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Hydrogenation of (1-phenylthiophene)Mn(CO)$_3$ (thiophene = 3-methylthiophene and 3,4-dimethylthiophene) complexes: formation of tetrakis(tricarbonyl-phenylthiomanganese)

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Abstract

For the hydrogenation of (1-phenylthiophene)Mn(CO)$_3$ (**2**), the nature of the thiophene derivatives strongly affect the yields and distribution of reaction products. When 3-methyl- and 3,4-dimethylthiophene were used as thiophene derivatives, the dimer [Mn(CO)$_4$(SPh)]$_2$ (**7**) and the tetramer [Mn(CO)$_3$(SPh)]$_4$ (**8**) was obtained as major products and the hydrodesulfurized product, isoprene or 2,3-dimethyl-1,3-butadiene were obtained in a high yield. Structures of **7** and **8** were verified by X-ray diffraction studies. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Thiophene; Manganese; Hydrodesulfurization; Cubane

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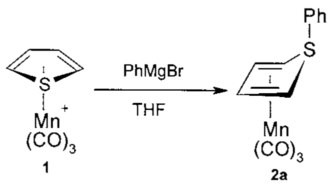
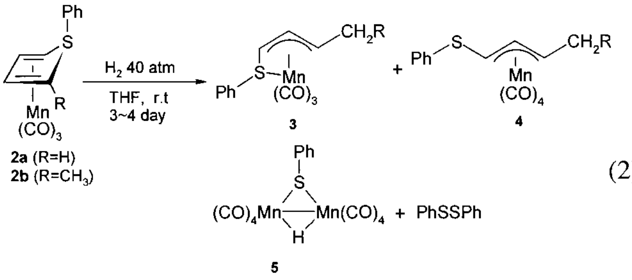
1. Introduction

Due to the great importance of hydrodesulfurization (HDS) in petroleum refining, a considerable amount of research has been directed to the study of homogeneous model systems that may mimic some of the chemical steps occurring during the heterogeneously catalyzed industrial process [1]. Thiophenic molecules are of particular interest in this regard due to their reluctance to undergo desulfurization. Recently, we reported [2,3] that neutral complexes **2a** are formed via nucleophilic addition of PhMgBr to the sulfur in (thiophene)Mn(CO)$_3^+$ (**1**) (1).



(1)

While **1** does not react with H$_2$, complexes **2a** and **2b** readily undergo hydrogenolysis of a C–S bond to afford compounds **3**–**5**, and diphenyl disulfide (2).



(2)

	3	4	5	PhSSPh
2a	60	14	trace	trace
2b	69	4	trace	trace

Such reactions may be relevant to the general problem of HDS of thiophenic molecules. In order to more thoroughly investigate this reaction, we report herein the hydrogenation of (1-phenyl-2,5-dimethylthiophene)Mn(CO)$_3$ (**2c**), (1-phenyl-3-methylthiophene)Mn-

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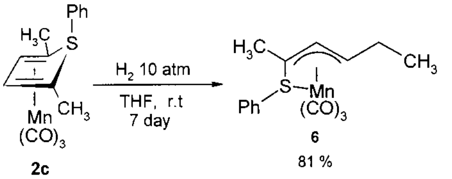
$(CO)_3$ (**2d**), and (1-phenyl-3,4-dimethylthiophene)Mn$(CO)_3$ (**2e**). It is shown that two of the hydrogenation products are the dimer $[Mn(CO)_4(SPh)]_2$ (**7**) and the cubane-type molecule $[Mn(CO)_3(SPh)]_4$ (**8**). We also report the X-ray crystal structures of **7** and **8**.

2. Results and discussion

The manganese thiophene complexes were prepared by the reaction of the appropriate thiophene with $Mn(CO)_5BF_4$ in dichloromethane [2–4]. Nucleophilic addition of PhMgBr to the sulfur in the manganese thiophene complexes led to reasonable yields of complexes **2c**, **2d** and **2e**.

