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Reaction of [(1-*H*-Hydronaphthalene)Mn(CO)$_3$] with Pyridine in the Presence of Halogenated Solvent: The Role of Ring-Slippage in [(1-*H*-Hydronaphthalene)Mn(CO)$_3$]

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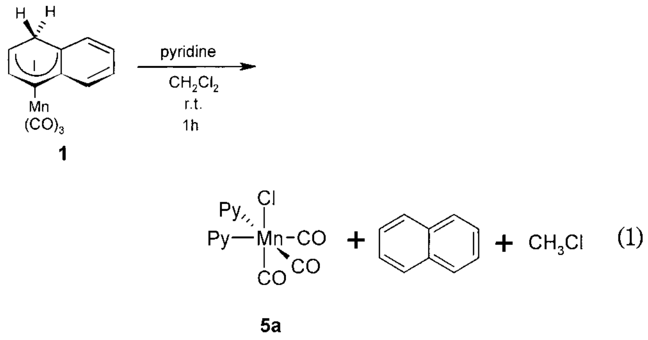
*Summary: Halogenated solvents such as dichloromethane, dibromomethane, bromochloromethane, chloroform, and carbon tetrachloride react with [(1-H-hydronaphthalene)Mn(CO)$_3$] (**1**) and pyridines (py′) to give the halogeno complex [Mn(CO)$_3$(py′)$_2$X] (X = Cl, Br) and naphthalene. The C−H and C−X cleavage reactions are dependent upon the electronic and steric properties of the pyridine. The structure of fac-[Mn(CO)$_3$(4-Me-py)$_2$Cl] (**5b**) has been established by X-ray diffraction study.*

Introduction

Recently we and others reported the chemistry of the η^5-1-*H*-hydronaphthalene complex $[(\eta^5\text{-}C_{10}H_9)Mn(CO)_3]$ (**1**).[1,2] In the reaction of **1** with P(OMe)$_3$, compounds $[(\eta^3\text{-}C_{10}H_9)Mn(CO)_3P(OMe)_3]$ (**2**), $[(\eta^5\text{-}C_{10}H_9)Mn(CO)_2P(OMe)_3]$ (**3**), and $[(\eta^3\text{-}C_{10}H_9)Mn(CO)_2\{P(OMe)_3\}_2]$ (**4**) were isolated and characterized. We recently attempted to synthesize pyridine analogues of **2**−**4**. To our surprise, when we used dichloromethane as a medium, [Mn(CO)$_3$(py)$_2$Cl] (**5**)[3] was isolated as the product. The formation of **5** implies that there must be C−H and C−Cl bond cleavage during the reaction. Herein we report the details of this unexpected reaction of **1** with halogenated solvents.

Results and Discussion

Treatment of **1** with pyridine in CH$_2$Cl$_2$ at room temperature for 1 h gave **5a** and naphthalene (eq 1).



(1)

The molecular structure of **5a** was inferred from the X-ray structure of the 4-methylpyridine derivative **5b** (Figure 1). Crystal data and selected bond distances and angles for **5b** are presented in Tables 1 and 2. The molecule consists of a manganese atom octahedrally coordinated to three (*facial*) terminal carbonyl groups, a chlorine atom, and two (*cis*) 4-methylpyridine ligands. The chlorine ligand is *trans* to a carbonyl, while the remaining two carbonyls and two pyridine ligands occupy *cis* positions. The Mn−Cl bond length of 2.3868(12) Å is slightly shorter than found for a Mn−Cl single bond in other organomanganese complexes, e.g., *fac*-[ClMn(CO)$_3$(L−L)] (L−L = 1,3-bis(dimethylarsino)propane, 2.415(9) Å; L−L = depe, 2.406(2) Å).[4,5]

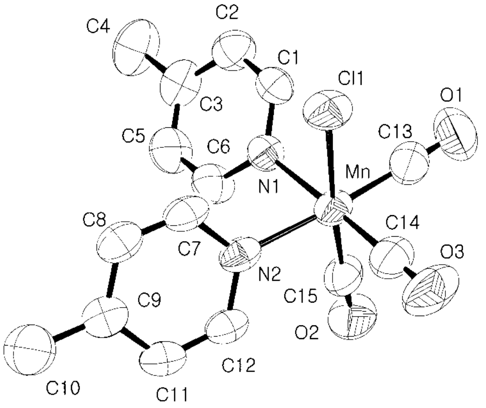
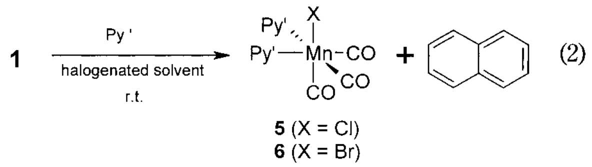


Figure 1. ORTEP drawing of **5b** (50% probability levels) with the atomic numbering.

