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Molybdenum-Mediated Dimerization of Norbornadiene and Derivatives

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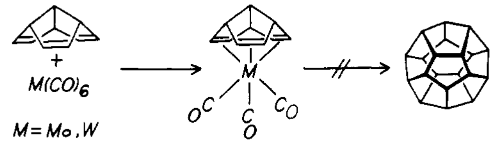
Abstract: Dimerizations of norbornadiene (NBD), 7-(benzoyloxy)norbornadiene (BzNBD), and 7-*tert*-butoxynorbornadiene (BuNBD) for the formation of heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (HCTD) are achieved regiospecifically by the mediation of hexacarbonylmolybdenum. Two major types of intermediates for these reactions, $LMo(CO)_4$ and isomers of $L_2Mo(CO)_2$, are identified, and for the latter there exist one, three, and five diastereomers for L = NBD, BzNBD, and BuNBD, respectively. X-ray crystallographic analysis for one of the five $(BuNBD)_2Mo(CO)_2$ isomers is completed, and the two BuNBD ligands on that structure are shown to chelate the metal in an endo and exo orientation. Bond strengths of C=C's to metal are discussed on the basis of their relative bond lengths, and trans effects are shown to be evident. The absolute geometry of other isomers is resolved either by ^1H NMR decoupling experiments or by 2D NOESY techniques. Heterolytic coupling between NBD and BuNBD for the production of monosubstituted HCTD is also reported.

Birdcage-like hydrocarbons are a special group of compounds. The chemistry of polyhedranes, prismanes, polyquinanes, adamantane and their derivatives has attracted wide interest among theoretical and synthetic chemists. However, the syntheses of these cage compounds are sometimes tedious since assembling a highly compact structure is an entropy-disfavored process. Organometallics have been suggested to facilitate the combination of two units of triquinacene to give dodecahedrane. A half-sandwich compound **1** was synthesized by Oudeman et al., but the subsequent triquinacene dimerization could not be achieved.[1] The structure of dodecahedrane represents a twelve-membered cyclic polyhedrane of the highest symmetry. Closely related to the formation of dodecahedrane from triquinancene is the formation of an eight-membered cyclic polyquinane **2a** (heptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane, HCTD) of D_{2d} symmetry by coupling two units of norbornadiene (NBD) through the catalysis of a metal nucleus.[2] This type of reaction has been known for more than 20 years.[3] Dimerizations of NBD in general have been shown to be catalyzed effectively by a variety of metal complexes such as $Fe(CO)_5$,[4] $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$,[5] $RhCl(PPh_3)_3$,[6] Ni,[7] $Ni(CO)_4$,[8] $Zn[Co(CO)_4]_2$,[9] etc.[10] In most cases more than five isomeric dimers and/or dimer ketones are produced simultaneously in addition to high molecular weight polymers.[8,11] This sets a major limitation on the production of HCTD. Only in the special case where both of the exo sides of NBD are blocked as shown on **2d**[12] can the yield be enhanced. This paper reports the details of a new catalytic system derived from $Mo(CO)_6$ which enables the production of HCTD and derivatives in high regiospecificity.[13-15] Thus compounds **2a-c** are synthesized from the corresponding norbornadienes without the formation of other dimeric products. The mechanism for the dimerization of NBD has been described involving intermediates with a metal nucleus holding two NBD ligands in geometries like **3-5**. Complexes of dimeric NBD coordinated to iridium **6**[16] in an exo-trans-exo geometry and to nickel **7**[17] in an exo-trans-endo geometry have previously been isolated. These complexes may be called later-stage intermediates since carbon-carbon σ linkages have already formed. Early-stage intermediates of the types **3-5** have seldom been identified. In the case of our molybdenum-



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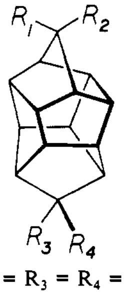

2a: $R_1 = R_2 = R_3 = R_4 = H$
b: $R_1 = R_3 = OCOPh$; $R_2 = R_4 = H$
c: $R_1 = R_3 = O\text{-}t\text{-}Bu$; $R_2 = R_4 = H$
d: $R_1, R_2 = R_3, R_4 = -(CH_2)_4-$
e: $R_1 = O\text{-}t\text{-}Bu$; $R_2 = R_3 = R_4 = H$

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(1) Codding, P. W.; Kerr, K. A.; Oudeman, A.; Sorensen, T. S. *J. Organomet. Chem.* **1982**, *232*, 193.
(2) (a) Lemal, D. M.; Shim, K. S. *Tetrahedron Lett.* **1961**, 368. (b) Bird, C. W.; Colinese, D. L.; Cookson, R. C.; Hudec, J.; Williams, R. O. *Tetrahedron Lett.* **1961**, 373.
(3) Schrauzer, G. N. *Adv. Catal.* **1968**, *18*, 373.
(4) (a) Marchand, A. P.; Earlywine, A. D. *J. Org. Chem.* **1984**, *49*, 1660. (b) Marchand, A. P.; Hayes, B. R. *Tetrahedron Lett.* **1977**, 1027. (c) Marchand, A. P.; Goodin, D. B.; Hossain, M. B.; van der Helm, D. *J. Org. Chem.* **1984**, *49*, 2897.
(5) (a) Ennis, M.; Manning, A. R. *J. Organomet. Chem.* **1976**, *116*, C31. (b) Ennis, M.; Foley, R. M.; Manning, A. R. *J. Organomet. Chem.* **1979**, *166*, C18.
(6) Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446.
(7) (a) Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376. (b) Yoshikawa, S.; Kiji, J.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1093.
(8) Arnold, D. R.; Treckor, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596.
(9) Schrauzer, G. N.; Bastian, B. N.; Fosselius, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 4890. (b) Schrauzer, G. N.; Ho, R. K. Y.; Schlesinger, G. *Tetrahedron Lett.* **1970**, 543.
(10) (a) Jolly, P. W.; Stone, F. G. A.; Mackenzie, K. *J. Chem. Soc.* **1965**, 6416. (b) Langenback, H. J.; Keller, E.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 188.
(11) (a) Elder, P. A.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1771. (b) Ealick, S. C.; van der Helm, D.; Hayes, B. R.; Marchand, A. P. *Acta Crystallogr.* **1978**, *B34*, 3219. (c) Leto, J. R.; Olsen, L. M. *Chem. Abstr.* **1965**, *63*, 11728c; U.S. Patent 3,192,191.
(12) Marchand, A. P.; Wu, A.-h. *J. Org. Chem.* **1985**, *50*, 396.
(13) Chow, T. J.; Wu, M.-Y.; Liu, L.-K. *J. Organomet. Chem.* **1985**, *281*, C33.
(14) Chow, T. J.; Liu, L.-K.; Chao, Y.-S. *J. Chem. Soc., Chem. Commun.* **1985**, 700.
(15) Chow, T. J.; Chao, Y.-S. *J. Organomet. Chem.* **1985**, *296*, C23.

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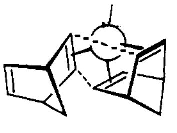
mediated dimerization, several key intermediates of type **3** and **5** have been isolated and characterized by spectroscopic methods. The reaction sequences are analyzed by monitoring the concentration of each intermediate throughout the course of the reaction. Several key structures were further confirmed by X-ray crystallographic analysis.



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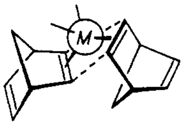

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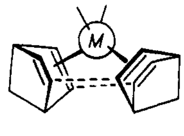

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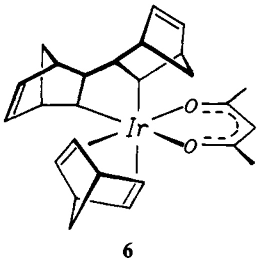

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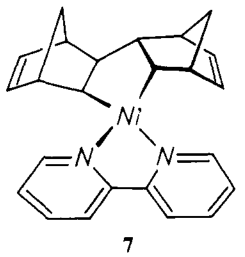

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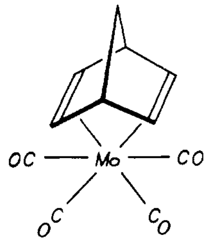
Results