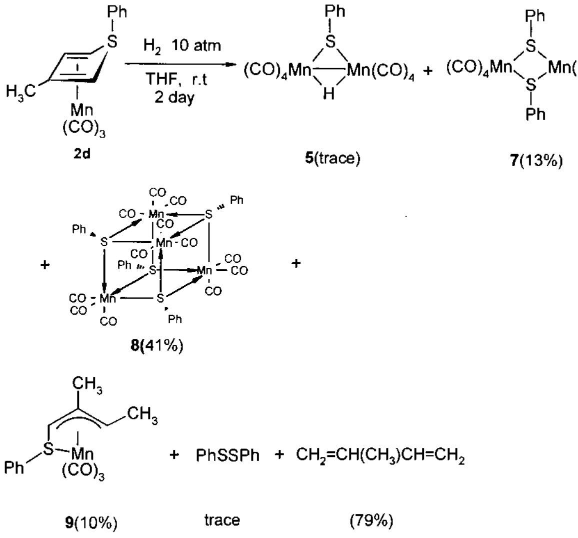
Treatment of **2c** in THF with 10 atm of H_2 at room temperature for 7 days led to the isolation of **6** in 81% yield (3).



(3)

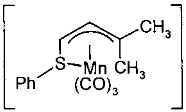
Compound $\{\eta^1{:}\eta^3\text{-PhSC(CH}_3\text{)CHCHCH}_2\text{CH}_3\}Mn(CO)_3$ (**6**) is the same type as **3**.

Treatment of **2d** in THF with 10 atm of H_2 at room temperature for 2 days afforded **5**, **7**, **8**, **9**, PhSSPh and isoprene (4).



(4)

Two of the isolated products are the dimer $[Mn(CO)_4(SPh)]_2$ (**7**) (13%) and the tetrameric cubane $[Mn(CO)_3(SPh)]_4$ (**8**) (41%). These compounds are newly characterized in this reaction. Compounds $[(\mu\text{-H})(\mu\text{-SPh})Mn_2(CO)_8]$ (**5**) and diphenyl disulfide were previously generated by the hydrogenation of **2a** and **2b** [3]. Compound $\{\eta^1{:}\eta^3\text{-PhSCHC(CH}_3\text{)CHCH}_3\}Mn(CO)_3$ (**9**) is the same type as **3** and **6**. In addition to these compounds, liberation of isoprene was confirmed by GC-MS (mass number: 68; yield: 79%) [5]. Formation of **7** and **8** was confirmed by the X-ray structure determinations. Compound **7** can be completely converted into **8** by heating in THF. However, neither **5** nor **9** is converted to **8** when heated or treated with CO or H_2. This means that the origin of **8** is from **7** and not from **5** or **9** and that **7** (or **8**) and **9** may come from different intermediates. Treatment of **7** with H_2 did not produce a noticeable amount of **5**. Compound **9** is derived from the C5–S cleavage. The C2–S cleaved product, presumably $\{\eta^1{:}\eta^3\text{-PhSCHCHC(CH}_3\text{)}_2\}$-Mn$(CO)_3$ (**A**) was not observed presumably due to the *gem*-dialkyl effect [6].

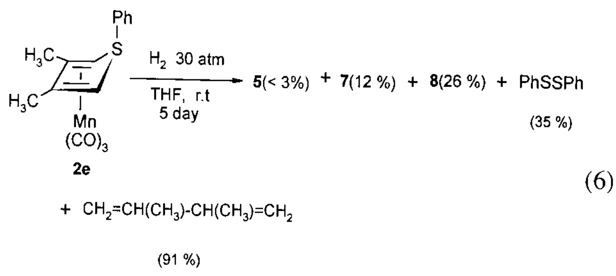


A

Instead of **A**, **7** and **8** were obtained. We can envisage that **7** and **8** may come from **A**. However, we do not have any evidence to support the relation between **A** and **7** (or **8**). Nevertheless, in addition to the C5–S cleavage there should be other reaction routes to explain formation of **7** and **8**.

