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Reinvestigation of Nucleophilic Addition to the $[(naphthalene)Mn(CO)_3]^+$ Cation: Hydrogen Migration in $[(\textit{exo}\text{-}R\text{-}\eta^5\text{-}C_{10}H_8)Mn(CO)_3]$

Seung Uk Son, Se-Jung Paik, Kang Hyun Park, Young-A Lee, In Su Lee, and Young Keun Chung*

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea

D. A. Sweigart

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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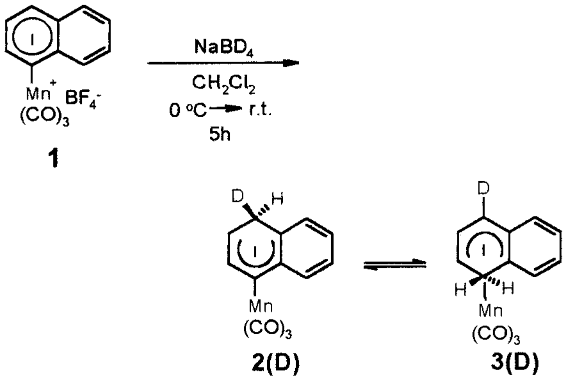
Summary: Treatment of RMgBr with **1** *at −78 °C led to the isolation of an equilibrium mixture of* $[(exo\text{-}1\text{-}R\text{-}\eta^5\text{-}C_{10}H_8)Mn(CO)_3]$ (**2a−h**) *and* $[(exo\text{-}1\text{-}H\text{-}\eta^5\text{-}C_{10}H_7\text{-}4\text{-}R)Mn(CO)_3]$ (**3a−h**). *The equilibrium ratio is dependent upon the R group. A single-crystal X-ray diffraction analysis confirms the formation of* **3d** *(R = p-tolyl). Treatment of the mixture of* **2a** *(R = Me) and* **3a** *(R = Me) with* Ph_3CBF_4 *led to the isolation of* $[(\eta^6\text{-}1\text{-}Me\text{-}C_{10}H_7)Mn(CO)_3]BF_4$ *in 94% yield.*

Introduction

Naphthalenes activated by coordination to transition metals are easily attacked by nucleophiles, including hydride and carbon donors. Recently, we reported[1] the nucleophilic addition to $(polyarene)Mn(CO)_3^+$ complexes containing naphthalene type ligands. According to our previous report, nucleophiles were added regiospecifically at the C1 position and all of the C-donor additions occurred in the usual stereospecific exo manner. However, we recently found that the situation was not as simple as reported. Thus, we have reinvestigated the nucleophilic addition to $(naphthalene)Mn(CO)_3^+$ and found the 1,4-hydride shift in the (1-Nu-naphthalene)-$Mn(CO)_3$ derivatives to give an equilibrium mixture of (1-Nu-naphthalene)$Mn(CO)_3$ and (4-Nu-naphthalene)-$Mn(CO)_3$. The 1,4-hydride migration was confirmed by solving an X-ray crystal structure of $[\{1\text{-}H\text{-}(NuC_{10}H_7)\}Mn(CO)_3]$ (Nu = 4-p-$CH_3C_6H_5$). While our work was in progress, Kreiter's and Cooper's groups reported a 1,4-hydride shift within $[Mn(\eta^5\text{-}C_{10}H_9)(CO)_3]$ and $[Mn(\eta^5\text{-}C_{14}H_{11})(CO)_3]$, respectively.[2,3]

Results and Discussion

Treatment of **1** with $NaBH_4$ in CH_2Cl_2 at 0 °C for 5 h led to the hydride adduct $(\eta^5\text{-}C_{10}H_9)Mn(CO)_3$ (**2(H)**) in 48% yield. However, the reaction of **1** with $NaBD_4$ resulted in the two chemical species **2(D)** and **3(D)** in the ratio 1:1 (eq 1).



(1)

Assignment of **2(D)** and **3(D)** is based on the ^{1}H NMR spectrum of the product: the integration of the proton of *exo*-H (δ 2.73 ppm) and the proton at C4 (δ 6.47 ppm) is half that of other protons. Recently, Kreiter's[2] and Cooper's groups[3,4] reported a 1,4-hydride shift within $[Mn(\eta^5\text{-}C_{10}H_9)(CO)_3]$ and $[Mn(\eta^5\text{-}C_{14}H_{11})(CO)_3]$, respectively. Cooper et al. prepared **2(H)** from the reaction of $M[Mn(\eta^4\text{-}C_{10}H_8)Mn(CO)_3]$ (M = K, PPN) with CF_3CO_2H and showed that **2(H)** participates in a 1,4-hydride shift reaction that involves exchange of the endo proton with the proton para to this position. However, they did not extend their study to $[Mn(1\text{-}R\text{-}\eta^5\text{-}C_{10}H_8)(CO)_3]$ ($R \neq H$).