We investigated the influence of the steric and electronic properties of pyridine nucleophiles (py′) (eq 2 and Table 3). With a more basic pyridine such as 3,4-dimethylpyridine and 3,5-dimethylpyridine, the reaction was observed to occur more rapidly. With 2-methyl-



(2)

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[1] (a) Sun, S.; Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Lee, S. S.; Chung, Y. K. *Inorg. Chim. Acta* **1997**, *262*, 213. (b) Son, S. U.; Paik, S.-J.; Lee, I. S.; Lee, Y.-A.; Chung, Y. K.; Seok, W. K.; Lee, H. N. *Organometallics* **1999**, *18*, 414. (c) Son, S. U.; Paik, S.-J.; Chung, Y. K. *J. Mol. Catal.* **2000**, *150*, 87.

[2] Georg, A.; Kreiter, C. G. *Eur. J. Inorg. Chem.* **1999**, 651.

[3] [Mn(CO)$_3$py$_2$Cl]: (a) McLean, R. A. N. *J. Chem. Soc.* **1974**, 1568. (b) Parker, P. J.; Wojoicki, A. *Inorg. Chim. Acta* **1974**, *11*, 9. (c) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501. [Mn(CO)$_3$py$_2$Br]: (d) Angelici, R. J. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2627. (e) Dalton, J.; Paul, I.; Smith, J. G.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1208.

[4] Bear, C. A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1973**, 673.

[5] Li, G. Q.; Feldman, J.; Krause, J. A.; Orchin, M. *Polyhedron* **1997**, *16*, 2041.

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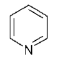
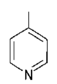
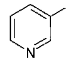
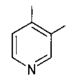
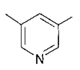
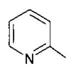
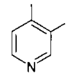
Table 1. Crystal Data and Structure Refinement for 5b

empirical formula	$2[C_{15}H_{14}ClMnN_2O_3]\cdot CH_2Cl_2$
fw	806.27
temperature	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	$a = 23.431(9)$ Å $b = 11.097(2)$ Å, $\beta = 90.19(2)°$ $c = 14.259(2)$ Å
volume	3708(2) $Å^3$
Z	4
density (calcd)	1.444 Mg/m^3
abs coeff	1.014 mm^{-1}
F(000)	1640
θ range for data collection	1.74−25.00°
index ranges	$0 \leq h \leq 27$, $0 \leq k \leq 13$, $-16 \leq l \leq 16$
no. of reflns collected	3351
no. of ind reflns	3265 [R(int) = 0.0413]
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	3264/0/215
goodness-of-fit on F^2	1.043
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0498, wR2 = 0.1333
R indices (all data)	R1 = 0.0731, wR2 = 0.1497
largest diff peak and hole	0.678 and −0.414 e $Å^{-3}$

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 5b

Mn−C(15)	1.787(4)	Mn−C(14)	1.802(5)
Mn−C(13)	1.805(5)	Mn−N(1)	2.089(3)
Mn−N(2)	2.101(3)	Mn−Cl(1)	2.3865(12)
C(15)−Mn−C(14)	90.0(2)	C(15)−Mn−C(13)	90.0(2)
C(14)−Mn−C(13)	90.0(2)	C(15)−Mn−N(1)	91.6(2)
C(14)−Mn−N(1)	177.3(2)	C(13)−Mn−N(1)	92.2(2)
C(15)−Mn−N(2)	93.8(2)	C(14)−Mn−N(2)	91.7(2)
C(13)−Mn−N(2)	175.8(2)	N(1)−Mn−N(2)	86.04(12)
C(15)−Mn−Cl(1)	176.03(14)	C(14)−Mn−Cl(1)	89.22(14)
C(13)−Mn−Cl(1)	86.10(14)	N(1)−Mn−Cl(1)	89.36(9)
N(2)−Mn−Cl(1)	90.06(9)		

Table 3. C−X Cleavage Reaction

entry	pyridines	solvents	time(h)	product	yield(%)[a]
1		CH_2Cl_2	1	5a	76
2		CH_2Cl_2	1	5b	72
3		CH_2Cl_2	3	5c	74
4		CH_2Cl_2	1	5d	84
5		CH_2Cl_2	2.5	5e	84
6		CH_2Cl_2	18		n.r.
7		$CHCl_3$	1	5d	81
8		CCl_4	1	5d	72
9		CH_2Br_2	1	6d	86
10		CH_2BrCl	1	5d/6d(2:1)	83

[a] Isolated yield.

pyridine, no reaction was observed, presumably due to the steric reasons. We conclude that the reaction in eq 2 is sensitive to the electronic and steric properties of the pyridine.