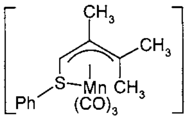
We have determined the X-ray crystal structures of **7** and **8**. Figs. 1 and 2 show the structures of **7** and **8** and Tables 1 and 2 give a summary of the crystallographic data and selected bond lengths and angles of **7** and **8**. Recently, $[Mn(CO)_4(SC_6H_4CH_3\text{-}p)]_2$ was characterized crystallographically [4]. The crystal structure of **7** is essentially the same as that of $[Mn(CO)_4(SC_6H_4CH_3\text{-}p)]_2$. The Mn–S bond distances are between 2.395(2) and 2.401(2) Å and the S–C bond distances are between 1.784(7) and 1.793(9) Å. Compound **8** has no metal–metal bonds, with the sulfur lying off the centers of the triangular faces. The Mn1–Mn2 distance is 3.763(1) Å, longer than the sum of covalent radii. The average Mn–S bond distance is 2.393 Å, slightly longer than those in tricarbonyl[(methylsulfidomethyl)phenyl-2-*C*,*S*]triphenylphosphinemanganese: $C_6H_4CH_2SCH_3Mn(CO)_3PPh_3$ (2.310 (4) Å) [7], trialkylphosphinedithiocarboxylato complex $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (2.282(2) and 2.335(2) Å) [8], the terminal thiolate complex $(\eta^6\text{-}C_6H_6)Mn(CO)_2SPh$ (2.350(3) Å), the bridging thiolate $\{[(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)(CO)_2Mn]_2(SPh)\}^+$ (2.347(2) and 2.358(2) Å) [9], and the bridging thietane complex $Mn_2(CO)_8[\mu\text{-}SCH_2CMe_2CH_2]$ (2.207(1) and 2.211(1) Å) [10]. Each manganese has an octahedral coordination geometry.

Hydrogenation of **2e** led to the isolation of various products (6).



(6)

When **2e** was treated with the 10 atm of H_2, the hydrogenation reaction did not go to completion. At 30 atm of H_2, the reaction went to completion and compounds **5**, **7**, **8** and diphenyl disulfide were isolated as products. It is almost the same result as the hydrogenation products of **2d**, but the distribution of products is quite different: a considerable amount of diphenyl disulfide was isolated for the hydrogenation of **2e**. Furthermore, formation of $\{(\eta^1{:}\eta^3\text{-PhSCHC(Me)C(Me)}_2\}\text{Mn(CO)}_3$ (**B**), which may be akin to the **9**, was not observed, presumably, due to the *gem*-dialkyl effect [6].



B

These observations imply that there will be a relation between the yield of diphenyl sulfide and **B**. Treatment of **2e** with a mixture of H_2 and CO (30 and 10 atm, respectively) led to an increase in the yield of **7** from 12 to 38% and to a decrease in the yield of **8** from 26 to 12%, respectively. This suggests that the yields of **7** and **8** are correlated to each other and depend upon the pressure of CO. Treatment of **2e** with 30 atm of H_2 for 5 days led to ca. 91% of 2,3-dimethyl-1,3-butadiene. The liberation of 2,3-dimethyl-1,3-butadiene was detected by GC-MS and ^{1}H-NMR [11].

The results for hydrogenation of **2d** and **2e** are quite different from the hydrogenation of **2a**, **2b** and **2c**. Hydrogenation products are quite dependent upon the nature of thiophene derivatives, e.g. the position(s) of the substituent(s) on the thiophene ring. We envision that the stability of the C–S cleaved product(s) depend(s) upon the position of substituent(s). Thus, when the substituent is located at the 2-position, the C2–S cleaved product **3** is stable, and when the substituent is situated at the 3-position, the C5–S cleaved product **9** is stable, but the C2–S cleaved products (presumably **A**) may be quite unstable to be isolated. When the substituents are at the 3- and 4-positions, we failed to observe the presence of the C2–S or C5–S cleaved product (presumably **B**). When the C2–S or C5–S cleaved product seems to be unstable, formation of **7** and **8** is observed. Thus, we envisage that there will be a relation between formation of **7** and **8** and the stability of C–S cleaved product(s). One notable thing in the hydrogenation for **2d** and **2e** is the high yield generation of the hydrodesulfurized organic compounds, i.e. isoprene and 2,3-dimethyl-1,3-butadiene. For the hydrogenation of **2a**, **2b** and **2c** we failed to detect hydrodesulfurized organic compounds. Right now we do not have any plausible mechanisms to explain the generation of the hydrodesulfurized organic compound. To firmly establish the mechanism, further investigation is needed.