The addition of Grignard reagent to **1** is highly dependent upon the reaction temperature. When the reaction temperature was 0 °C, the reaction product was always **2(H)**, independent of the nature of the nucleophile. Thus, treatment of **1** with MeMgBr in THF at 0 °C led to the isolation of **2(H)** in 28% yield. Formation of **2(H)** suggests the possibility of electron-transfer to **1** to give **1$^•$**, prior to the reaction with nucleophile. **1-(H)$^•$** would pick up a proton from water during workup. When deuterated naphthalene has been used, the proton, presumably from water, is situated at an endo position: in ^{1}H NMR ($CDCl_3$), a single peak appears at δ 3.32 ppm as a singlet. However, the poor yield suggests that there could be other uncharacterized reactions. However, when the reaction temperature was

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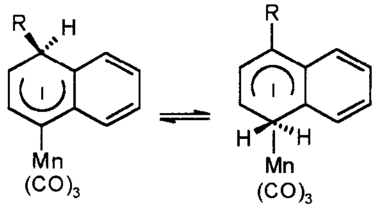
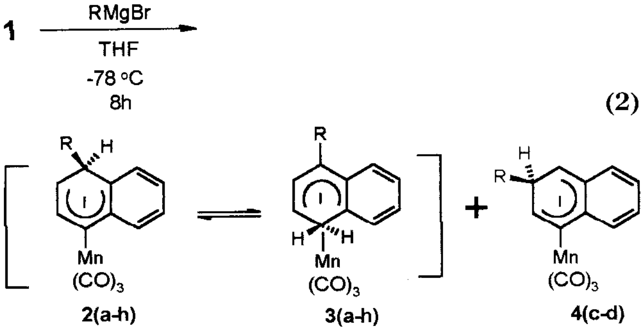
Table 1. Equilibrium Ratios at Room Temperature in $CDCl_3$



2(a-h) **3(a-h)**

entry	R		ratio 2	ratio 3	yield (%)
1	Me	**a**	1.24	1	48
2	*t*-Bu	**b**	1	0	43
3	Ph	**c**	1	1.08	69
4	*p*-tolyl	**d**	1	1.13	69
5	3,5-dimethylphenyl	**e**	1	1.15	47
6	4-*tert*-butylphenyl	**f**	1	1.21	44
7	4-methoxyphenyl	**g**	1	1.45	48
8	4-thioanisolyl	**h**	1	1.42	54

−78 °C, a mixture of **2a**−**h** and **3a**−**h** was isolated (eq 2 and Table 1). Interestingly, when R was phenyl or *p*-tolyl, a trace amount of **4c** or **4d** was observed. Similar temperature-dependent reactions were found in the reaction of CpFe(arene)$^+$ with nucleophiles.[5]



(2)

Treatment of **1** with MeMgBr in THF at −78 °C afforded the isolation of **2a** and **3a** in a ratio of 5:4. They were inseparable because they formed an equilibrium mixture, presumably via a 1,4-hydride shift, as suggested by Kreiter's and Cooper's groups.

Slow diffusion of pentane into a diethyl ether solution of a mixture of **2d** and **3d** followed by slow evaporation in a freezer led to the growth of single crystals of the regioisomer **3d** suitable for an X-ray study. The X-ray crystal structure of **3d** (Figure 1) confirms the molecular structure of **3d** in the solid state. Table 2 gives a summary of the crystallographic data. The bond distances and angles of **3d** are ordinary and require no comment. When the single crystals of **3d** were dissolved in d_{12}-cyclohexane after an X-ray crystallographic study, the ^{1}H NMR spectrum (Figure 2) of the solution showed the presence of **2d** and **3d** in a ratio of 32:68, which was the same ratio as the initial mixture in d_{12}-cyclohexane (see the Supporting Information).

