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Reactivity of [(1,2,3,4-tetrahydronaphthalene)Mn(CO)$_3$]PF$_6$: molecular structure of [(1,2,3,4-tetrahydronaphthalene)Mn(CO)$_2$(C(O)Me)]

Tae-Young Lee [a], Su Seong Lee [a], Young Keun Chung [a,*], Soon W. Lee [b]

[a] *Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, South Korea*
[b] *Department of Chemistry, Sung Kyun Kwan University, Su-Won 440-746, South Korea*

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Abstract

[(1,2,3,4-Tetrahydronaphthalene)Mn(CO)$_3$]PF$_6$ (**1**) was synthesized in 78% yield, starting from Mn(CO)$_5$Br, AlCl$_3$ and tetralin in refluxing cyclohexane. The reactivity of **1** with nucleophiles has been studied. When **1** was reacted with nucleophiles such as NaBH$_3$CN (NaBD$_4$), PhMgBr, NaP(O)(OMe)$_2$, and LiCH$_2$CN, α-position adducts were always obtained. However, when the nucleophile was MeMgBr, α-position adduct and acyl compound (**4**) were obtained in the ratio of 5.2 : 1. Compound **4** crystallizes in the orthorhombic system, space group $P2_12_12_1$ with cell parameters $a = 7.141(6)$, $b = 11.741(4)$, $c = 15.158(3)$ Å, and $Z = 4$. Least-squares refinement of the structure led to a R (wR_2) factor of 0.0357 (0.0791) for 902 unique reflections of $I > 2\sigma(I)$ and for 163 variables.

Keywords: Manganese; Tetrahydronaphthalene; Nucleophilic addition; X-ray structure; Acyl compound; Cyclohexadienyl

1. Introduction

In recent studies, we and others have established the utility of [(arene)Mn(CO)$_3$]$^+$ cations in difunctionalizing cyclohexadienes by nucleophilic addition to coordinated arenes [1]. In pursuing the chemistry of organomanganese, we have been very interested in the chemistry of [(polycyclic arene)Mn(CO)$_3$]$^+$. Although coordination chemistries of polycyclic aromatic hydrocarbons with iron [2], ruthenium [3], and chromium [4] have been reported, there has been less interest in the chemistry of [(polycyclic arene)Mn(CO)$_3$]$^+$ [5].

The [(1,2,3,4-tetrahydronaphthalene)Mn(CO)$_3$]$^+$ cation (**1**) has been known for several years [6], but there has been no report on the reactivity of **1**. In this paper, we report on this topic and on the molecular structure of the manganese acyl compound (1,2,3,4-tetrahydronaphthalene)Mn(CO)$_2$(C(O)Me) (**4**). This is the first report of the X-ray crystal structure of an (arene)manganese acyl compound.

2. Experimental section

All solvents were purified by standard methods and all synthetic procedures took place under a nitrogen atmosphere. THF was freshly distilled from sodium benzophenone ketyl prior to use, and reagent grade chemicals were used without further purification.

Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Mass spectra were recorded on a VG ZAB-E double-focusing mass spectrometer. ^{1}H NMR spectra were obtained using a Varian XL-200 instrument. Elemental analyses were performed at the Korea Basic Science Center.

2.1. Synthesis of [(1,2,3,4-tetrahydronaphthalene)Mn(CO)$_3$]PF$_6$ (1)

Mn(CO)$_5$Br (2.0 g, 7.3 mmol), tetralin (2 ml, 14.7 mmol), AlCl$_3$ (2.0 g, 15.0 mmol), and cyclohexane (50 ml) were placed in a flask and refluxed for 5 h. After cooling to room temperature, ice-water (30 ml) was added and the aqueous layer was collected. The aqueous solution was treated with aqueous NH$_4$PF$_6$ solution to precipitate compound **1**. The resulting precipi-

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* Corresponding author.