Reaction Profile. The syntheses of **2** were accomplished by boiling a solution of hexacarbonylmolybdenum (1 equiv) and norbornadiene (3 equiv) in petroleum ether (100–140 °C) under reflux for a few days. The formation of mono(norbornadiene)tetracarbonylmolybdenum (**8**) was noticed first after a few hours, followed by the appearance of bis(norbornadiene)dicarbonylmolybdenum (**9a**). The concentration of **9a** increased at the expense of **8** until it reached an optimum quantity at ca 20 h. Both **8** and **9a** may be collected in good yields (60% for **8** and 45% for **9a**) at appropriate stages by fractional crystallizations. The X-ray single-crystal structures of **9a**[13] and **2a**[14] have already been reported by us. HCTD (**2a**) was isolated after 100 h in 26% yield, and the yield was expected to increase slightly if the heating was prolonged. The reaction profile is shown in Figure 1.[18] The relative concentrations of NBD, **8**, and **9a** were determined by both ^{1}H NMR spectra and TLC–FID chromatographs. The yields of **2a** were measured by periodic isolation of the pure product. Therefore the following reaction sequence is unambiguously illustrated.

$$\text{NBD} + \text{Mo(CO)}_6 \rightarrow \mathbf{8} \rightarrow \mathbf{9a} \rightarrow \mathbf{2a}$$



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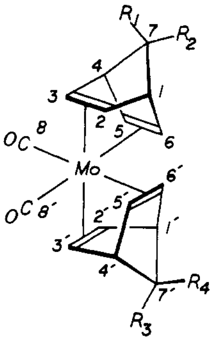

9a: $R_1 = R_2 = R_3 = R_4 = H$
b: $R_1 = R_3 = \text{OCOPh}$; $R_2 = R_4 = H$
c: $R_1 = R_4 = \text{OCOPh}$; $R_2 = R_3 = H$
d: $R_1 = R_3 = H$; $R_2 = R_4 = \text{OCOPh}$
e: $R_1 = R_3 = \text{O-}t\text{-Bu}$; $R_2 = R_4 = H$
f: $R_1 = R_4 = \text{O-}t\text{-Bu}$; $R_2 = R_3 = H$
g: $R_1 = R_3 = H$; $R_2 = R_4 = \text{O-}t\text{-Bu}$
h: $R_1 = \text{O-}t\text{-Bu}$; $R_2 = R_3 = R_4 = H$
i: $R_2 = \text{O-}t\text{-Bu}$; $R_1 = R_3 = R_4 = H$

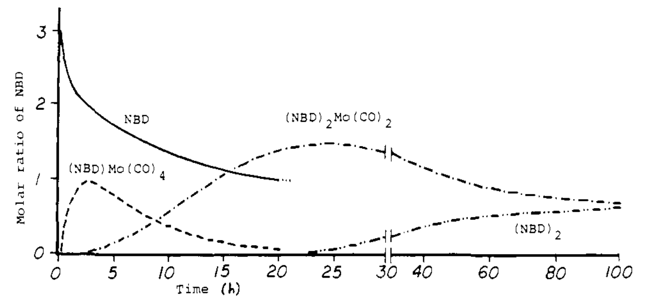

Figure 1. The reaction profile for the thermolysis of NBD with Mo(CO)$_6$.

Reactions for 7-Substituted Norbornadienes. Similar reactions were also observed between Mo(CO)$_6$ and two other 7-substituted NBDs, i.e., the 7-(benzoyloxy)norbornadiene (BzNBD) and the 7-*tert*-butoxynorbornadiene (BuNBD). In the reaction of BzNBD, three stable intermediates were isolated and found to have the same molecular formula of (BzNBD)$_2$Mo(CO)$_2$ (combined yield of 42% after 48 h of heating), and in the reaction of BuNBD, five isomeric Mo complexes were found and identified as (BuNBD)$_2$Mo(CO)$_2$ (combined yield of 60% after 24 h of heating). The isomers for BzNBD were the diastereomers **9b**, **9c**, and **9d**, depending on the orientations of the benzoyloxy group. It had been shown by us that the NBD ligands coordinate to the molybdenum nucleus in a tilted fashion (Figure 2). The double bond trans to a carbonyl is in a different chemical environment from the one cis to a carbonyl. The distinctive polarities of **9b–d** make them easily separable on a silica gel column chromatograph. All of them crystallize to form light yellow needles and are quite stable in air. The ^{1}H NMR signals of the four vinylic protons spread over a very wide range at ca. δ 2.1, 3.3, 4.9, and 5.5 with small variations between **9b** and **9d** (Table I). For **9c** there should exist a *d,l*-pair, and likewise for the dimeric adduct 7,12-dibenzoyloxy-HCTD (**2b**). The presence of a benzoyloxy group on the exo side of NBD does not seem to influence the regioselectivity of the coupling reaction to any significant degree. The adduct **2b** was found to be the only dimeric product in this reaction.

The reaction became somewhat more complicated for BuNBD since an oxygen moiety with lone pairs can act as an effective ligand, therefore a BuNBD molecule may chelate the metal through either its endo or exo face. Both types of complexes of chromium have been identified previously.[19] A careful analysis of the products indicated the existence of another two complexes **10a** and **10b** in addition to the three isomers **9e–g**.[15] Both of them were purified to form light-yellow crystals, and one of their BuNBD ligands was shown to chelate the metal through the exo side. The structure of **10b** was confirmed by X-ray crystallography, and its ORTEP drawing is shown in Figure 3. This analysis resolved the question of assigning the absolute geometries of **10a** and **10b**. Similar assignments for the stereoorientations of complexes **9b–d** and **9e–g** were determined by ^{1}H NMR two-dimensional NOESY techniques which will be discussed later in this

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(16) Fraser, A. R.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597.

(17) Blackborow, J. R.; Feldhoff, U.; Grevels, F.-W.; Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1979**, *173*, 253.

(18) This Figure was used as part of a presentation at the Third IUPAC Symposium on Organometallic Chemistry Directed Toward Organic Synthesis, 1985, Kyoto, Japan.

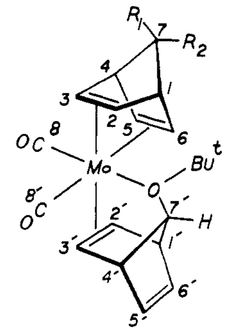
(19) Wege, D.; Wilkinson, S. P. *J. Chem. Soc., Chem. Commun.* **1972**, 1335.

Table I. ^{1}H NMR Signals of the Metal–NBD Complexes[a]

	vinyls	other signals
8	5.0 (t, J = 2 Hz, 4 H)	3.8 (m, 2 H), 1.3 (t, J = 2 Hz, 2 H)
9a	2.2, 3.4, 5.1, 5.6 (4 t, J = 4 Hz)	3.5, 3.7 (2 m, 2 H), 1.2 (AB pattern, J = 8 Hz, 2 H)
9b	2.15, 3.4, 4.9, 5.45 (4 t, J = 4 Hz)	3.7–4.0 (m, 2 H), 4.55 (m, 1 H), 7.5, 8.0 (2 m, 5 H, phenyl)
9c	2.0, 2.15, 3.2, 3.4 (4 t, J = 4 Hz) 4.8–5.0, 5.3–5.5 (2 m, 2 H each)	3.7, 3.9 (2 m, 2 H each), 4.5 (2 t overlap, J = 2 Hz, 2 H) 7.3–7.6, 7.8–8.1 (2 m, 10 H, phenyl)
9d	2.0, 3.2, 4.95, 5.5 (4 t, J = 4 Hz)	3.7, 3.9 (2 m, 2 H), 4.5 (t, J = 2 Hz, 1 H) 7.5, 8.0 (2 m, 5 H, phenyl)
9e	2.1, 3.2, 4.8, 5.3 (4 t, J = 4 Hz)	3.2–3.55 (m, 3 H), 1.10 (s, 9 H)
9e[b]	2.15, 3.05, 4.5, 4.85 (4 m)	3.2–3.5 (m, 3 H), 1.1 (s, 9 H)
9g	2.0, 3.15, 4.9, 5.45 (4 t, J = 4 Hz)	3.35, 3.42, 3.55 (3 m), 1.10 (s, 9 H)
9g[b]	1.9, 3.1, 4.8, 5.2 (4 m, 4 H)	3.3–3.5 (2 m, 3 H), 1.05 (s, 9 H)
9h,i[c]	1.9, 3.0, 4.8, 4.9, 5.25, 5.45 (6 t, J = 4 Hz) 2.2 (m, 3 H), 5.0, 5.55 (2 m, 2 H each)	1.11, 1.12 (2 s, 9 H each), 1.2–1.3 (m, 4 H) 3.35–3.5 (m, 11 H), 3.7 (m, 2 H)
10a	2.4, 3.2 (2 m), 4.2, 5.1 (2 t, J = 4 Hz) 2.9 (m, 2 H), 6.2 (t, J = 2 Hz, 2 H)	1.08, 1.10 (2 s, 9 H each) 3.45 (s, 2 H), 3.6–3.75 (m and s, 4 H)
10b	2.5, 3.2 (2 m), 4.4, 5.3 (2 t, J = 4 Hz) 2.9 (m, 2 H), 6.2 (t, J = 2 Hz, 2 H)	1.06, 1.18 (2 s, 9 H each) 3.4 (m, 2 H), 3.5 (m, 1 H), 3.7 (m, 3 H)
11	1.6, 3.1 (2 t, J = 6 Hz), 4.9, 5.5 (2 t, J = 4 Hz)	0.90 (m, 2 H), 3.65, 4.0 (2 m)

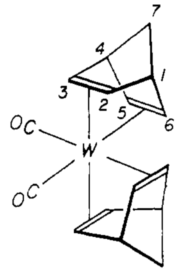
[a] Spectra were taken in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in δ units downfield from tetramethylsilane. [b] Spectrum taken in deuterated benzene. [c] Complexes isolated as a 1/1 mixture of diastereomers. Some of their vinyl signals are overlapped with the signals of bridgeheads.

report. The ^{1}H NMR signals of **9e,g** and **10a,b** are also listed in Table I.