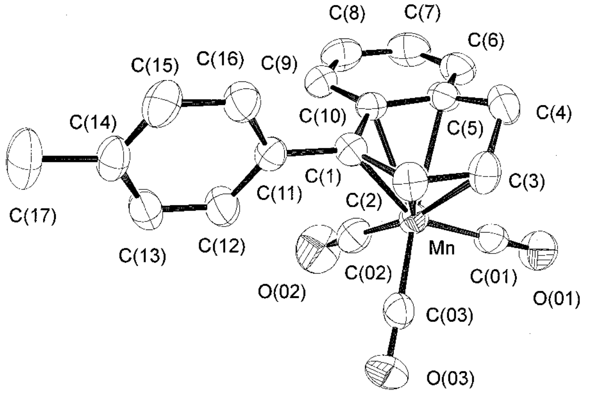
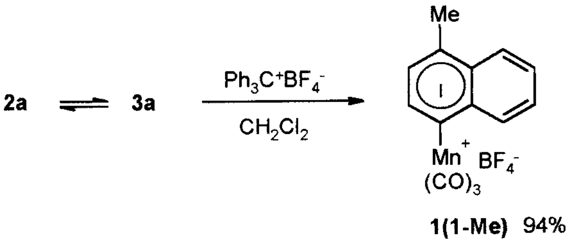


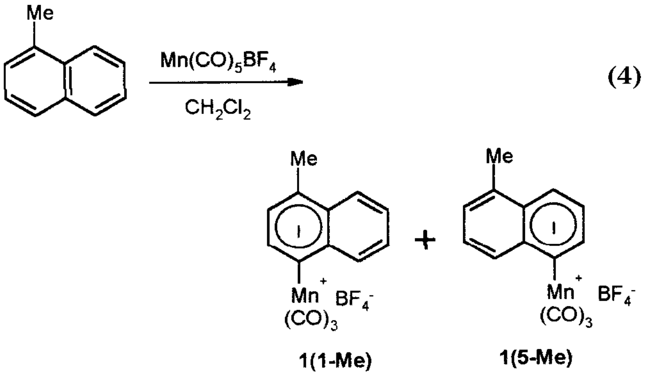
Figure 1. ORTEP drawing of **3d** with the atomic labeling scheme. Selected bond distances (Å) and angles (deg): Mn−C(03) = 1.785(3), Mn−C(02) = 1.796(3), Mn−C(01) = 1.808(3), Mn−C(2) = 2.119(3), Mn−C(1) = 2.130(3), Mn−C(3) = 2.190(3), Mn−C(10) = 2.247(2), Mn−C(5) = 2.375(2); C(03)−Mn−C(02) = 86.03(13), C(03)−Mn−C(01) = 93.77(11), C(02)−Mn−C(01) = 96.83(13).

The ratio **2a**−**h**:**3a**−**h** seemed to be slightly dependent upon the steric and electronic properties of the R group. When R was an alkyl group, steric effect such as allylic 1,3-strain[6] may prevail. When R was an aryl group, electronic properties may be more prevalent than steric effects.

The equilibrium between **2a**−**h** and **3a**−**h** can be seen in a reaction of a mixture of **2a**−**h** and **3a**−**h** with trityl cation. Thus, treatment of a mixture of **2a** and **3a** in CH_2Cl_2 with Ph_3CBF_4 resulted in the isolation of **1(1-Me)** in 94% yield (eq 3). Usually, trityl cation abstracts hydrogen from an exo hydrogen.[7] Thus, the high yield suggests that **2a** has to rearrange to **3a** as **3a** is used up. Reaction of 1-methylnaphthalene with $Mn(CO)_5BF_4$ in CH_2Cl_2 gave a mixture of **1(1-Me)** and **1(5-Me)** in 90% yield with a ratio 1:1 (eq 4).[8] Thus, eq 3 can be used



(3)



(4)

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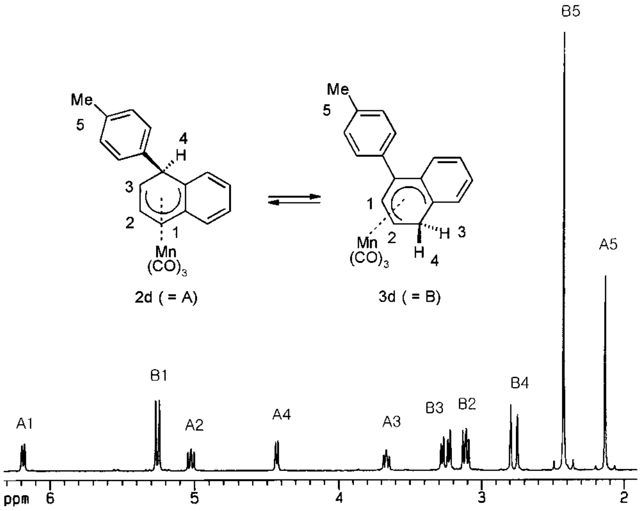

Figure 2. ^{1}H NMR spectrum of an equilibrium mixture of **2d** and **3d** in d_{12}-cyclohexane.

