiting Alexander von Humboldt Fellow at the Institut für Organische Chemie und Makromolekulare Chemie der Universität Düsseldorf, West Germany.



(IA: R = CH_3;
IB: R = Ph ;
IC: R = $OSi(CH_3)_3$;
ID: R = $Si(CH_3)_3$)



(II)

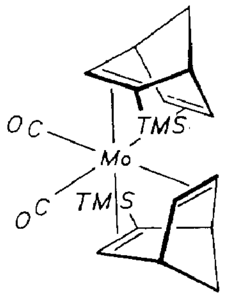
Heating of either IA, IB, or IC with an equal molar amount of hexacarbonylmolybdenum in heptane for several hours resulted only in the decomposition of the starting materials. For the reaction of IA, a double bond migration from the endocyclic C2=C3 to the exocyclic C2=C8 bond proceeds in 56% yield during 56 hours [10]. For IB, polymerization is exclusive without the formation of any identifiable products. For IC, desilylation takes place during 48 hours to give 2,5-norbornenone in 60% yield. In all these reactions, no stable diene-metal complexes were detected.

After each of these reactions, the nonpolar products were examined by use of a GC-MS spectrometer in order to identify any possible cage dimer adducts, with negative results.

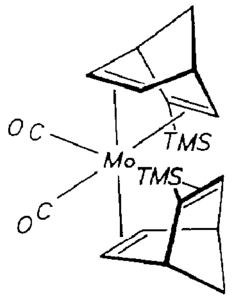
The reaction of ID with hexacarbonylmolybdenum in petroleum ether (b.p. 100–140 °C) under reflux yields two types of molybdenum complex, i.e. $Mo(CO)_4(ID)$ (II) and $Mo(CO)_2(ID)_2$ (III). The structure of II is readily determined from its spectroscopic data. The olefinic protons in the ^1H NMR spectrum show upfield shifts (2H at δ 4.84 and 1H and δ 4.98 ppm) compared with those in the free ligand (2H at 6.64, 1H at 7.00 ppm). In the ^{13}C NMR spectra, the olefinic carbons appear at δ 78.15, 79.72, 85.69, and 86.21 ppm, and the four carbonyl ligands in ^{13}C NMR appear at δ 214.29, 214.69, 217.75, 217.96 ppm. In the IR spectrum the carbonyl groups have strong absorptions at 1885, 1914, and 2037 cm^{-1}. The structure of III is more complicated than that of II since several diastereotopic isomers are possible [5].

One of the two major isomers of III exhibits a very simple pattern in its ^1H NMR spectrum. The olefinic proton signals from NBD appear at δ 3.30, 5.30, and 5.45 ppm, those from the bridgehead at 3.36 and 3.70 ppm, and those from the methylene group at 1.04 and 1.26 ppm. III shows nine distinct absorptions in its ^{13}C NMR spectrum, indicating the existence of a two-fold symmetry in its structure. To comply with the spectroscopic data, isomers IIIA and IIIB are probable. However, it is known that in the ^1H NMR spectra the olefinic protons *transoid* to a C=C ligand appear at a much higher field than those *transoid* to a C=O ligand [4]. The observed olefinic ^1H signal pattern, viz., one at higher field and two at lower field, suggests that IIIA is the prefered structure as opposed to IIIB.

The other isomer of III shows the presence of two kinds of NBD ligands in its configuration, thus IIIC, in which the two NBD ligands are enantiomers is proposed. A two-dimensional ^1H–^1H COSY spectrum confirms such an assignment.



(IIIA)



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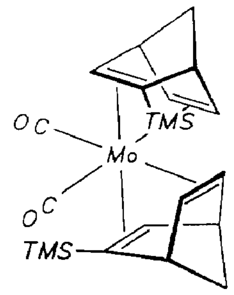

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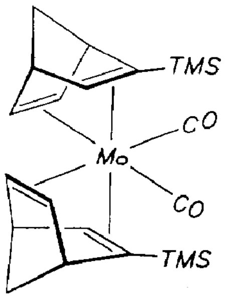
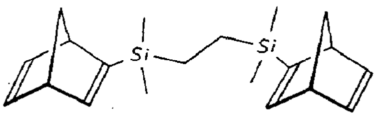


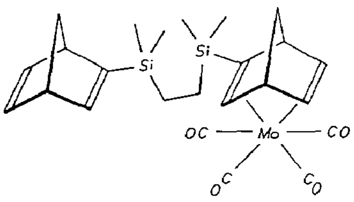
(IIID)

Complexes IIIA and IIIC are stable at ambient temperature and can be recrystallized. Their prolonged heating does not produce the desired cage dimers.