10a: R_1 = O-*t*-Bu; R_2 = H
b: R_1 = H; R_2 = O-*t*-Bu

Tungsten and Chromium Analogues. The tungsten analogue $(NBD)_2W(CO)_2$ (**11**) was also synthesized by heating $(CH_3CN)_3W(CO)_3$ with NBD in petroleum ether for 48 h. Complex **11** is stable at ambient temperatures and crystallizes as light orange needles (mp 92–94 °C).



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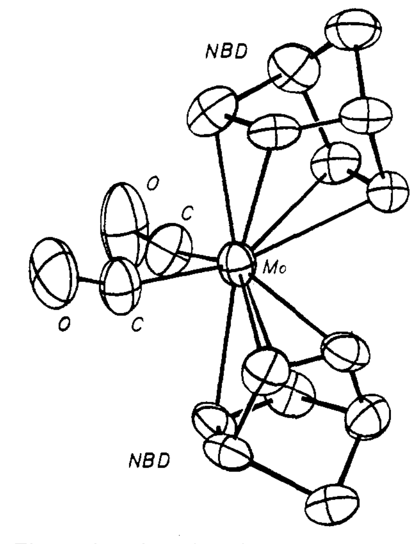


Figure 2. The spatial orientation of **9a**.

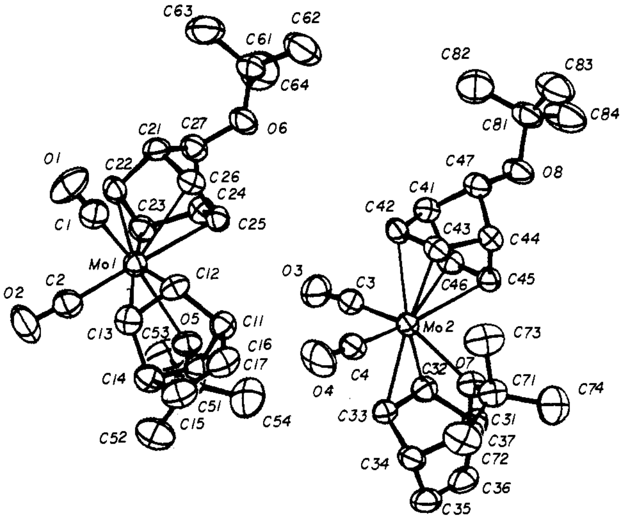


Figure 3. An ORTEP view of **10b** showing the numbering scheme for the X-ray data. This numbering is not used for the discussions in text.

The ^{1}H NMR of **11** shows seven well-separated groups of signals at δ ($CDCl_3$) 5.5 and 4.9 (2 dd, J = 4 and 6 Hz, vinyl), 4.0 and 3.65 (2 m, bridgeheads), 3.1 and 1.6 (2 t, J = 6 Hz, vinyl), and 0.9 (AB pattern, J = 8 Hz, 2 H) (Table I). Homonuclear ^{1}H decoupling experiments showed that the absorptions at δ 5.5 (H6) and 4.9 (H5) are protons attached on the same double bond, while the peaks at δ 3.1 (H3) and 1.6 (H2) are protons attached to the other double bond. Irradiations on the bridgeheads' protons indicated that the peaks at δ 4.9 (H5), 4.0 (H4), and 3.1 (H3) correspond to adjacent protons on one side of the NBD structure, while the peaks at δ 5.5 (H6), 3.65 (H1), and 1.6 (H2) represent those protons on the other side. This seems to be a general phenomenon for complexes of **8**, **9**'s, and **11** in that the vinyl protons appearing both at the highest field (H2) and at the lowest field (H6) are located on the same side of an NBD structure. The diamagnetic environment of each proton is believed to be strongly influenced by the proton's orientation relative to the carbonyl groups so that the protons' chemical shifts are not determined solely by their distances from the metal (i.e., Mo–C2 is the shortest

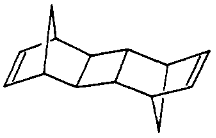
Table II. ^{13}C NMR Signals of the Metal–NBD Complexes[a]

	C2,3 (C2′,3′)	C5,6 (C5′,6′)	C1,4 (C1′,4′)	C7 (C7′)	C7 substituent
8	78.5 (d, J = 179 Hz)		49.0 (d, J = 150 Hz)	64,9 (t, J = 134 Hz)	
9a	44.2, 51.6 (2 d, J = 178 Hz)	79.0, 82.5 (2 d, J = 176 Hz)	48.8, 48.9 (2 d, J = 149 Hz)	60.9 (t, J = 133 Hz)	
9b	40.4, 47.3	74.6, 77.3	51.3, 51.4	92.1	128.2, 129.5, 130.2, 132.9, 166.2
9c	39.2, 40.4, 44.3, 47.3 (4 d, J = 180 Hz)	74.6, 77.3 (2 d, J = 184 Hz)	51.3 (br) (d, J = 150 Hz)	92.1, 92,5 (2 d, J = 165 Hz)	128.2, 129.5, 130.1, 132.9, 166.2
9g	36.4, 42.3 (2 d, J = 168 Hz)	72.1, 74.9 (2 d, J = 172 Hz)	48.7 (d, J = 150 Hz)	90.3 (d, J = 147 Hz)	68.1 (s) 23.6 (q, J = 126 Hz)
11	31.1, 39.5 (2 d, J = 180 Hz)	72.1, 74.9 (2 d, J = 182 Hz)	48.5, 48.8 (2 d, J = 144 Hz)	63.4 (t, J = 132 Hz)	

[a] All spectra were taken in $CDCl_3$ using tetramethylsilane as internal standard.

bond, and Mo–C5 is the longest one instead of Mo–C6).[13] Prolonged heating of **11** unfortunately did not yield the expected HCTD.

Both the thermochemical[19] and the photochemical[20] reactions of NBD with $Cr(CO)_6$ have already been investigated by other workers. Nevertheless they were reexamined by us. The major product of the reaction was dimer **12** formed via coupling through an exo-trans-exo mode, which should be the most favored one from the viewpoint of stereochemistry. The formation of complexes analogous to $(NBD)_2Cr(CO)_2$ could not be detected,



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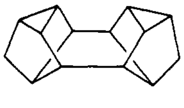
Discussion

MO Correlations. The metal nucleus has two functions in this reaction. First, only by chelating to the metal could the two NBDs be fixed in an endo-cis-endo geometry with respect to each other prior to the coupling;[21] and second, the coupling reaction would not be able to proceed without the mediation of the metal since a concerted dimerization of two NBDs is symmetry-disallowed. A portion of orbital interactions for a concerted dimerization according to a structure of D_{2d} symmetry can be obtained from the supplementary material. When two NBDs approach each other, the energy of π electrons in b2 will be rapidly elevated to a high-energy σ antibonding mode. A metal nucleus with partially filled d-orbitals can help the electrons find a path to cross such an energy obstacle through an electron donating–back donating mechanism.

A stepwise mechanism is rather preferred in the case of molybdenum mediation based on an analysis of the structure of intermediate **9a**. The spatial distance of C6–C6′ is much shorter than that of C3–C3′ (Figure 3). To form a cage adduct, the C–C bonds on one side of the structure should form prior to those on the other side. An immediate result of this bond formation would be the production of a σ-bonded metallocycle such as those of **6** and **7**. Then the metal nucleus would leave the ligand followed by closure of the cage. This mechanism can be verified if any of the σ-bonded metallocycles is isolated. However, we were unable to identify any of them from the reactions. This probably was due to their short lifetimes. Neither have we found the formation of Binor-S (**13**) which might be considered as a direct consequence of a metallocycle with half of the cage sealed.