Table 2. Crystal Data and Structure Refinement Details for 3d

empirical formula	$C_{20}H_{15}Mn O_3$
fw	358.26
temp	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 7.9529(8)$ Å
	$b = 9.7075(10)$ Å
	$c = 21.934(2)$ Å
	$\alpha = 90.019(8)°$
	$\beta = 99.289(8)°$
	$\gamma = 89.988(8)°$
V	1671.2(3) Å^3
Z	4
density (calcd)	1.424 mg/m^3
abs coeff	0.803 mm^{-1}
$F(000)$	736
θ range for data collection	1.88−24.97°
index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 11$, $-26 \leq l \leq 25$
no. of rflns collected	3171
no. of indep rflns	2944 (R(int) = 0.0380)
refinement method	full-matrix least squares on F^2
no. of data/restraints/ params	2943/0/277
goodness of fit on F^2	1.084
final R indices ($I > 2\sigma(I)$)	R1 = 0.0332, wR2 = 0.0829
R indices (all data)	R1 = 0.0524, wR2 = 0.0930
largest diff peak and hole	0.343 and −0.210 e Å^{-3}

to synthesize [(η^6-1-methylnaphthalene)Mn(CO)$_3$]BF$_4$. This reaction can be generalized to the synthesis of [(η^6-1-R-naphthalene)Mn(CO)$_3$]BF$_4$.

In conclusion, we have demonstrated that the nucleophilic addition to [(η^6-$C_{10}H_8$)Mn(CO)$_3$]BF$_4$ (**1**) is quite dependent upon the reaction temperature. At 0 °C, the hydrogen adduct **2(H)** was isolated as a product, and at −78 °C an equilibrium mixture of **2a**−**h** and **3a**−**h** was isolated. The equilibrium ratio **2a**−**h**:**3a**−**h** is quite dependent upon the steric bulkiness of R. Treatment of a mixture of **2a**−**h** and **3a**−**h** with trityl cation gave [(η^6-1-R-naphthalene)Mn(CO)$_3$]BF$_4$ as the sole product.

Experimental Section

General Considerations. All solvents were purified by standard methods, and all synthetic procedures were carried out 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, and Inter-University Center Natural Science Facilities, Seoul National University. ^{1}H NMR spectra were obtained with Bruker 500 and 300 MHz instruments. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. The compounds **1(H)**, **1(Me)**, **2(H)**, and **2a** were previously reported.[1,8,9]

^{1}H NMR (CDCl$_3$) of **2(H)**: δ 7.30−7.06 (m, 4 H), 6.49 (d, 5.4 Hz, 1 H), 5.24 (t, 5.6 Hz, 1 H), 3.32 (m, 1 H, endo H), 3.29 (t, 5.5 Hz, 1 H), 2.75 (d, 13.0 Hz, 1 H, exo H) ppm.

Synthesis of a Mixture of 2a and 3a. The published method has been employed in the synthesis of **2a** and **3a**. Physical properties for **2a** have already been reported. We only report the ^{1}H NMR of **3a**. ^{1}H NMR (CDCl$_3$): δ 7.63 (d, 8.6 Hz, 1 H), 7.26−7.11 (m, 3 H), 5.28 (d, 7.4 Hz, 1 H), 3.21 (dd, 5.2, 14.3 Hz, 1 H), 3.14 (dd, 5.5, 6.9 Hz, 1 H), 2.93 (s, 3 H), 2.67 (d, 13.9 Hz, 1 H) ppm.

Synthesis of a Mixture of 2c, 3c, and 4c. To a solution of **1(H)** (0.30 g, 0.85 mmol) in 15 mL of THF was added dropwise PhMgBr (0.34 mL in 3.0 M in Et$_2$O, 0.10 mmol) at −78 °C for 5 min. The resulting solution was stirred at −78 °C for 4 h, quenched with 10 mL of saturated NH$_4$Cl solution, and extracted with 20 mL of Et$_2$O. The ethereal solution was dried over anhydrous MgSO$_4$, evaporated, and chromatographed on a silica gel column with hexane as eluent. Removal of the solvent gave a red oil (0.20 g, 69%). The distribution of products was calculated by the integration of characteristic peaks for **2c**, **3c**, and **4c**. Yield of **4c**: ca. 5%.