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tate was collected and recrystallized by diethyl ether/acetone. Yield: 78%. Mp. 250°C. IR: (NaCl): ν(CO) 2056, 2016 cm^{-1}, ν(PF) 842 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 6.72 (s, 4H, H^{1-4}), 3.08 (dm, $J = 17.7$ Hz, 1H, H^5 or H^8) and 2.91 (dm, $J = 17.7$ Hz, 1H, H^5 or H^8), 1.93 (m, 2H, $H^{6,7}$) ppm. Anal: Found: C, 37.44; H, 2.92. $C_{13}H_{12}F_6MnO_3P$ calcd.: C, 37.52; H, 2.91%.

2.2. Reaction between 1 and $NaBH_3CN$

Excess $NaBH_3CN$ was added to the suspension of **1** (0.30 g, 0.72 mmol) in 20 ml of THF at room temperature. After stirring for 10 min, diethyl ether (100 ml) and water (50 ml) were added to the reaction flask and the neutral compound was extracted with diethyl ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel eluting with hexane. The concentrated hexane solution of the purified compound was kept in the freezer overnight. Bright yellow crystalline solids were precipitated. After filtration, compound **2** (H) was obtained in the yield of 92%. Mp 60.0°C. IR (NaCl): ν(CO) 2000, 1910 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.60 (dd, $J = 1.2$, 5.1 Hz, 1H, H^1), 4.85 (ddd, $J = 1.0$, 5.4, 7.4 Hz, 1H, H^2), 2.83 (ddt, $J = 1.0$, 5.8, 7.2 Hz, 1H, H^3), 2.57 (dd, $J = 5.6$, 13.2 Hz, 1H, $H^{4\text{-endo}}$), 2.29 (d, $J = 13.0$ Hz, 1H, $H^{4\text{-exo}}$), 2.57 (m, 1H, H^8), 2.27–1.36 (m, 7H, $H^{5,6,7,8}$) ppm. HRMS: m/z (M^+) calcd. 272.0245, obsd. 272.0243. Anal: Found: C, 57.29; N, 4.82. $C_{13}H_{13}MnO_3$ calcd.: C, 57.37; H, 4.81%.

2.3. Reaction between 1 and $NaBD_4$

In the same way as above, $NaBD_4$ was added to **1**. After work-up, **2** (D) was obtained in the yield of 87.5%. Mp. 63.9°C. IR (NaCl): ν(CO) 1998, 1914 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.59 (dd, $J = 1.0$, 5.0 Hz, 1H, H^1), 4.84 (ddd, $J = 0.6$, 5.4, 6.4 Hz, 1H, H^2), 2.82 (ddd, $J = 1.4$, 5.6, 7.2 Hz, 1H, H^3), 2.53 (d, $J = 5.0$ Hz, 1H, $H^{4\text{-endo}}$), 2.56 (m, 1H, H^8), 2.44–1.28 (m, 7H, $H^{5,6,7,8}$) ppm. HRMS: m/z, (M^+) calcd. 273.0308, obsd. 273.0301. Anal: Found: C, 56.63; H, 4.80. Calcd. for $C_{13}H_{12}DMnO_3$: C, 57.16; H, 4.42%.

2.4. Reaction between 1 and MeMgBr

To the suspension of **1** (0.15 g, 0.36 mmol) in 20 ml of THF was added 2 equiv of MeMgBr at 0°C. The reaction mixture was stirred until the colour of the reaction mixture changed to orange. Excess diethyl ether (100 ml) and water (50 ml) were added to the reaction flask and the neutral compound was extracted with diethyl ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel eluting with hexane and diethyl ether. After evaporation of the hexane solution, compound **3** was obtained as a yellow solid (yield: 73%). From the ether extract, compound **4** was obtained as a yellow solid (yield: 14%) after evaporation of diethyl ether. Crystals suitable for X-ray analysis were grown in hexane.

3: IR (NaCl): ν(CO) 2000, 1920 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.51 (d, $J = 4.8$ Hz, 1H, H^1), 4.74 (dd, $J = 5.4$, 6.8 Hz, 1H, H^2), 3.02 (ddd, $J = 0.6$, 6.2, 6.8 Hz, 1H, H^3), 2.56 (m, 1H, H^4), 2.44–1.32 (m, 8H, $H^{5,6,7,8}$), 0.47 (d, $J = 6.4$ Hz, 3H, Me) ppm. HRMS: m/z (M^+) calcd. 286.0401, obsd. 286.0401.