In conclusion, we have demonstrated that for the hydrogenation of **2**, the nature of thiophene derivatives

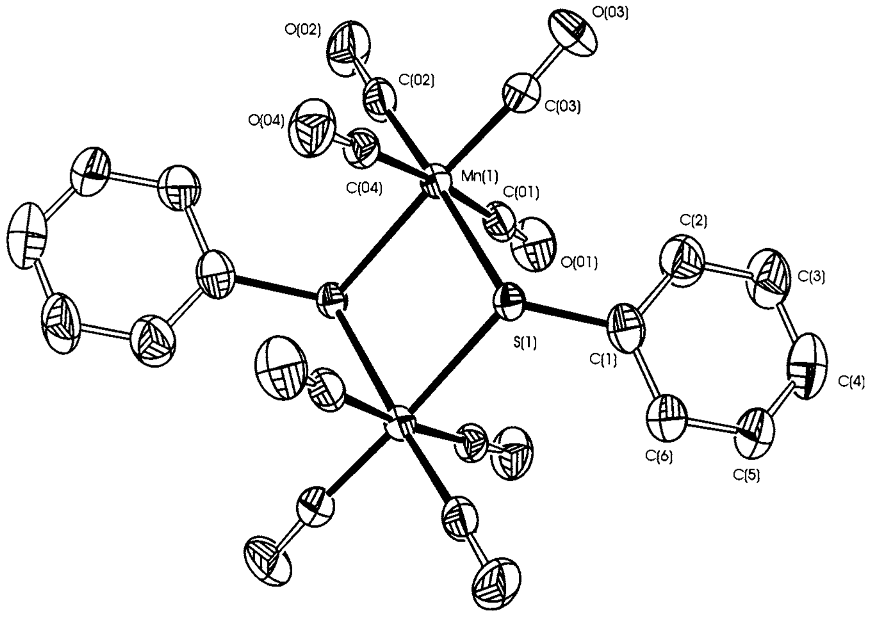


Fig. 1. ORTEP drawing and atomic numbering scheme for **7**.

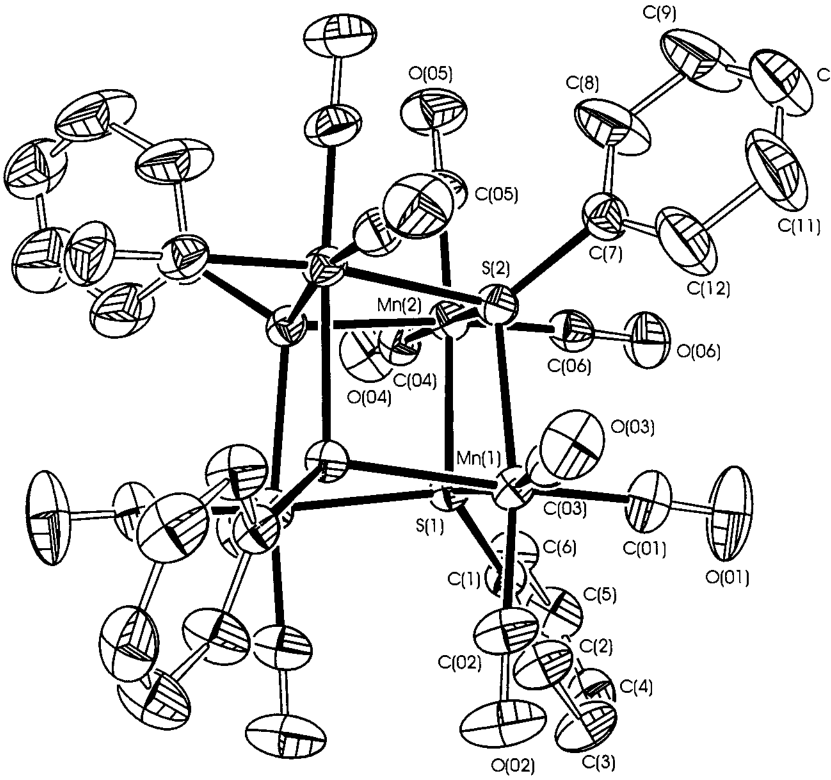


Fig. 2. ORTEP drawing and atomic numbering scheme for **8**.