IR (NaCl): ν(CO) 2000, 1906 cm^{-1}. HRMS: m/z 344.0242 (M$^+$). ^{1}H NMR (CDCl$_3$) of **2c**: δ 7.53−7.07 (m, 7 H), 6.60 (d, 6.8 Hz, 2 H), 6.35 (d, 5.4 Hz, 1 H), 5.19 (t, 5.9 Hz, 1 H), 4.54 (d, 5.3 Hz, 1 H), 3.81 (t, 5.8 Hz, 1 H) ppm. ^{1}H NMR (CDCl$_3$) of **3c**: δ 7.88 (d, 6.9 Hz, 2 H), 7.53−7.07 (m, 7 H), 5.39 (d, 7.6 Hz, 1 H), 3.33−3.29 (m, 2 H), 2.82 (d, 12.8 Hz, 1 H) ppm. ^{1}H NMR (CDCl$_3$) of **4c**: δ 7.72 (d, 8.5 Hz, 1 H), 7.54−7.03 (m, 6 H), 6.73 (d, 6.5 Hz, 2 H), 5.73 (d, 7.3 Hz, 1 H), 3.97 (t, 5.8 Hz, 1 H), 3.87 (dd, 5.3, 7.3 Hz, 1 H), 3.68 (d, 5.5 Hz, 1 H) ppm.

2b: yellowish red oil; yield 43%; IR (NaCl) ν(CO) 2000, 1909 cm^{-1}; HRMS (EI) m/z 324.0551 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.27−7.04 (m, 4 H), 6.20 (d, 5.4 Hz, 1 H), 5.22 (t, 5.9 Hz, 1 H), 3.50 (t, 5.8 Hz, 1 H), 3.07 (d, 5.2 Hz, 1 H), 0.44 (s, 9 H) ppm; ^{13}C NMR (cyclohexane-d_{12}) δ 223.5, 136.5, 129.7, 128.4, 125.8, 111.5, 95.9, 92.5, 73.4, 52.2, 51.5, 38.9, 26.3 ppm.

2d, **3d**, and **4d**: reddish yellow solids; mp 123−124 °C; yield 69%; IR (NaCl) ν(CO) 2002, 1908 cm^{-1}; Anal. Calcd for $C_{20}H_{15}MnO_3$: C, 67.05; H, 4.22. Found: C, 67.43; H, 4.04. ^{1}H NMR (CDCl$_3$) of **2d**: δ 7.45−7.09 (m, 4 H), 6.92 (d, 7.9 Hz, 2 H), 6.50 (d, 8.0 Hz, 2 H), 6.35 (d, 5.0 Hz, 1 H), 5.19 (t, 5.7 Hz, 1 H), 4.50 (d, 5.3 Hz, 1 H), 3.80 (t, 5.3 Hz, 1 H), 2.20 (s, 3 H) ppm. ^{1}H NMR (CDCl$_3$) of **3d**: δ 7.75 (d, 8.1 Hz, 2 H), 7.34 (d, 7.8 Hz, 2 H), 7.45−7.09 (m, 4 H), 5.37 (d, 7.4 Hz, 1 H), 3.32−3.27 (m 2 H), 2.82 (d, 13.2 Hz, 1 H), 2.48 (s, 3 H) ppm. ^{1}H NMR (CDCl$_3$) of **4d**: δ 7.72 (d, 8.0 Hz, 1 H), 7.25 (d, 7.9 Hz, 1 H), 7.68−6.90 (m, 4 H), 6.79 (d, 7.9 Hz, 1 H), 6.52 (d, 8.0 Hz, 1 H), 5.54 (d, 7.4 Hz, 1 H), 3.86 (t, 5.8 Hz, 1 H), 3.70 (dd, 7.4, 5.4 Hz, 1 H), 3.53 (d, 5.6 Hz, 1 H), 2.13 (s, 3 H) ppm.