13

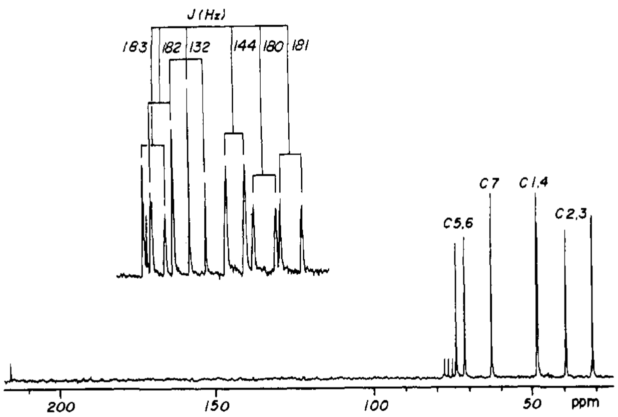


Figure 4. ^{13}C NMR spectra of **11**. Plot at the top shows ^{13}C–^{1}H coupling constants.

Characters of the Double Bonds. The structural characters of the bis-chelated NBD–metal complexes are worthy of special discussion. As mentioned earlier, the bonding between C=C bonds and metal is directly related to the coupling efficiency of the NBDs. As more of the bonding electrons in b2 are transferred to the antibonding mode of b1, the C=C π bonding should become weaker and the C—Mo bonding should become stronger. The extreme case of a C–Mo bond strengthening would lead to a σ-bond. It has been shown recently that molybdenum is capable of forming stable σ-bonded metallocyclopropanes with ethylenes.[22] The nature of these bonds should be revealed by their spectroscopic properties as well as by their corresponding bond distances. The ^{1}H NMR spectra of these complexes indeed show unusually high field chemical shifts at ca 2.0 ppm for some of the vinyl protons[23] (Table I). However, this information alone is not sufficient to establish the existence of σ-bonds. The degree of hybridization of carbons may best be judged by measuring their ^{13}C–^{1}H coupling constants. The ^{13}C NMR data for **9a**, **9b**, **9c**, **9g**, **11**, and **8**, including the coupling constants of interest, are listed in Table II.[25] The magnitudes of the coupling constants are found to appear in a range of 168–184 Hz which is typical for carbons of sp^2 hybridizations. One example is shown in Figure 4 for the complex **11**, including both the COM (completely proton decoupled) and NOE (proton undecoupled with NOE) spectra. Only by observing the ^{13}C–^{1}H coupling constants can the signals be correctly assigned. One of the double bonds (C2=C3) shifts more upfield than both the bridgeheads and C7, yet the coupling constants stay in the range of 180–181 Hz. The relative positions

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(20) Jennings, W.; Hill, B. *J. Am. Chem. Soc.* **1970**, *92*, 3199.

(21) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1967**, 2601.

(22) (a) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507. (b) Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350. (c) Eichner, M. E.; Alt, H. G. *J. Organomet. Chem.* **1984**, *264*, 309. (d) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418.

(23) Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2037.

(24) Kuhn, N,; Schwenk, U.; Winter, M. *J. Organomet. Chem.* **1984**, *260*, C43.

(25) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

Table III. Selected Averaged Bond Distances of **10b** and **9a**

bond	**10b** lengths (Å)		**10b** av	**9a**[a] lengths	**9a**[a] av
Mo—C(8)O	1.915 (5)	1.906 (5)	1.911		
C(8)≡O	1.164 (6)	1.164 (6)	1.164		
Mo—OBu-*t*	2.408 (3)	2.403 (3)	2.406		
Mo—C(8′)O	1.958 (5)	1.976 (5)	1.967	1.968 (2)	
C(8′)≡O	1.161 (6)	1.153 (6)	1.157	1.148 (3)	
Mo—C(5)	2.422 (4)	2.411 (4)		2.457 (2)	
Mo—C(6)	2.444 (4)	2.449 (4)	2.432	2.492 (2)	2.475
C(5)═C(6)	1.342 (6)	1.357 (6)	1.350	1.348 (3)	
Mo—C(2)	2.332 (4)	2.330 (4)		2.301 (2)	
Mo—C(3)	2.297 (4)	2.287 (4)	2.312	2.251 (2)	2.276
C(2)═C(3)	1.392 (6)	1.387 (6)	1.390	1.392 (3)	
Mo—C(2′)	2.198 (4)	2.212 (4)			
Mo—C(3′)	2.289 (4)	2.300 (4)	2.250		
C(2′)═C(3′)	1.402 (7)	1.404 (6)	1.403		
C(5′)═C(6′)	1.322 (8)	1.327 (8)	1.325		

[a] Data abstracted from ref 13.

of C2 and C3, C1 and C4, and C5 and C6 cannot be distinguished in these spectra. The absolute assignment for the position of each atom is accomplished by their 2D NOESY spectra which will be discussed later.

The bonding character of Mo—C should be reflected not only by $J(^{13}C-^{1}H)$ but also on the bond order of C═C which can be estimated by measuring the C═C bond length. The bond lengths observed in an X-ray crystallographic analysis are shown in Table III. The C═C distances appear to be slightly elongated but not yet beyond the limits of typical double bonds. This information indicates that σ-bonded molybdenocyclopropanes do not exist among these complexes.

Influence of a Substituent on C7. The presence of both types of substituent on C7 does not decrease the regiospecificity of the dimerization. Compounds **2b** and **2c** are formed exclusive of other dimeric products. However, the isolation of **10a** and **10b** has shown the feasibility of exo-coordination for BuNBD toward molybdenum. It was expected that complexes with geometries of **10a** and **10b** should produce dimers linked in an endo-exo mode. However, heating **10a** or **10b** in the presence of 1 equiv of BuNBD produced only **2c** in >50% yield. The mechanism apparently involves intermediates **9e–g**. Ligand exchange with exo-bonded BuNBD replaced by endo-bonded BuNBD must have happened before formation of the product. The isolation of **9e–g** from heating pure **10a,b** demonstrated the conversion. Transformation of **10a,b** to **9e–g** proceeded steadily throughout the course of heating, and the authenticity of **9e–g** was confirmed by isolation and comparison with pure samples. However, the reversal of this reaction is not feasible, i.e., heating pure **9e–g** does not produce **10a,b**. These facts strongly suggest a higher stability for **9e–g** than for **10a,b**. It is further supported by observations on TLC that complexes **10a,b** appear earlier than complexes **9e–g** when the coupling reaction is continuously monitored. The complete sequence of reaction may be summarized as follows:

$$\mathrm{BuNBD} \rightarrow \mathbf{10a,b} \rightarrow \mathbf{9e\text{–}g} \rightarrow \mathbf{2c}$$

The corresponding BzNBD analogues of **10a,b** were not observed. The oxygen moieties of BzNBD do not act as effective coordination sites compared to those of BuNBD.

Properties of the Ligands on 10b. The X-ray structure of **10b** indicates three kinds of coordination around the Mo center, CO, C═C, and O—*t*-Bu, arranged in three types of pairings: (1) CO trans to C═C, (2) CO trans to O—*t*-Bu, and (3) C═C trans to C═C. With a free C═C in the same X-ray structure available as a reference, the structure thus provides a good model for comparing the trans influences in this molecule. The observed structural parameters could be summarized as follows (Table III): The Mo—C(8)O (trans to O—*t*-Bu) is 0.056 Å shorter than the Mo—C(8′)O (trans to C═C). The former C≡O distance is seemingly longer than the latter. The averaged Mo—C of C2═C3 and C2′═C3′ (trans to each other) is shorter than the Mo—C of C5═C6 (trans to CO) by a range of 0.120 to 0.182 Å. The former C═C is 0.046 Å longer than the latter and is 0.071 Å longer than the free C5′═C6′.

The above bond lengths are in excellent agreement with the degree of electron back-donation from the d-orbitals of Mo to the ligands whose π acidity is taken into account. As CO is the best π acid of all three, the back-donation to CO is much preferred. For the CO and its trans O-*t*-Bu pair, the electron density due to back-donation is almost wholly accepted by CO, resulting in a shortened Mo—C(CO) distance and a lengthened C═O distance. For the CO and its trans C═C pair, the electron density due to back-donation is primarily taken by CO. For the C═C and its trans C═C pair, the electron density due to back-donation should be more or less equally shared. The averaged Mo—C distance of C2═C3 and C2′═C3′ (trans to each other) is thus shorter than the averaged distance of Mo—C of C5═C6 (trans to CO). On the other hand, the C═C distance decreases according to the order of C═C (trans to C═C) > C═C (trans to C═O) > C═C (free).