Stimulated by the above observations, other halogenated solvents such dibromomethane, bromochloromethane, chloroform, carbon tetrachloride, and chlorobenzene were studied with 3,4-dimethylpyridine. In all cases except chlorobenzene, the C−X bond was cleaved within 1 h and the corresponding product was obtained in 72−86% yield. With carbon tetrachloride, the formation of $CHCl_3$ was confirmed by ^1H NMR spectroscopy. When bromochloromethane was used as a solvent, C−Cl and C−Br cleaved products were obtained in the ratio of 2:1, as determined by the inspection of the ^1H NMR spectra of **5d** and **6d**.

It has been reported[6,7] that the reaction of $[Mn(CO)_5CH_2Cl]$ with PPh_3 in CH_3CN at room temperature gave $[Mn(CO)_3(PPh_3)_2Cl]$. This suggests $[Mn(CO)_3(py)_2CH_2Cl]$ as a plausible intermediate in eq 1. However, treatment of **1** with 3,4-dimethylpyridine in CH_2Cl_2 at −42 °C led to the isolation of **5d** as a sole product, with no halogenoalkyl intermediates being observed.

Dehalogenation reactions are shown to be promoted by metals in the presence of hydride donors.[8] Thus, many hydrides react with excess CCl_4 to give $CHCl_3$ and the metal chloride.[9] For example, Orchin et al.[10] have demonstrated that treatment of $Mn(CO)_3(dppe)H$ in refluxing CCl_4 affords $Mn(CO)_3(dppe)Cl$ and $CHCl_3$. To observe the formation of a manganese hydride intermediate, the reaction of **1** with 3,4-dimethylpyridine was carried out in benzene-d_6. During the reaction, a small peak appeared at δ −4.5 ppm. This is likely due to a manganese hydride, even though most manganese hydride species appear at higher fields than −4.5 ppm. The peak remained for only a limited time and then disappeared. This observation suggests the generation of a manganese hydride species in eq 1.

A plausible mechanism for the formation of **5** is provided in Scheme 1. The first step is formation of $[(\eta^3\text{-}C_{10}H_8)Mn(CO)_3(py)]$ in analogy with the formation of **2** from the reaction of **1** with $P(OMe)_3$. The second step might be an *endo* C−H activation by the basic metal to yield $[(\eta^2\text{-}C_{10}H_8)Mn(H)(CO)_3(py)]$, which rapidly reacts with py to give $[HMn(CO)_3(py)_2]$ and naphthalene. $[HMn(CO)_3(py)_2]$ then reacts further with CH_2Cl_2 to give $[ClMn(CO)_3(py)_2]$ and CH_3Cl. In accordance with this scheme, the manganese complexes such as (indenyl)$Mn(CO)_3$, $CpMn(CO)_3$, (cyclohexadienyl)$Mn(CO)_3$, and $[(C_{10}H_8)Mn(CO)_3]BF_4$ were found to activate neither C−X nor C−H cleavage.

When the reaction was carried out using a mixture of $[(exo\text{-}p\text{-}MeOC_6H_4\text{-}\eta^5\text{-}C_{10}H_8)Mn(CO)_3]$ (**7a**) and [(*exo*-

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[6] Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221.

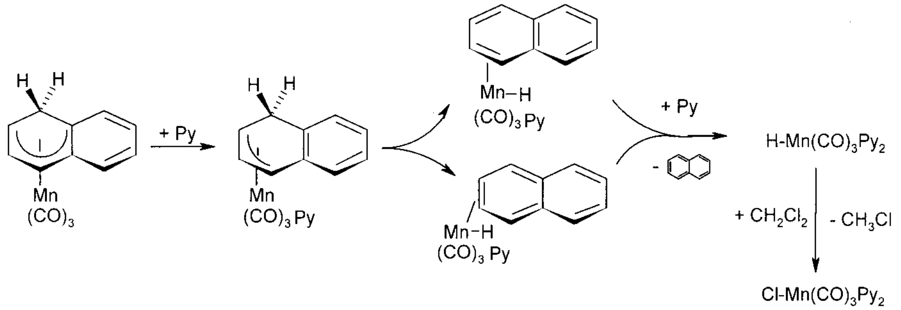
[7] Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495.