2e and **3e**: orange solids; mp 107−108 °C; yield 47%; IR (NaCl) ν(CO) 2000, 1908 cm^{-1}. Anal. Calcd for $C_{21}H_{17}MnO_3$: C, 67.75; H, 4.60. Found: C, 67.59; H, 4.63. ^{1}H NMR (CDCl$_3$) of **2e**: δ 7.48−7.11 (m, 7 H), 6.36 (d, 5.6 Hz, 1 H), 5.20 (t, 5.6 Hz, 1 H), 4.48 (d, 5.3 Hz, 1 H), 3.79 (t, 5.3 Hz, 1 H), 2.06 (s, 6 H) ppm. ^{1}H NMR (CDCl$_3$) of **3e**: δ 7.48−7.11 (m, 7 H), 5.38 (d, 6.3 Hz, 1 H), 3.32−3.24 (m, 2 H), 2.77 (d, 13.0 Hz, 1 H), 2.44 (s, 6 H) ppm.

2f and **3f**: orange solids; mp 127−128 °C; yield 44%; IR (NaCl) ν(CO) 2004, 1920 cm^{-1}. Anal. Calcd for $C_{23}H_{21}MnO_3$: C, 69.00; H, 5.29. Found: C, 69.13; H, 5.29. ^{1}H NMR (CDCl$_3$)

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of **2f**: δ 7.80−6.53 (m, 8 H), 6.35 (d, 5.3 Hz, 1 H), 5.19 (t, 5.7 Hz, 1 H), 4.51 (d, 5.0 Hz, 1 H), 3.81 (t, 5.6 Hz, 1 H), 1.20 (s, 9 H) ppm. ^{1}H NMR ($CDCl_3$) of **3f**: δ 7.80−6.53 (m, 8 H), 5.39 (d, 6.1 Hz, 1 H), 3.32−3.28 (m, 2H), 2.81 (d, 13.0 Hz, 1 H), 1.43 (s, 9 H) ppm.

2g and **3g**: orange solids; mp 123−124 °C; yield 48%; IR (NaCl) νCO 1998, 1906 cm^{-1}. Anal. Calcd for $C_{20}H_{15}MnO_4$: C, 64.18; H, 4.04. Found: C, 64.22; H, 3.72. ^{1}H NMR ($CDCl_3$) of **2g**: δ 7.80−6.54 (m, 8 H), 6.36 (d, 5.3 Hz, 1 H), 5.20 (t, 5.6 Hz, 1 H), 4.48 (d, 5.2 Hz, 1 H), 3.81 (t, 5.4 Hz, 1 H), 3.68 (s, 2 H) ppm. ^{1}H NMR ($CDCl_3$) of **3g**: δ 7.80−6.54 (m, 8 H), 5.37 (d, 7.2 Hz, 1 H), 3.92 (3 H, s), 3.33−3.27 (m, 2 H), 2.80 (d, 13.0 Hz, 1 H) ppm.

2h and **3h**: orange solids; mp 113−114 °C; yield 54%; IR (NaCl) ν(CO) 1998, 1908 cm^{-1}. Anal. Calcd for $C_{20}H_{15}MnO_3S$: C, 61.54; H, 3.87. Found: C, 61.51; H, 3.78. ^{1}H NMR ($CDCl_3$) of **2h**: δ 7.72−6.45 (m, 8 H), 6.28 (d, 5.4 Hz, 1 H), 5.12 (t, 6.0 Hz, 1 H), 4.42 (d, 5.2 Hz, 1 H), 3.70 (t, 5.8 Hz, 1 H), 2.29 (s, 3 H) ppm. ^{1}H NMR ($CDCl_3$) of **3h**: δ 7.72−6.45 (m, 8 H), 5.30 (d, 6.3 Hz, 1 H), 3.27−3.21 (m, 2 H), 2.73(d, 13.0 Hz, 1 H), 2.51 (s, 3 H) ppm.

Synthesis of 1(Me) from a Mixture of 2a and 3a. To a solution of **2a** and **3a** (0.10 g, 0.35 mmol) in 5 mL of CH_2Cl_2 was added Ph_3CBF_4 (0.117 g, 0.39 mmol). The solution was stirred for 1 h and quenched with excess Et_2O (50 mL). Filtration gave the yellow solid **1(Me)** (0.12 g, 94%).

X-ray Crystal Structure of 3d. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer with a $\omega/2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 2. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. 144142. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, int. code + (1223)-336-033; e-mail, deposit@ccdc.ac.uk).

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **3d** and equilibrium ratios (between **2** and **3**) in various solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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