The norbornadiene skeleton apparently imposes a strain such that the coordination around Mo is a distorted octahedral and the C═C to Mo coordination is not isosceles for either the endo or the exo norbornadiene. Also because O-*t*-Bu is not a π acid, less geometrical adjustment would be necessary for the exo norbornadiene. As expected the exo norbornadiene reveals a C═C to Mo coordination stronger than that of the endo norbornadiene.

The molecule is also seen to possess a chiral center at Mo. Both molecular chiralities are present and paired up by the inversion centers as required by the crystallographic considerations. The left molecule of the ORTEP drawings reveals one chirality while the other independent molecule on the right reveals the other kind.

2D NOESY NMR Analyses. The orientation of the substituent on C7 of **10b** is clearly shown on its ORTEP view; however, assignments for the orientation of the 7-substituents on isomers **9b–d** (i.e., the benzoyloxy group) and **9e–g** (the *tert*-butoxy group) are not so apparent without X-ray crystallographic data. This problem may be solved better by a two-dimensional NOESY (Nuclear Overhauser Effect Spectroscopy) NMR technique. The cross-relaxations of proximately located hydrogens (within a spatial distance of ca. 5 Å) are indicated by the presence of NOE correlation signals. The appearance of clear cross-relaxations between H7 and H5, H6 as well as the absence of such signals between H7 and H2, H3 point out that the orientation of H7 on **9e** must be syn to the double bond C5═C6 and anti to C2═C3. Therefore the absolute geometries of **9e–g** and **10a,b** are confirmed in order of increasing polarity on silica gel as **10a** < **10b** < **9e** < **9f** < **9g**. The absolute geometry of **9d** was similarly determined and shown to have the 7-benzoyloxy group oriented anti to the bond C2═C3. The relative polarity observed on silica gel is **9d** < **9c** < **9b**.

There is another interesting problem encountered in the structural analyses of the **9** complexes. Although it is a relatively easy matter to assign the ^{1}H NMR signals of H(2,3) and H(5,6) as pairs of triplets, it is very difficult to identify the signals of H2 and H6 from those of H3 and H5, and vice versa. Even X-ray crystallography is not of any help. However, after closely examining the structures of the **9**'s, we have found a way to distinguish the protons located on one side of a 7-R-NBD ligand, i.e., H(2,1,6), from those located on the other side, i.e., H(3,4,5), by examining 2D NOESY spectra. The presence of cross-relaxations among H2, H1, H6 and among H3, H4, H5 are quite clear on both of the 2D NOESY of **9d** and **9e**. Besides that, it is noticed that the distance between H2 and H5′ should also be close enough for an effective through-space interaction, which should not exist between H3 and H6′. This correlation will make a distinction between H2 and H3 as well as between H5′ and H6′ (also H5 and H6 since they are chemically equivalent to H5′ and H6′). Indeed on the 2D NOESY of **9d** and **9e** we observed strong correlation signals between the two pairs of vinyl hydrogens.[26] Consequently the peak at high field is assigned H2 and the one at low field H5′ (or H5), and all the ^{1}H NMR signals can be unambiguously identified.

The Chemistry of HCTD Derivatives. Compound **2a** and its derivatives are of potential usefulness for theoretical as well as organic chemists. This structure is more rigid than those of adamantanes yet the strain is not much higher. We have found that all the bond lengths of **2a** are within the range of 1.52–1.57 Å, and most of the bond angles are within 103–108° except the one on the methylene bridge which is 95°.[14,27] The substituents on **2b** and **2c** may be transformed into other functionalities such as ketones and ethylenes. The hydrophobic nature of the cage could be beneficial to special drug designs. The poly-nitro derivatives are compact "energetic" molecules comparable to the recently developed analogues of cubanes,[28] bishomocubanes,[29] and bishomopentaprismanes.[30] Among all of the norbornadiene dimers, HCTD possesses the most stable skeleton since it has been shown to be the end product of acidic rearrangements for several structural isomers.[31] The presence of two substituents on **2b** and **2c** renders variations in dipole moment and chirality. No attempts have yet been made to resolve the optical isomers. However, it would be interesting to synthesize derivatives with only one substituent. This would require a heterolytic coupling between an NBD and a BuNBD. The key intermediate (NBD)(BuNBD)Mo$(CO)_2$ (**9h**) was isolated as an 1:1 mixture of two diastereomers **9h** and **9i** in addition to **9a** and **9e–g** from refluxing a petroleum ether solution of NBD and BuNBD. Prolonged heating of **9h**,**i** produced **2e** as expected, which was purified by preparative GC. The structure of **2e** stands for the first example of HCTD derivatives possessing a single substituent.

Conclusion

Molybdenum plays a crucial role in the dimerization of norbornadiene and derivatives via d-orbital intervention in electron-orbital correlations. The endo-endo bis-chelated complexes **9** are proven to be key intermediates in these processes. In the case of BuNBD, another pair of isomers **10a**,**b** with endo-exo geometry are found to form prior to the **9**'s. Although evidence shows that an exo-coordination of BuNBD to Mo seems to be stronger than an endo-coordination per C=C to Mo, the overall stabilities of **9e**,**g** are shown to be higher than those of **10a**,**b**. Detailed structural features of **9**'s and **10**'s are carefully analyzed according to their spectra. With the aid of 2D ^{1}H NMR, each proton is unambiguously assigned to the spectra. The degree of large-scale upfield chemical shifts for certain vinyl protons is determined not only by their bonding distances to Mo but also by their electronic environments which is particularly influenced by their trans-ligands.

Experimental Section

Melting points were determined with use of a Yamato Model MP-21 melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Proton nuclear magnetic resonance (NMR) spectra were obtained either on a Jeol JNM-C-60HL spectrometer or on a Jeol JNM-FX 100 FT spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in hertz (Hz). Two-dimensional NOESY spectra were done on a Bruker AM 400-MHz NMR spectrometer. Elemental analyses were obtained on a Perkin-Elmer 240 EA instrument. Mass spectra were carried out on a Jeol JMS-D300 mass spectrometer. For analytical gas chromatography (GC), a Perkin-Elmer Sigma 300 chromatograph equipped with a dual flame ionization detector was used with nitrogen as carrier gas. Either a 7 ft × $^1/_8$ in. stainless steel column packed with 10% carbowax 20M on 80/100 chromosorb W A/W DMCS or a 20 ft × $^1/_8$ in. stainless steel column packed with 3% OV-101 on Supelcoport 80/100 mesh was used. For GC/MS studies a Hewlett-Packard 5995 Gas Chromatograph/Mass Spectrometer fitted with a 2 ft × $^1/_8$ in. glass column packed with 5% OV-101 on WHP 80/100 mesh was used.

Hexacarbonylmolybdenum and hexacarbonyltungsten were purchased from MERCK. Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) was purchased from Alfa Products (Morton Thiokol, Inc.) and was distilled before use. 7-*tert*-Butoxynorbornadiene (BuNBD)[32] and 7-(benzoyloxy)norbornadiene (BzNBD)[33] were synthesized by the published procedures.

Heptacyclo[6,6,0,0^{2,6},0^{3,13},0^{4,11},0^{5,9},0^{10,14}]tetradecane (2a, HCTD) and Bis(norbornadiene)dicarbonylmolybdenum (9a). In a round-bottomed flask fitted with a condenser was refluxed a 25-mL petroleum ether solution (100–140 °C) of norbornadiene (1.00 g, 11 mmol) and hexacarbonylmolybdenum (1.00 g, 3.80 mmol) for 40 h under nitrogen. It was then allowed to cool, and the liquid was decanted. The dark brown precipitate was extracted several times with *n*-hexane. All the liquid parts were combined and evaporated to dryness. Complex **9a** was directly recrystallized from *n*-hexane to form light yellow needles, mp 85 °C (585 mg, 1.74 mmol, 46%).[34] The crystals are quite stable under nitrogen at 0 °C but slowly decompose upon exposure to the air at room temperature. It darkens in a few hours when dissolved in chloroform or benzene but stays intact for many days in methanol in a sealed tube. ^{1}H NMR ($CDCl_3$) δ 1.2 (AB pattern with multiplets, 2 H, $J = 8$ Hz), 2.2, 3.4 (2 t, $J = 4$ Hz, 2 H), 3.7 and 3.5 (2 m, 2 H), 5.1 (t, 1 H, $J = 4$ Hz), 5.6 (t, 1 H, $J = 4$ Hz); IR (KBr) 1880 (s), 1930 (s) cm^{-1}; mass spectrum (*m*/*z*) 338 (M^+ for Mo = 98), 310 ($M^+ - CO$), 278, 254, 241, 228, 214, 202, 188. Anal. Calcd for $C_{16}H_{16}MoO_2$: C, 57.10; H, 4.76. Found: C, 57.51; H, 4.76.