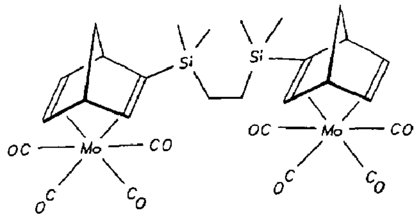
Photolysis of pure IIIA in a quartz vessel under UV light from a medium-pressure Hg lamp induces a rearrangement of IIIA to IIID. The appearance of IIID is evident in both the ^{1}H and ^{13}C NMR spectra. The olefinic protons appear at δ 2.14, 4.83, and 5.52 ppm, a pattern similar to that for IIIA. There are nine signals in the ^{13}C NMR spectrum, suggesting the existance of a two-fold symmetry in the structure. The major difference between IIIA and IIID is in their relative orientation of the NBD ligands with respect to the carbonyls. The high field ^{1}H absorptions at δ 3.30 (IIIA) and 2.14 (IIID), used as the criterion, are compared with the known geometry of $Mo(CO)_2(NBD)_2$ [4], to differentiate their respective configurations. The conversion from IIIA to IIID must involve bond cleavage between Mo and C=C, probably initiated by the absorption of the irradiated light. The structure of IIIA is believed to be in a lower energy state than that of IIID, since the thermodecomposition of IIID proceeds faster than that of IIIA, and IIID is not a product of the thermal reactions. Furthermore, the ratio of IIIA/IIID approaches 1/1 after prolonged UV irradiation. It should be noted that the decomposition of IIIA happens predominantly during the photolysis, and free molecules of ID are also found in the reaction mixture.



(IV)



(V)



(VI)

In the structures of IIIA, IIIC, and IIID, the of the TMS -substituted C=C bonds are always *transoid* to each other. Structures analogous to IIIB, containing TMS-substituted C=C bonds *cisoid* to each other, have never been observed. The ligand orientation in IIIB must be highly disfavored. The geometrical selectivity is further demonstrated by the reaction of IV with $Mo(CO)_6$. The structure of IV contains two units of ID which are linked together by silylmethyl groups. Under suitable conditions, IV can act as a quadridentate ligand. However, because of the inherent geometrical strain of the linkage, the two TMS-substituted C=C bonds are forced into a *cisoid* configuration. The formation of such a complex should provide a direct estimation of the stability of IIIB.

Compound IV is obtained from the reaction of NBD with 1,2-bis(chlorodimethylsilyl)ethane in good yield. Heating equimolar amounts of IV and $Mo(CO)_6$ in petroleum ether at ca. 120 °C for several days yields the unimetallic complex V and the bimetallic complex VI. Both complexes contain $Mo(CO)_4$ units chelated by the NBD moieties. Prolonged heating of the mixture does not give the quadridentate molybdenum complex of IV. This result is consistent with our previous observations that the silyl-substituted NBD ligands have geometrical preference in forming the complexes. Any cage products which might have formed in this reaction were not detected.

Present information indicates that a change in the olefinic substituents in NBD, to either electron-withdrawing or electron-releasing, does not enhance its efficiency in forming the cage dimer. Adding substituents to the double bonds inevitably increases steric hindrance to an *endo–cis–endo* coupling. However, the variation in the yields of C7-substituted NBDs indicates that steric hindrance is not the only factor in operation. In order to achieve optimal coupling efficiency, the structure of the molybdenum complexes should be understood from both electronic and steric view points.

Experimental

Melting points were determined on a Yamato model MP-21 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer

297 infrared spectrophotometer. Proton and carbon-13 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 the tetramethylsilane standard in δ units and coupling constants are in hertz (Hz). Mass spectra were carried out on a JEOL JMS-D300 mass spectrometer.