4: IR (NaCl): ν(CO) 1955, 1895 cm^{-1}, ν(C=O) 1610 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.67 (td, $J = 2.0$, 5.0 Hz, 2H, $H^{2,3}$), 4.55 (m, 2H, $H^{1,4}$), 2.66 (s, 3H, C(O)Me), 2.31 (dt, $J = 5.6$, 16.8 Hz, 2H, H^{5or8}), 1.89 (dt, $J = 5.6$, 16.8 Hz, 2H, H^{5or8}), 1.38–1.12 (m, 4H, $H^{6,7}$) ppm. HRMS: m/z (M^+) calcd. 286.0401, obsd. 286.0514.

2.5. Reaction between 1 and PhMgBr

To the suspension of **1** (0.25 g, 0.60 mmol) in 20 ml of THF was added 3 equiv of PhMgBr at 0°C. After stirring for 10 min, diethyl ether (100 ml) and water (50 ml) were added to the reaction flask and the neutral compound was extracted with diethyl ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel eluting with hexane. The concentrated hexane solution of the purified compound was kept in the freezer overnight. Bright yellow crystalline solids were precipitated. After filtration, compound **5** was obtained in the yield of 70%. Mp. 116.6°C. IR (NaCl): ν(CO) 2004, 1916 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.21 (m, 3H, Ph), 6.93 (m, 2H, Ph), 5.53 (dd, $J = 1.0$, 5.4 Hz, 1H, H^1), 4.84 (dd, $J = 5.5$, 6.8 Hz, 1H, H^2), 3.76 (d, $J = 6.1$ Hz, 1H, H^4), 3.31 (ddd, $J = 1.5$, 5.9, 7.1 Hz, 1H, H^3), 2.70 (dt, $J = 6.3$, 17.6 Hz, 1H, H^8), 2.36–1.56 (m, 7H, H^{5-8}) ppm. HRMS: m/z (M^+) calcd. 348.0558, obsd. 348.0566. Anal: Found: C, 65.50; H, 4.89. $C_{19}H_{17}MnO_3$ calcd.: C, 65.53; H, 4.92%.

2.6. Reaction between 1 and $NaP(O)(OMe)_2$

To the suspension of **1** (0.30 g, 0.72 mmol) in 20 ml of THF was added 1.1 equiv of $NaP(O)(OMe)_2$ (generated in situ by the reaction of NaH and $HP(O)(OMe)_2$) at room temperature. After stirring for 30 min, diethyl ether (100 ml) and water (50 ml) were added to the reaction flask and the neutral compound was extracted with diethyl ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel eluting with diethyl ether. The concentrated hexane solution of the purified compound was kept in the freezer overnight. Bright yellow crystalline solids were precipitated. After filtration, compound **6** was obtained in the yield of 73%. Mp.

77.4°C. IR (NaCl): ν(CO) 2004, 1913 cm^{-1}, ν(P=O) 1244 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.66 (dd, $J = 1.2$, 5.4 Hz, 1H, H^1), 4.95 (ddd, $J = 0.6$, 5.6, 6.2 Hz, 1H, H^2), 3.67 (d, $J = 10.5$ Hz, 3H, POMe), 3.66 (d, $J = 10.5$ Hz, 3H, POMe), 3.23 (dd, $J = 5.6$, 11.4 Hz, 1H, H^4), 2.82 (br t, $J = 6.2$ Hz, 1H, H^3), 2.65 (m, 1H, H^8), 2.42–1.39 (m, 9H, $H^{5,6,7,8}$) ppm. HRMS: m/z (M^+) calcd. 296.0372, obsd. 296.0364.