strongly affect the yields and distribution of reaction products. When 3-methyl- or 3,4-dimethylthiophene was used as thiophene derivatives, **7** and **8** were obtained as major products and formation of hydrodesulfurized organic compounds, such as isoprene and 2,3-dimethyl-1,3-butadiene, was confirmed by GC-MS and ^{1}H-NMR. Structures of **7** and **8** were solved by X-ray diffraction studies.

3. Experimental

3.1. General

All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen atmosphere. Reagent grade chemicals were used without further purification.

Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University. ^{1}H-NMR spectra were obtained with a Bruker BPX-300 or AMX-500. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. GC-MS spectra were recorded on a HP 6890 Series GC system with HP 5973 mass selective detector.

3,4-Dimethylthiophene was prepared by the published procedure [12]. Compounds [(thiophene)Mn-(CO)$_3$]BF$_4$ (thiophene = 3-methylthiophene, 2,5-dimethylthiophene and 3,4-dimethylthiophene: **2a**, **2b** and **2d**, respectively) were previously reported [2–4].

Table 1
Crystal data for **7** and **8**

	7	**8**
Formula	$C_{20}H_{10}Mn_2O_8S_2$	$C_{36}H_{20}Mn_4O_{12}S_4$
Formula weight	552.28	992.52
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073
Crystal size (mm^3)	0.7 × 0.4 × 0.3	0.3 × 0.3 × 0.2
Space group	$P\bar{1}$	$C2/c$
a (Å)	7.7353(14)	11.524(2)
b (Å)	9.2820(7)	22.018(2)
c (Å)	15.552(2)	16.514(2)
α (°)	90.709(8)	90
β (°)	96.634(13)	108.231(13)
γ (°)	101.727(11)	90
V (Å^3)	1085.2(3)	3979.7(10)
Z	2	4
ρ_{calc} (g cm^{-3})	1.690	1.657
2θ range	4.48–50.00	3.70–49.90
Data	3809	1952
Parameters	289	253
R (all data)	0.0785	0.0476
wR^2 (all data)	0.2346	0.1041
S	1.238	1.109

Table 2
Selected bond distances (Å) and angles (°) for **7** and **8**

		7			
Mn1–S	2.389(2)	Mn2–S2	2.401(2)	S1–C1	1.793(9)
C02–Mn1–S	177.0(3)	C1–S1–Mn1	114.2(3)	C7–S2–Mn2	113.7(3)
		8			
Mn1–C02	1.794(8)	Mn1–S1	2.391(2)	Mn1–S2	2.395(2)
Mn2–S2	2.393(2)	Mn2–S1	2.395(2)	S1–C1	1.805(6)
S2–C7	1.800(7)	C01–O01	1.126(8)	C02–O02	1.144(8)
C02–Mn1–C03	93.6(3)	C02–Mn1–S1	171.6(3)	C03–Mn1–S1	92.2(2)
S1–Mn1–S2	76.18(6)	C05–Mn2–C04	91.5(4)	C05–Mn2–S2	171.7(3)
C1–S–Mn(2)	117.0(2)	Mn1–S1–Mn2	103.66(7)	C1–S1–Mn1	117.0(2)