To collect **2a** as a major product the reaction had to be refluxed for a longer period of time. After 110 h the solution was worked up following the same procedures and **2a** was purified by passing the solution through a silica gel chromatographic column eluted with *n*-hexane. The colorless solids were recrystallized from ether/methanol to form cube clusters, mp 161–162 °C (lit.[2] mp 165–165.5 °C), yield 29% (200 mg, 1.10 mmol). ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 2 H), 2.34 (s, 6 H); mass spectrum (*m*/*z*) 184 (M^+, base peak). Its IR[2] and X-ray crystallographic data[14] have been reported previously.

Kinetic Measurements for the Synthesis of 2a (HCTD). The profile of the reaction was completed by combining the information collected from three types of independent tests: (A) quantitative TLC–FID analyses; (B) measurements of ^{1}H NMR integrals; and (C) yields of isolated products.

(A) An Iatroscan TH-10 TLC/FID Analyzer (Iatron Lab., Inc., Tokyo, Japan) was used for tracing the relative quantities of **8** and **9a** produced in the reaction mixture after various time intervals. A small amount of liquid sample was withdrawn from the reaction flask each time. It was spotted onto the lower end of a quartz rod coated with silica gel (Chromarod-SII, TM). The rod was then fitted vertically into a metal frame and was eluted with ethyl acetate/*n*-hexane (1/10 v/v) just like ordinary TLC plates. After the solvent had evaporated the rod was scanned by a FID collector electrode. The signals were integrated to give a quantitative plot of each spot developed on the rod. In these analyses **9a** appeared on the rod with R_f 0.60 and **8** with R_f 0.45. A small amount of tetraglyme (ca. 0.1 mol ratio with respect to NBD) was used as an internal standard (R_f 0.0) which was added to the solution prior to the refluxing.

However, volatile components such as NBD could not be accurately measured by this method. Therefore the relative concentration of NBD at different stages of the reaction was estimated by ^{1}H NMR integrals as follows: (B) The integrals used for comparisons on ^{1}H NMR were the vinyl protons of NBD (triplet at δ 6.9), **8** (triplet at δ 4.9), and **9a** (two triplets at δ 5.1 and 5.6). No absorptions of other materials from the reaction were interfering in these regions. Chloroform was used as the internal standard and quantitative amounts were added before taking the spectra.

(C) The quantities of **2a** were measured by yields of isolation, since its ^{1}H NMR absorptions were overlaid with the strong solvent signals of petroleum ether, and also it was too volatile to be detected by a TLC–FID spectrometer.

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(26) Spurious signals occasionally appear in NOESY spectra which may cause misinterpretation. See: Bax, A. In *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Delft, Holland, 1982; p 75. In our cases the cross-relaxation signals between H(2) and H(5′) seem to be quite clear. Copies of the NOESY spectra can be obtained from supplementary materials.

(27) Neely, S. C.; van der Helm, D.; Marchand, A. P.; Hayes, B. R. *Acta Crystallogr.* **1976**, *B32*, 561.

(28) Eaton, P. E.; Ravi Shanker, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185.

(29) Marchand, A. P.; Reddy, D. S. *J. Org. Chem.* **1984**, *49*, 4078.

(30) Paquette, L. A.; Fischer, W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524.

(31) (a) Hollowood, F. S.; McKervey, A. *J. Org. Chem.* **1980**, *45*, 4954. (b) Scharf, H.-D.; Weisgerber, G.; Hover, H. *Tetrahedron Lett.* **1967**, 4227.

(32) Story, P. R.; Fahrenholtz, S. R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 151.

(33) Tanida, H.; Tsiji, T. *Chem. Ind.* **1963**, 212.

(34) Chow, T. J.; Wang, C.-Y.; Sheu, S.-C.; Peng, S.-M. *J. Organomet. Chem.* **1986**, *311*, 339.

7,12-(Dibenzoyloxy)heptacyclo[6,6,0,$0^{2,6}$,$0^{3,13}$,$0^{4,11}$,$0^{5,9}$,$0^{10,14}$]tetradecane (2b) and Bis(7-benzoyloxynorbornadiene)dicarbonylmolybdenum Isomers (9b, 9c, and 9d). In a round-bottomed flask was refluxed a 20-mL petroleum ether (100–140 °C) solution of 7-(benzoyloxy)norbornadiene (1.01 g, 4.8 mmol) and hexacarbonylmolybdenum (0.421 g, 1.60 mmol) for 110 h under nitrogen. The dark solution was filtered and the solids were extracted with several portions of ethyl acetate. The liquid parts were combined and concentrated. The products were separated from a silica gel column chromatograph eluted with ethyl acetate/*n*-hexane (1/10 v/v). Compound **2b**[4a] was collected first (20 mg, 0.05 mmol, 3%): ^{1}H NMR ($CDCl_3$) δ 2.6 (s, 3 H), 2.7 (br s, 1 H), 2.9 (s, 2 H), 5.5 (s, 1 H), 7.5 (m, 3 H), 8.0 (m, 2 H); IR (CH_2Cl_2) 1710 cm^{-1}; mass spectrum (m/z) 424 (M^+, base peak), 406, 319, 302. The three isomeric complexes came out of the column in an order of **9d**, **9c**, and **9b** (combined yield of 286 mg, 0.50 mmol, 30%). Each of them shows distinctive melting point as well as spectroscopic characters. **9b**: mp 126–128 °C; ^{1}H NMR ($CDCl_3$) δ 2.15, 3.4 (2 t, J = 4 Hz, 2 H), 3.7–4.0 (m, 2 H), 4.55 (t, J = 2 Hz, 1 H), 4.9, 5.45 (2 t, J = 4 Hz, 2 H), 7.5 (m, 3 H), 8.0 (m, 2 H); IR ($CDCl_3$) 1960 (s), 1905 (s), 1720 (s) cm^{-1}; mass spectrum (m/z) 578 (M^+ for Mo = 98), 550 ($M^+ - CO$), 522 ($M^+ - 2CO$), 430, 406, 310. Anal. Calcd for $C_{30}H_{24}MoO_6$: C, 62.51; H, 4.20. Found: C, 62.64; H, 4.36. **9c**: mp 142–144 °C; ^{1}H NMR ($CDCl_3$) δ 2.0, 2.15, 3.2, 3.4 (4 t, J = 4 Hz, 4 H), 3.7, 3.9 (2 m, 2 H), 4.5, 4.55 (2 t, J = 2 Hz, 2 H), 4.8 (m, 1 H), 4.9 (m, 1 H), 5.3–5.5 (m, 2 H), 7.3–7.6 (m, 6 H), 7.8–8.1 (m, 4 H); IR ($CDCl_3$) 1960 (s), 1905 (s), 1720 (s) cm^{-1}; mass spectrum (m/z) 578 (M^+ for Mo = 98), 550 ($M^+ - CO$), 522 ($M^+ - 2CO$), 430, 406, 310. Anal. Calcd for $C_{30}H_{24}MoO_6$: C, 62.51; H, 4.20. Found: C, 62.61; H, 4.28. **9d**: mp 132–134 C; ^{1}H NMR ($CDCl_3$) δ 2.00, 3.20 (2 t, J = 4 Hz, 2 H), 3.7, 3.9 (2 m, 2 H), 4.5 (t, J = 2 Hz, 1 H), 4.95 (t, J = 4 Hz, 1 H), 5.5 (m, 1 H), 7.5 (m, 3 H), 8.0 (m, 2 H); IR ($CDCl_3$) 1960 (s), 1905 (s), 1720 (s) cm^{-1}; mass spectrum (m/z) 578 (M^+ for Mo = 98), 550 ($M^+ - CO$), 522 ($M^+ - 2CO$), 430, 406, 310. Anal. Calcd for $C_{30}H_{24}MoO_6$: C, 62.51; H, 4.20. Found: C, 62.77; H, 4.34.