2.7. Reaction between 1 and $LiCH_2CN$

To the suspension of **1** (0.30 g, 0.72 mmol) in 20 ml of THF at −78°C was added 1.1 equiv of $LiCH_2CN$ (generated in situ by the reaction of LDA and CH_3CN at −78°C). While stirring for 30 min, the reaction mixture was allowed to warm to room temperature. Diethyl ether (100 ml) and water (50 ml) were added to the reaction flask and the neutral compound was extracted with diethyl ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel eluting with hexane. The concentrated hexane solution of the purified compound was kept in the freezer overnight. Bright yellow crystalline solids were precipitated. After filtration, compound **7** was obtained in the yield of 21%. Mp. 123.9°C. IR (NaCl): ν(CN) 2238 cm^{-1}, ν(CO) 2002, 1926 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.58 (d, $J = 5.4$ Hz, 1H, H^1), 4.93 (dd, $J = 5.4$, 6.3 Hz, 1H, H^2), 3.06 (ddd, $J = 1.$, 5.6, 6.0 Hz, 1H, H^3), 2.95 (ddd, $J = 5.2$, 5.6, 7.0 Hz, 1H, H^4), 2.68 (m, 1H, H^8), 2.48–1.36 (m, 7H, $H^{5,6,7,8}$), 1.89 (dd, $J = 5.2$, 16.7 Hz, 1H, CH_2CN), 1.73 (dd, $J = 6.9$, 16.7 Hz, 1H, CH_2CN) ppm. HRMS: m/z(M^+) calcd. 311.0354, obsd. 311.0349. Anal. Found: C, 57.60; H, 4.61; N, 4.43. $C_{15}H_{14}MnNO_3$ calcd.: C, 57.89; H, 4.53; N, 4.50%.

2.8. X-ray structure analysis for 4

All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centred reflections with $8° < 2\theta < 24°$. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out on a personal computer with use of the SHELXS-86, SHELXL-93 programs.

Table 1
Crystallographic data and summary of data collection and structure refinement

Formula	$C_{14}H_{15}O_3Mn$	$F(000)$	592
Fw	286.20	no. of unique data	917
Crystal system	orthorhombic		
Space group	$P2_12_12_1$	no. of reflns used, $I > 2\sigma(I)$	902
a, Å	7.141(6)		
b, Å	11.741(4)	no. of params	163
c, Å	15.158(3)	Z	4
V, $Å^3$	1270(1)	scan range	$3 < 2\theta < 50°$
d_{calc}, g cm^{-3}	1.496	scan type	ω-2θ
μ, mm^{-1}	1.035	GOF	1.071
Max. in Δρ (e $Å^{3-}$)	0.25	R	0.0357
		wR_2 [a]	0.0791

[a] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

A white crystal, shaped as a block, of approximate dimensions 0.2 × 0.2 × 0.3 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) unambiguously indicated $P2_12_12_1$ as the space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. Final atomic positional parameters for non-hydrogen atoms are given in Table 2 and the selected bond distances and angles are shown in Table 3; complete bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, hydrogen atom coordinates, and tables of observed and calculated factors are available as supplementary material.

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Mn	−1163(1)	−941(1)	−6296(1)	37(0)
O(1)	1193(8)	1032(5)	−6535(3)	72(2)
O2	1545(8)	−2818(4)	−6310(4)	74(2)
O3	287(8)	−375(5)	−4536(3)	77(2)
C1	834(10)	88(6)	−6806(5)	48(2)
C2	463(10)	−2072(5)	−6326(5)	51(2)
C3	−297(10)	−585(6)	−5229(5)	50(2)
C4	−3362(9)	−331(6)	−6618(4)	37(2)
C5	−3978(10)	−315(5)	−5898(4)	39(2)
C6	−3998(11)	−1515(6)	−5965(5)	54(2)
C7	−3360(11)	−2065(7)	−6707(5)	62(2)
C8	−2795(10)	−1427(7)	−7445(5)	54(2)
C9	−2767(10)	−248(7)	−7382(5)	52(2)
C10	−4065(11)	259(7)	−5061(4)	54(2)
C11	−3941(11)	1490(8)	−5019(6)	88(3)
C12	−4229(16)	2125(8)	−5811(6)	88(3)
C13	−3280(11)	1608(6)	−6595(5)	54(2)
C14	1900(10)	−324(7)	−7616(5)	64(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond distances (Å) and angles (deg) for compound **4**