3.2. Synthesis of [(3,4-dimethylthiophene)Mn(CO)$_3$]BF$_4$

$AgBF_4$ (1.42 g, 7.3 mmol) was added to $Mn(CO)_5Br$ (2.0 g, 7.3 mmol) in CH_2Cl_2 (40 ml), and the mixture was stirred for 1 min at room temperature in the absence of light. At this stage 3,4-dimethylthiophene (0.98 g, 8.76 mmol) was added and the mixture was heated at reflux for 12 h. The volume was then reduced to 5 ml, and the product was precipitated as the BF_4^- salt by addition of Et_2O. Yield: 65% (1.61 g). IR (CH_3NO_2) ν(CO): 2065, 1966 cm^{-1}; ^{1}H-NMR (CD_3NO_2): δ 6.60 (s, 2H), 2.49 (s, 6H) ppm; Anal. Found: C, 31.63; H, 2.06. Calc. for $C_9H_8BF_4MnO_3S$: C, 31.99; H, 2.39.

*3.3. Synthesis of **2***

These complexes were prepared by a procedure previously described for **2a**,**b**,**d** [3]. In a typical synthesis of **2e**, to a solution of [(3,4-dimethylthiophene)-Mn(CO)$_3$]BF$_4$ (0.91 g, 2.69 mmol) in 30 ml of THF, PhMgBr (1.2 equivalents, 3.48 mmol) was added at 0°C under N_2. The reaction mixture was stirred for 30 min and allowed to warm to room temperature. To this solution diethyl ether (30 ml) and saturated aq. NH_4Cl (30 ml) were added. The organic layer was collected, dried over $MgSO_4$, concentrated, and chromatographed on a silica gel column with *n*-hexane and diethyl ether (v/v, 10:1) as eluant to give the product **2e** as a yellow solid. Yield: 55% (0.49 g). IR (CH_2Cl_2) ν(CO): 1984, 1899 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.36 (m, 3H, Ph), 7.18 (m, 2H, Ph), 2.57 (s, 2H), 2.20 (s, 6H, CH_3) ppm; Anal. Found: C, 54.82; H, 3.68; S, 9.88. Calc. for $C_{15}H_{13}MnO_3S$: C, 54.88; H, 3.97; S, 9.77. For **2c**: Yield: 31%. IR (hexane) ν(CO): 1975, 1869 cm^{-1}; ^{1}H-NMR (CD_2Cl_2): δ 7.6–7.5 (m, 5H, Ph), 5.12 (s, 2H), 1.79 (s, 6H, CH_3) ppm; Anal. Found: C, 54.79; H, 4.12. Calc. for $C_{15}H_{13}MnO_3S$: C, 54.89; H, 3.96.

*3.4. Reaction of **2c** with H_2*

Compound **2c** (0.150 g, 0.457 mmol) and THF (10 ml) were put in a 100 ml stainless steel high pressure reactor. The reactor was charged with 10 atm of H_2. The solution was stirred at room temperature for 5 days. After releasing the pressure, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane gave 0.122 g of **6** (81%). IR (hexane) ν(CO): 2050, 1933, 1921 cm^{-1}; ^{1}H-NMR ($CDCl_3$): one diastereomer δ 7.56 (m, 2H, Ph), 7.44 (m, 1H, Ph), 7.39 (m, 2H, Ph), 4.80 (d, 9.3 Hz, 1H), 2.24 (s, 3H, CH_3), 2.01 (m, 1H), 1.90 (m, 1H), 1.32 (m, 1H), 1.19 (t, 7.4 Hz, 3H, CH_3); other diastereomer δ 7.24 (m, 1H, Ph), 7.19 (m, 2H, Ph), 6.98 (m, 2H, Ph), 5.09 (d, 9.5 Hz, 1H), 2.69 (s, 3H, CH_3), 1.92–1.87 (m, 2H), 1.23 (m, 1H), 0.96 (t, 7.4 Hz, 3H, CH_3) ppm; Anal. Found: C, 54.32; H, 4.41; S, 10.11. Calc. for $C_{15}H_{15}MnO_3S$: C, 54.55; H, 4.58; S, 9.71.