2-Trimethylsilylnorbornadienetetracarbonylmolybdenum (II) and the isomers of bis(2-trimethylsilylnorbornadiene)dicarbonylmolybdenum (IIIA and IIIC)

Petroleum ether was degassed in a round-bottom flask by bubbling dry nitrogen gas through the liquid during irradiation with ultrasound. 2-Trimethylsilylnorbornadiene (ID) (1.64 g, 10 mmol) and hexacarbonylmolybdenum (2.64 g, 10 mmol) were then dissolved in the petroleum ether. A refluxing condenser was fitted to the top of the flask and the solution was heated in an oil bath under reflux. After several hours, the presence of II could be detected by TLC. The unimetallic complex II was collected in ca. 56% yield after 20 h heating. To collect the bimetallic complexes IIIA and IIIC, the reaction time was extended to ca. 70 h. At the end of the reaction, the solution was cooled and filtered. The filtrate was concentrated in vacuo, and the resulting mixture was chromatographed on a silica gel column eluting with hexane/ethyl acetate. Complexes IIIA and IIIC were eluted first, followed by the complex II. Complex II (yield 10%) was recrystallized from hexane, m.p. 58–59 °C; IR (KBr): ν(CO) 1885, 1914, 2037 cm^{-1}; ^{1}H NMR: ($CDCl_3$) 0.11 (9H, s), 1.15 (1H, dt, *J* 1.5, 8.2 Hz), 1.32 (1H, dt, *J* 1.5, 8.2 Hz), 3.68 (1H, m), 3.77 (1H, m), 4.84 (2H, m), 4.98 (1H, d, *J* 3.5 Hz); ^{13}C NMR: ($CDCl_3$) −0.62, 49.05, 51.78, 65.20, 78.15, 79.72, 85.69, 86.21, 214.29, 214.69, 217.75, 217.96; MS (70 eV) *m/e* (relative intensity) 374 (M^+ for Mo = 98, 8.5%), 318 ($M^+ - 2CO$, 11), 290 ($M^+ - 3CO$, 8.5), 258 (44), 244 (47), 73 (TMS, 100). The combined yield of IIIA and IIIC was 25% in a roughly equimolar ratio. Complex IIIA was recrystallized from hexane, m.p. 129–130 °C; IR (KBr): ν(CO) 1884, 1941 cm^{-1}; ^{1}H NMR: ($CDCl_3$) −0.13 (9H, s), 1.04 (1H, dm, *J* 8.2 Hz), 1.26 (1H, dm, *J* 8.2 Hz), 3.30 (1H, d, *J* 4.0 Hz), 3.36 (1H, m), 3.70 (1H, m), 5.30 (1H, tm, *J* 3.6 Hz), 5.45 (1H, tm, *J* 3.6 Hz); ^{13}C NMR: ($CDCl_3$) −0.43, 45.14, 48.79, 51.50, 59.28, 60.73, 79.76, 87.20, 227.27; MS (70 eV): *m/e* (relative intensity) 482 (M^+ for Mo = 98, 10%), 454 ($M^+ - CO$, 8.3), 426 ($M^+ - 2CO$, 6.4), 228 (Cp_2Mo, 37), 73 (TMS, 100); Anal. Found: C, 55.10; H, 6.63. $C_{22}H_{32}O_2Si_2Mo$ calc: C, 54.98; H. 6.71%. Complex IIIC: IR (KBr): ν(CO) 1884, 1941 cm^{-1}; ^{1}H NMR: ($CDCl_3$) −0.16 (9H, s), 0.07 (9H, s), 0.98 (1H, dm, *J* 8.0 Hz), 1.06 (1H, dm, *J* 8.0 Hz), 1.24 (1H, dm, *J* 8.0 Hz), 1.29 (1H, dm, *J* 8.0 Hz), 2.14 (1H, d, *J* 3.5 Hz), 3.18 (1H, d, *J* 3.5 Hz), 3.43 (1H, m), 3.46 (1H, m), 3.51 (1H, m), 3.72 (1H, m), 4.96 (1H, m), 5.19 (1H, m), 5.50 (2H, m); ^{13}C NMR: ($CDCl_3$) −0.89, −0.59, 42.25, 48.73, 49.03, 51.02, 51.92, 55.75, 57.73, 58.93, 60.70, 61.05, 78.84, 81.72, 85.20, 86.12, 228.52, 229.66.