7,12-Di-*tert*-butoxyheptacyclo[6,6,0,$0^{2,6}$,$0^{3,13}$,$0^{4,11}$,$0^{5,9}$,$0^{10,14}$]tetradecane (2c) and Bis(7-*tert*-butoxynorbornadiene)dicarbonylmolybdenum Isomers (9e, 9f, 9g and 10a, 10b). A similar operation as outlined for the benzoyloxy derivatives had been followed for the preparation of these *tert*-butoxy analogues. 7-*tert*-Butoxynorbornadiene (5.51 g, 33.6 mmol) and hexacarbonylmolybdenum (3.00 g, 11.4 mmol) were refluxed in 90 mL of petroleum ether (100–140 °C) for 24 h. The dark brown solution was then concentrated on a rotary evaporator and applied onto a silica gel chromatographic column eluted with ethyl acetate/*n*-hexane (1/10 v/v). Five isomeric complexes were washed out of the column in a sequence of **10a**, **10b**, **9e**, **9f**, **9g**. The combined yields were 46% (2.5 g, 5.2 mmol) for **9e–g** and 15% (0.83 g, 1.73 mmol) for **10a,b**. Four of them were further purified by recrystallizations from *n*-hexane. **9e**: mp 130–131 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 2.1 (t, J = 4 Hz, 1 H), 3.2–3.55 (m, 4 H), 4.8, 5.3 (2 t, J = 4 Hz, 2 H); IR (KBr) 1920 (s), 1860 (s) cm^{-1}; mass spectrum (m/z) 482 (M^+ for Mo = 98), 454 ($M^+ - CO$), 426 ($M^+ - 2CO$), 391, 311, 310, 335, 279, 267, 221, 205. Anal. Calcd for $C_{24}H_{32}MoO_4$: C, 60.01; H, 6.68. Found: C, 59.92; H, 6.76. **9g**: mp 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 2.00, 3.15 (2 t, J = 4 Hz, 2 H), 3.35, 3.42, 3.55 (3 m, 3 H), 4.92, 5.45 (2 t, J = 4 Hz, 2 H); IR (KBr) 1940 (s), 1890 (s) cm^{-1}; mass spectrum (m/z) 454 ($M^+ - CO$ for Mo = 98), 426 ($M^+ - 2CO$), 391, 335, 310, 279, 267, 254, 221, 205. **10a**: mp 112–113 °C; ^{1}H NMR ($CDCl_3$) δ 1.08, 1.18 (2 s, 18 H), 2.4 (m, 1 H), 2.9 (m, 2 H), 3.2 (m, 1 H), 3.45 (s, 2 H), 3.6–3.75 (s and m, 4 H), 4.2, 5.1 (2 t, J = 4 Hz, 2 H), 6.2 (t, J = 2 Hz, 2 H); IR ($CDCl_3$) 1940 (s), 1860 (s) cm^{-1}; mass spectrum (m/z) 482 (M^+ for Mo = 98), 454 ($M^+ - CO$), 426 ($M^+ - 2CO$), 391, 363, 335, 307. Anal. Calcd for $C_{24}H_{32}MoO_4$: C, 60.01; H, 6.68. Found: C, 59.99; H, 6.80. **10b**: mp 123–126 °C; ^{1}H NMR ($CDCl_3$) δ 1.06, 1.18 (2 s, 18 H), 2.5 (m, 1 H), 2.9 (m, 2 H), 3.2 (m, 1 H), 3.4 (m, 2 H), 3.5 (m, 1 H), 3.7 (m, 3 H), 4.4, 5.3 (2 t, J = 4 Hz, 2 H), 6.2 (t, J = 2 Hz, 2 H); IR ($CDCl_3$) 1940, 1860 cm^{-1}; mass spectrum (m/z) 482 (M^+ for Mo = 98), 454 ($M^+ - CO$), 426 ($M^+ - 2CO$), 391, 363, 335, 307, 279, 262, 205. Anal. Calcd for $C_{24}H_{32}MoO_4$: C, 60.01; H, 6.68. Found: H, 60.22; H, 6.72.

To collect **2c** as the major component of the products, the above refluxing time was prolonged to 90 h before working-up. White solids of **2c** were isolated from a silica gel chromatographic column eluted with *n*-hexane to give a yield of 45%: mp 123–125 °C (lit.[27] mp 131–132 °C); ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 2.3 (m, 1 H), 2.4 (m, 3 H), 2.8 (m, 2 H), 4.4 (br s, 1 H); mass spectrum (m/z) 328 (M^+), 313, 255, 199 (base peak), 187.

7-*tert*-Butoxyheptacyclo[6,6,0,$0^{2,6}$,$0^{3,13}$,$0^{4,11}$,$0^{5,9}$,$0^{10,14}$]tetradecane (2e) and (7-*tert*-Butoxynorbornadiene)dicarbonyl(norbornadiene)molybdenum Isomers (9h,i). The procedure was similar to previous preparations of **2**'s and **9**'s except a molar ratio of 1/3 for NBD/BuNBD was chosen as substrate in order to optimize the production of **2e**. In a typical run, NBD (760 mg, 8.3 mmol) was mixed with BuNBD (4.00 g, 24 mmol) and $Mo(CO)_6$ (4.30 g, 16 mmol) in petroleum ether (100–140 °C) which then was refluxed for 10 days. After a standard workup procedure, the crude product was applied onto a silica gel column eluted with hexane/ethyl acetate. The first component coming out of the column was a mixture of **2a**, **2c**, and **2e** with a combined yield of 1.1 g. The components were further separated by a preparative GC (3% OV101, 2 m × $^1/_4$ in., 190 °C isothermal elution with hydrogen as carier gas and with a TCD detector). The relative abundance of **2a**:**2c**:**2e** was shown on GC to be ca. 1:9:10 (uncorrected FID peak area). Pure **2e** was recrystallized to form white solids: mp 58.5–59.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.85 (s, 2 H), 2.30 (br s, 4 H), 2.43 (br s, 6 H), 2.72 (br s, 2 H), 4.22 (s, 1 H); mass spectrum (m/z) 256 (M^+), 241 ($M^+ - CH_3$), 183 (M^+ - O-*t*-Bu, base peak), 171, 141, 129, 117, 105, 91, 79. Anal. Calcd for $C_{18}H_{24}O$: C, 84.37; H, 9.37. Found: C, 84.24; H, 9.30. One of the more polar components eluted out of the silica gel column as yellowish dense liquid was identified to be a 1/1 mixture of **9h** and **9i**, yield 660 mg (1.6 mmol, 10%). ^{1}H NMR ($CDCl_3$) δ 1.11, 1.12 (2 s, 9 H each), 1.2–1.3 (m, 4 H), 1.9 (t, J = 4 Hz, 1 H), 2.2 (m, 3 H), 3.0 (t, J = 4 Hz, 1 H), 3.35–3.5 (m, 11 H), 3.7 (m, 2 H), 4.8, 4.9 (2 t, J = 4 Hz, 1 H each), 5.0 (m, 2 H), 5.25, 5.45 (2 t, J = 4 Hz, 1 H each), 5.55 (m, 2 H); IR ($CDCl_3$) 1880, 1935 cm^{-1}.

Crystal Data of 10b. A single crystal of the endo-and-exo isomer **10b** was grown from *n*-hexane for X-ray analysis. The X-ray intensity data ($2° < 2\theta < 50°$) were collected with use of a Nonius CAD-4 automated diffractometer with monochromated Mo Kα radiation (λ = 0.7093 Å, μ = 5.83 cm^{-1}, $F(000)$ = 999.73) which employed the ω–2θ scan method at varying speeds from 2.0° to 6.7° per minute such that more time was devoted to the weaker reflections. Each reflection was scanned from $-(0.7 + 0.35 \tan \theta)°$ to $+(0.7 + 0.35 \tan \theta)°$ around the maximum. Crystal is triclinic, P-1, a = 12.638 (2) Å, b = 13.363 (3) Å, c = 13.719 (4) Å, α = 90.71 (2)°, β = 98.52 (2)°, γ = 92.33 (2)°, M_r = 480.46, Z = 4, V = 2289.1 (8) Å^3, D_x = 1.394 g/cm^3. Three standard reflections (6 1 −3), (−6 −1 3), and (−5 3 3) were monitored after every 7200 s. Analysis of standard reflections showed no decay of intensity or decomposition of the crystal. Out of 8013 unique reflections measured and reduced, 5158 were found to have intensity above $2.5\sigma(I)$ and were used as observations in the crystal structure solution and refinements. No absorption corrections were applied in the analysis.