*3.5. Reaction of **2d** with H_2*

Compound **2d** (0.10 g, 0.32mmol) and THF (10 ml) were put in a 100 ml stainless steel high pressure reactor. The reactor was charged with 10 atm of H_2. The solution was stirred at room temperature for 5 days. After releasing the pressure, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane gave the hydride (trace), diphenyl disulfide (trace), the dimer (23 mg, 13%), {η^1:η^3-PhSCHC(CH_3)CH(CH_3)}Mn(CO)$_3$ (10 mg, 10%), and the cubane (32 mg, 41%). {η^1:η^3-PhSCHC(CH_3)CH(CH_3)}Mn(CO)$_3$: IR (hexane) ν(CO) 2010, 1933, 1920 cm^{-1}; ^{1}H-NMR ($CDCl_3$) of one isomer: δ 7.3–7.0 (m, 5H, Ph), 5.11 (s, 1H), 2.03 (s, 3H, CH_3), 1.61 (d, 6.1 Hz, 3H, CH_3), 1.36 (q, 6.1 Hz, 1H) ppm; ^{1}H-NMR ($CDCl_3$) of the other isomer: δ 7.6–7.3 (m, 5H, Ph), 5.29 (s, 1H), 2.06 (s, 3H, CH_3), 1.69 (d, 6.1 Hz, 3H, CH_3), 1.11 (q, 6.1 Hz, 1H) ppm; Anal. Found: C, 52.98; H, 4.23; S, 10.02. Calc. for $C_{14}H_{13}MnO_3S$: C, 53.17; H, 4.14; S, 10.14. Dimer: IR (hexane) ν(CO) 2064, 2002, 1994, 1959 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.58 (d, 8.0 Hz, 4H), 7.32 (dd, 7.2 Hz, 8.0 Hz, 4H), 7.25 (t, 7.2 Hz, 2H) ppm; Anal. Found: C, 43.19; H, 1.80; S, 11.91. Calc. for $C_{20}H_{10}Mn_2O_8S_2$: C, 43.50; H, 1.83; S, 11.61. Cubane: IR (hexane) ν(CO) 2010, 1942 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 8.0 (d, 7.2 Hz, 8H), 7.53 (dd, 7.2 Hz, 8H), 7.44 (t, 7.2 Hz, 4H) ppm; Anal. Found: C, 43.42; H, 1.84. Calc. for $C_{36}H_{20}Mn_4O_{12}S_4$: C, 43.56; H, 2.03.

3.6. Reaction of **2e** with H_2

Compound **2e** (0.10 g, 0.296 mmol) and THF (10 ml) were put in a 100 ml stainless steel high pressure reactor. The reactor was charged with 30 atm of H_2. The solution was stirred at room temperature for 5 days. After releasing the pressure, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane gave the hydride (trace), diphenyl disulfide (0.011 g, 35%), and the dimer (0.011 g, 7%) and eluting with hexane/diethyl ether (v/v, 60:1) gave cubane (0.019 g, 26%).

3.7. Reaction of **2e** with H_2 and CO

Compound **2e** (0.10 g, 0.29 mmol) and THF (10 ml) were put in a 100 ml stainless steel high pressure reactor. The reactor was charged with 30 atm of H_2 and 10 atm of CO. The solution was stirred at room temperature for 5 days. After releasing the pressure, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane gave the hydride (trace), diphenyl disulfide (13 mg, 40%), and the dimer (31 mg, 38%) and eluting with hexane/diethyl ether (v/v, 60:1) gave cubane (9 mg, 12%).

3.8. Synthesis of **8** from **7**

Compound **7** (70 mg) in 10 ml of THF was vigorously refluxed for 8 h. The solution was cooled and concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v, 60:1). Yield: 59 mg (94%).

3.9. X-ray structure determination of **7** and **8**

Diffraction was measured by an Enraf–Nonius CAD4 diffractometer with a ω–2θ scan method. Unit cells were determined by centering 25 reflections in the approximate 2θ range. Other relevant experimental details are given in the Supporting Information. The structure was solved by direct method using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were refined isotropically using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Supplementary materials for **7** and **8** (tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen atom positional and displacement parameters, and observed and calculated structure factors) have been deposited with the Cambridge Crystallographic Data Center.

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