Photolysis of IIIA

A small amount of pure IIIA was dissolved in hexane in a quartz vessel, and the solution was irradiated with a medium-pressure mercury lamp under nitrogen. The reaction was monitored by TLC until the production of IIID was maximal. The resulting mixture was purified by column chromatography, and IIID (ca. 12% yield) was collected as a 1/2 mixture with IIIA. Physical data of IIID: IR (KBr): ν(CO) 1884, 1941 cm^{-1}; ^{1}H NMR: ($CDCl_3$) 0.05 (9H, s), 0.98 (1H, dm, *J* 8.0 Hz), 1.22

(1H, dm, *J* 8.0 Hz), 2.14 (1H, m), 3.54 (2H, m), 4.83 (1H, m), 5.52 (1H, m); ^{13}C NMR: ($CDCl_3$) −0.75, 49.35, 51.34, 54.06, 60.80, 79.75, 83.26, 230.62. It was also observed that the thermodecomposition of IIID in $CHCl_3$ was more rapid than that of IIIA.

Preparation of IV and its reaction with $Mo(CO)_6$

To a flask containing hexane (3 ml) at −78° C was added potassium t-butoxide (0.38 g, 3.4 mmol) and n-butyllithium (2.3 ml of 1.5 *M* in hexane, 3.5 mmol) under a nitrogen atmosphere. The resulting mixture was warmed up gradually to −40° C, and to it was added dropwise tetramethylethylenediamine (0.39 g, 3.4 mmol), followed by norbornadiene (0.31 g, 3.4 mmol). The pale yellow suspension was stirred at −40° C for 1 h, and to it was added 1,2-bis(chlorodimethylsilyl)ethane (0.36 g, 1.7 mmol); white precipitates formed immediately. The mixture was stirred for 30 min, then was quenched with ice water, and neutralized with 5% HCl solution. The organic products were extracted with ether. The combined ether solution was washed with saturated $NaHCO_3$ and NaCl solutions, dried over anhydrous $MgSO_4$, and concentrated in vacuo. Pure IV was obtained by column chromatography on silica gel as a mixture of diastereomers (0.40 g, 1.2 mmol, 73%). ^{1}H NMR: ($CDCl_3$) −0.013 & 0.003 (12H, 2s), 0.397 & 0.383 (4H, 2s), 1.80–1.88 (4H, dm, *J* 6 Hz), 3.61 (2H, m), 3.66 (2H, m), 6.64 (4H, m), 7.00 (2H, m); ^{13}C NMR: ($CDCl_3$) −4.47, −4.35, 7.10, 51.88, 53.41, 74.04, 142.2, 143.1, 153.9, 154.7. Thermolysis of IV with $Mo(CO)_6$ was performed as described for ID. The reaction was stopped after 4 days, and the metallic products were isolated by column chromatography using hexane as an eluent. Yield of the unimetallic compound V was ca. 10%. IR ($CDCl_3$): ν(CO) 1893, 1954, 2045 cm^{-1}; ^{1}H NMR: ($CDCl_3$) 0.0 12H, 2s), 0.35–0.40 (4H, m), 1.15–1.33 (2H, m), 1.84 (2H, dm, *J* 6 Hz), 3.61 (1H, m), 3.67 (2H, m), 3.77 (1H, m), 4.85 (2H, m), 5.01 (1H, d, *J* 3 Hz), 6.65 (2H, m), 7.24 (1H, d *J* 3 Hz); ^{13}C NMR: ($CDCl_3$) −5.00, −4.35, −3.94, −2.71, 7.88, 9.61, 49.13, 51.94, 53.39, 65.14, 74.03, 77.86, 79.45, 85.40, 86.65, 142.26, 143.08, 153.92, 154.72, 214.30, 214.71, 217.83. Yield of the bimetallic compound VI was < 3%. ^{1}H NMR: ($CDCl_3$) 0.0 (12H, s), 0.35 (4H, s), 1.15–1.33 (4H, m), 3.67 (2H, m), 3.78 (2H, m), 4.85 (4H, m), 5.01 (2H, m). However, the NMR signals corresponding to the silylmethyl groups of V and VI have been tentatively assigned owing to the interference from some silicon-containing impurities.

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