[8] (a) Love, C. J.; McQuillin, F. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2509. (b) Imai, H.; Nishiguchi, T.; Tanaka, M.; Fukuzumi, K. *J. Org. Chem.* **1977**, *42*, 2309. (c) Carfagna, C.; Musco, A.; Pontellini, R.; Terzoni, G. *J. Mol. Catal.* **1989**, *54*, L23. (d) Qian, C.; Zhu, D.; Gu, Y. *J. Mol. Catal.* **1990**, *63*, L1. (e) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. (f) Scrivanti, A.; Vicentini, B.; Beghetto, V.; Chessa, G.; Matteoli, U. *Inorg. Chem. Commun.* **1998**, *1*, 246. (g) Esteruelas, M. A.; Herrero, J.; López, F. M.; Martín, M.; Oro, L. A. *Organometallics* **1999**, *18*, 1110.

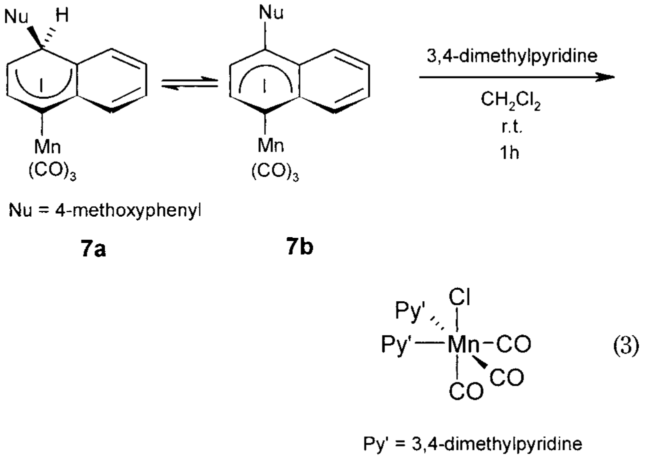
[9] (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John and Wiley & Sons: New York, 1994; p 63. Halogen−hydrogen exchange reactions starting with $MnH(CO)_{5-n}(L)_n$: (b) Hieber, W.; Faulhaber, G.; Theubert, F. *Z. Anorg. Allg. Chem.* **1962**, *314*, 125. (c) Osborne, A. G.; Stibbard, M. H. B. *J. Chem. Soc.* **1964**, 634. (d) Booth, B. L.; Haszeldine, R. N. *J. Chem. Soc. (A)* **1966**, 157. (e) Clegg, W.; Morton, S. *J. Chem. Soc., Dalton Trans.* **1978**, 1452.

[10] Li, G. Q.; Feldman, J.; Krause, J. A.; Orchin, M. *Polyhedron* **1997**, *16*, 2041.

Scheme 1



H-η^5-3-(p-MeOC$_6$H$_4$C$_{10}$H$_7$)Mn(CO)$_3$] (**7b**) as a hydride source, **5d** was obtained as a product (eq 3). This suggests that ring-slippage in the η^5-benzocyclohexadienyl ring may play a crucial role in the C−H cleavage reaction.



Nu = 4-methoxyphenyl

7a **7b**

Py' = 3,4-dimethylpyridine

5d

In conclusion we have demonstrated that the reaction of **1** with pyridines in the halogenated solvents leads to the isolation of [Mn(CO)$_3$(py')$_2$X] through C−H and C−X bond activation. The C−H activation in the η^5-1-H-hydronaphthalene ring in **1** may be related to facile ring-slippage, and the C−X activation may occur via a manganese hydride intermediate.

Experimental Section

General Comments. All reactions were performed under nitrogen using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. Routine ^{1}H NMR spectra were recorded with a Bruker 300 or 500 spectrometer. Elemental analyses were done at the Inter-University Center Natural Science Facilities, Seoul National University. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus 6427-H10 and not corrected. Compounds [(C$_{10}$H$_9$)Mn(CO)$_3$] (**1**) and a mixture of **8a** and **8b** were prepared according to literature procedures.[1a]

Synthesis. Typical procedure: To 5 mL of CH$_2$Cl$_2$ in a Schlenk flask were added **1** (0.20 g, 0.76 mmol) and pyridine (0.18 mL, 2.3 mmol). The resulting solution was stirred for 1 h at room temperature. After evaporation of the solvent, the residue was dissolved in dichloromethane (1 mL) and then precipitated by adding excess diethyl ether (15 mL). The precipitates were filtered out, washed with pentane, and dried (0.19 g, 75%). The residue was chromatographed on a silica gel column eluting with diethyl ether. Removal of the solvent gave the product.