The structure was solved by the two heavy-atom Patterson method. With the Mo atoms located, other non-hydrogen atoms were found in the following Fourier maps. Full-matrix least-squares refinement with all non-hydrogen atoms as anisotropic ellipsoids resulted in R = 0.053. Hydrogen atoms were then calculated and held fixed as isotropic thermal ellipsoids in the structure refinements. At full convergence, the agreement factors R = 0.035 and R_w = 0.028, with the weights from counting statistics and the quantity minimized in the full-matrix least-squares being $\sum\omega||F_o| - |F_c||^2$, where $|F_o|$ and $|F_c|$ were observed and calculated structure factors, respectively. The scattering factors used in this calculation were from the International Table for X-ray crystallography (1974). R was calculated as $\sum||F_o| - |F_c||/\sum|F_o|$ and R_w as $(\sum(\omega(|F_o| - |F_c|)^2)/\sum\omega|F_o|^2)^{1/2}$. The maximum parameter shift in the last cycle of refinement was 0.65. The final difference map calculated with the reported atomic fractional coordinates revealed only ripples with maximum and minimum as 0.62 and −0.45 e/Å^3, respectively. All computations were carried out on a VAX 780 computer with an NRCC package. The final atomic fractional coordinates and temperature factors, bond lengths, and bond angles are listed in the supplementary material. Because there are two independent molecules per asymmetric unit, chemically equivalent bond distances are averaged and relevant ones listed in Table III.

The Thermolysis of 10a,b. A mixture of **10a,b** (ca. 1/1 ratio) was purified to eliminate the trace contaminations of **9e–g**. A petroleum ether (100–140 °C) solution of this mixture (51 mg, 0.11 mmol) and 7-*tert*-butoxynorbornadiene (29 mg, 0.18 mmol) was refluxed for 65 h. The reaction was monitored during this period by eluting TLC plates. It was observed that new spots corresponding to **9e–g** appeared at the expense of **10a,b**. After reaching their maxima the spots of **9e–g** disintegrated to produce the cage compound **2c** in 56% yield (19 mg, 0.059 mmol). It was isolated from silica gel column, purified by washing with methanol, and showed identical features on ^{1}H NMR and GC spectra with an authentic sample. In another independent analysis, pure **10a,b** (1.00 g, 2.1 mmol) were refluxed in petroleum ether for ca. 30 h, and then all the products were applied onto a silica gel chromatographic column eluted with ethyl acetate/*n*-hexane (10% v/v). The components corresponding to **9e–g** (50 mg, 0.10 mmol) were collected and showed ^{1}H NMR, IR, and mass spectroscopic characters identical with the authentic samples. There were also 300 mg (0.62 mmol) of starting materials **10a,b** recollected. The quantity of **2c** for the second test was not measured.

Bis(norbornadiene)dicarbonyltungsten (11). A 100-mL two-necked round-bottomed flask equipped with a refluxing condenser was filled with a solution of hexacarbonyltungsten (1.00 g, 28 mmol) and acetonitrile (25 mL) in 50 mL of petroleum ether (100–140 °C).[35] The solution was refluxed for 44 h, then through the second neck the solvent and the unreacted acetonitrile were distilled off. To the remaining yellow-greenish residue of $(CH_3CN)_3W(CO)_3$ was added a solution of 50 mL of petroleum ether containing norbornadiene (1.15 g, 12.5 mmol). The solution was again brought to reflux for another 46 h. The liquid was decanted and the solids were extracted twice with *n*-hexane. The liquid portions were combined and evaporated to dryness on a rotary evaporator. Complex **11** was purified by passing through a silica gel column chromatograph eluted with ethyl acetate/*n*-hexane (2% v/v) and was recrystallized from *n*-hexane to form light orange crystals (140 mg, 0.36 mmol, 12%): mp 92–94 °C; ^1H NMR ($CDCl_3$) δ 0.90 (m, 2 H), 1.60, 3.10 (2 t, J = 6 Hz, 2 H), 3.65, 4.00 (2 m, 2 H), 4.90, 5.50 (2 t, J = 4 Hz, 2 H); IR ($CDCl_3$) 1980 (s), 1920 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2W$: C, 45.30; H, 3.77. Found: C, 45.40; H, 3.78.

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Supplementary Material Available: Table of final fractional coordinates of **10b** with its thermal parameters, bond angles, and bond distances; 2D NOESY spectra of **9d** and **9e**; and an orbital correlation diagram for concerted dimerization of NBD (11 pages); listing of structure factors (53 pages). Ordering information is given on any current masthead page.

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[35] King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 2. Solvolysis of 4-(Trimethylsilyl)-2-butyl *p*-Bromobenzenesulfonates

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Abstract: The solvolysis of 4-(trimethylsilyl)-2-butyl *p*-bromobenzenesulfonate produces racemic substitution products and a minor amount of methylcyclopropane at a rate which is several-fold faster than the solvolysis of its carbon analogue; polarimetric and conductometric rates are not significantly different. Added $LiClO_4$, KOH, KOBs, and LiOBs produced normal salt effects on the polarimetric rate; *b* values varied from 0.2 to 130, depending on the nature of the salt and solvent. The deuterium isotope rate effects vary somewhat with solvent as follows: α-*d*, 1.12–1.15; β-d_3, 1.115–1.16; β-d_2, 0.975–1.07. It is concluded that the γ-silyl group promotes the solvolysis and stabilizes the intermediate carbonium ion. The "W" and "sickle" conformations of the transition states for the formation and/or reaction of the carbonium ion intermediate have approximately equal energies.

The effects of silicon substituents on carbonium ion reactions have been examined previously by several authors.[1-3] Apeloig[1c] concluded from his study of the solvolysis of 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate as compared to 2-methyl-2-adamantyl *p*-nitrobenzoate that relative to carbon, an α-silyl substituent retards sovolysis. Lambert[3] found that a β-silicon substituent greatly accelerated the solvolysis of *cis*- and *trans*-2-(trimethylsilyl)cyclohexyl trifluoroacetates. The cis isomer reacted 33 500 times faster than the unsubstituted parent but 75 times slower than the trans isomer. He suggested that electron release from the 2-Me_3Si group occurred by both inductive and hyperconjugative interactions, but later ab initio calculations by Jorgensen[4] indicated only a very small inductive effect. Fessenden[5] showed that relative to carbon, substitution by silicon at the 4-position in cyclohexyl *p*-toluenesulfonate had little or no effect on the rate of acetolysis. Fleming and Patel[6] found that treatment of γ-Me_3Si-substituted tertiary alcohols with a boron trifluoride–acetic acid complex in methylene chloride led to olefin formation via Wagner–Meerwein rearrangment and loss of the Me_3Si group. Davis was the first to report the solvolysis of γ-silyl-substituted alkyl sulfonates.[7,8] In connection with his studies of cyclopropane formation via 1,3-deoxystannylation, he solvolyzed 4-(trimethylsilyl)-2-butyl methanesulfonate. He found that the solvolysis of this compound was accelerated relative to the 2-butyl analogue in acetic acid/water solutions, even though no methylcyclopropane was found. He concluded that there was no evidence for silicon-stabilized ionic intermediates.[7] Recently we reported the study of the solvolysis of *cis*- and *trans*-3-(trimethylsilyl)-cyclohexyl *p*-bromobenzenesulfonate (brosylate or OBs). In the trans isomer we found little or no acceleration relative to the 4-*tert*-butyl analogue and large β-d_4 isotope effects on the rate. The major products were derived by direct substitution, and by a process like that reported by Fleming and Patel,[6] β-hydrogen migration followed by elimination of the Me_3Si group. In the cis compound we found a large acceleration relative to its 4-*tert*-butyl analogue with small or inverse β-d_4 isotope effects; the major products were bicyclo[3.1.0]hexane from 1,3-deoxysilylation and direct substitution with retention of configuration.[10] It was concluded that the Me_3Si group stabilizes the carbonium ion and the transition state for its formation through the "W" conformation.[11] Theoretical calculations on model compounds by Davidson[12] support this conclusion, showing that a γ-silyl-sub-

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[1] (a) Sommer, L. H.; Goldberg, G. M.; Dorfman, E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 1083. (b) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, H.; Schiavelli, M. D.; Hughey, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6852. (c) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

[2] Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153.

[3] Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

[4] Jorgensen, W. L.; Wierschke, S. G.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

[5] Fessenden, R. J.; Seeler, K.; Dagani, M. *J. Org. Chem.* **1966**, *31*, 2483.

[6] Fleming, I.; Patel, S. K. *Tetrahedron Lett.* **1981**, *22*, 2321.

[7] Davis, D. D.; Black, R. H. *J. Organomet. Chem.* **1974**, *82*, C30–C34.

[8] Sommer studied the reactions involving 1,3-elimination of trimethylsilyl halides yielding cyclopropanes in primary systems.[9]

[9] Sommer, L. H.; Van Strien, R. E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056–3060.

[10] Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842–844.

[11] Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914.