***fac*-[Mn(CO)$_3$(py)$_2$Cl] (5a)**. Yield: 75%; mp 141 °C. IR: ν(CO) 2024, 1941, 1899 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.78 (d, 5.1 Hz, 4 H), 8.00 (t, 7.5 Hz, 2 H), 7.51 (m, 4 H) ppm. Anal. Calcd for C$_{13}$H$_{10}$ClMnN$_2$O$_3$: C, 46.94; H, 3.03; N, 8.42. Found: C, 46.69; H, 3.01; N, 8.29.

***fac*-[Mn(CO)$_3$(4-Me-py)$_2$Cl] (5b)**. Yield: 72%; mp 141 °C. IR: ν(CO) 2022, 1938, 1898 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.59 (s, 4 H), 7.28 (br s, 4 H), 2.43 (s, 6 H) ppm. Anal. Calcd for C$_{15}$H$_{14}$ClMnN$_2$O$_3$: C, 49.95; H, 3.91; N, 7.77. Found: C, 49.47; H, 3.90; N, 7.63.

***fac*-[Mn(CO)$_3$(3-Me-py)$_2$Cl] (5c)**. Yield: 74%; mp 144 °C. IR: ν(CO) 2022, 1939, 1897 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.67 (s, 2 H), 8.53 (s, 2 H), 7.80 (s, 2 H), 7.37 (s, 2 H), 2.33 (s, 6 H) ppm. Anal. Calcd for C$_{15}$H$_{14}$ClMnN$_2$O$_3$: C, 49.95; H, 3.91; N, 7.77. Found: C, 49.86; H, 4.01; N, 7.64.

***fac*-[Mn(CO)$_3$(3,4-Me$_2$-py)$_2$Cl] (5d)**. Yield: 84%; mp 157 °C. IR: ν(CO) 2022, 1938, 1894 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.55 (s, 2 H), 8.38 (d, 3.0 Hz, 2 H), 7.23 (d, 3.0 Hz, 2 H), 2.35 (s, 6 H), 2.25 (s, 6 H) ppm. Anal. Calcd for C$_{17}$H$_{18}$ClMnN$_2$O$_3$: C, 52.53; H, 4.67; N, 7.21. Found: C, 52.58; H, 4.83; N, 7.16.

***fac*-[Mn(CO)$_3$(3,5-Me$_2$-py)$_2$Cl] (5e)**. Yield: 84%; mp 156 °C. IR: ν(CO) 2024, 1939, 1904 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.42 (s, 4 H), 7.61 (s, 2 H), 2.28 (s, 12 H) ppm. Anal. Calcd for C$_{17}$H$_{18}$ClMnN$_2$O$_3$: C, 52.53; H, 4.67; N, 7.21. Found: C, 52.16; H, 4.89; N, 6.92.

***fac*-[Mn(CO)$_3$(3,4-Me$_2$-py)$_2$Br] (6d)**. Yield: 86%; mp 154 °C. IR: ν(CO) 2018, 1935, 1903 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.59 (s, 2 H), 8.41 (d, 5.4 Hz, 2 H), 7.23 (d, 5.4 Hz, 2 H), 2.36 (s, 6 H), 2.25 (s, 6 H) ppm. Anal. Calcd for C$_{17}$H$_{18}$BrMnN$_2$O$_3$: C, 47.14; H, 4.19; N, 6.47. Found: C, 46.98; H, 4.57; N, 6.90.

Crystal Structure Determination of 5b. Crystals of **5b** were grown by slow evaporation of a solution of **5b** in pentane and dichloromethane (2:3, v/v). Diffraction was measured by an Enraf-Nonius CAD4 diffractometer with the $\omega-2\theta$ scan method. The unit cell was determined by centering 25 reflections in the approximate 2θ range. Systematic absences and diffraction symmetry were uniquely consistent for the reported space group, whose correctness was subsequently confirmed by computationally stable results of refinements. The structure was solved by direct methods using SHELX-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 the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Details on the crystal data for **5b** are given in Table 1.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (KOSEF) (1999-1-122-001-5) and the KOSEF through the Center for Molecular Catalysis. S.U.S. thanks the BK21 Fellowship.

Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, anisotropic displacement, and hydrogen coordinates for **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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