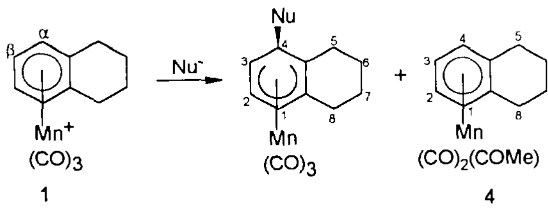
Mn–C(1)	2.023(7)	Mn–C(2)	1.765(7)
Mn–C(4)	2.222(7)	Mn–C(6)	2.191(8)
Mn–C(7)	2.143(8)	C(1)–C(14)	1.523(10)
C(1)–O(1)	1.210	C(4)–C(5)	1.400(9)
C(14)–C(1)–Mn	118.1(5)	O(1)–C(1)–Mn	124.5(6)
O(1)–C(1)–C(14)	117.3(7)	C(2)–Mn–C(1)	88.6(3)
O(2)–C(2)–Mn	177.3(8)	C(5)–C(4)–C(9)	118.3(7)
C(5)–C(6)–C(7)	121.6(7)	C(7)–C(8)–C(9)	118.9(8)

3. Results and discussion

Compound **1** was synthesized in 78% yield, starting from $Mn(CO)_5Br$, $AlCl_3$, and tetralin in refluxing cyclohexane. We completely characterized compound **1**. Stobart and Zaworotko reported the preparation of compound **1** by two kinds of method [6]. The first procedure started from $Mn(CO)_5Br$, $AlCl_3$, and refluxing tetralin and afforded compound **1** (ca. 70% yield) and a tricyclic ring compound (ca. 25%). The tricyclic ring compound had to be removed by sequential refrigeration of CH_2Cl_2 solutions. The other method was to use naphthalene as an arene substrate instead of tetralin. However, after work-up, they obtained compound **1** in only 10% yield. We improved the yield of formation of **1** by changing the reaction medium, i.e. by using cyclohexane as a solvent.

To find any special regioselectivities related to the saturated fused ring, the reactivity of **1** with nucleophiles has been studied (Scheme 1). There are two positions on the coordinated arene ring to be attacked by nucleophiles. One position (α) is *meta* and *ortho* to the saturated fused ring and the other (β) is *meta* and *para* to it.

Addition of hydride to **1** was found to be directed exclusively to the α position. To verify this, a decoupling experiment was carried out. When H^3 was decoupled, H^1 and H^2 appeared as doublets (5.12 Hz) and $H^{4\text{-endo}}$ and $H^{4\text{-exo}}$ also appeared as doublets (13.0 Hz). If the hydride had been added to the α-position, the above results could not be explained. Addition of deuteride to **1** also confirms that the deuteride is added to α-position in an exo fashion.



2 (Nu = H)
3 (Nu = Me)
5 (Nu = Ph)
6 (Nu = $P(O)(OMe)_2$)
7 (Nu = CH_2CN)

Scheme 1.

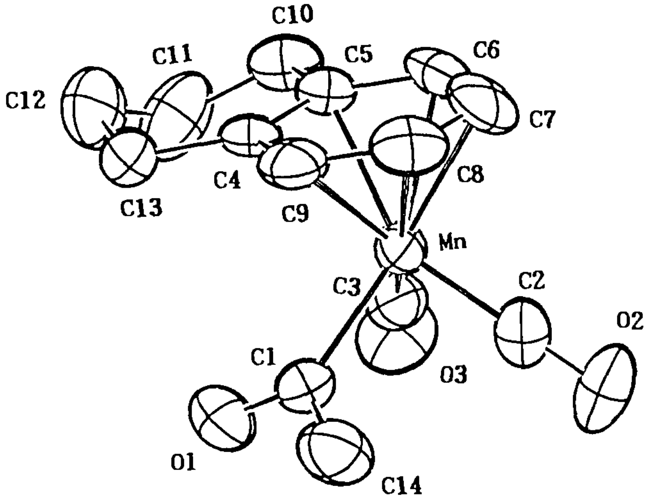


Fig. 1. ORTEP drawing of compound 4.

Treatment of **1** with MeMgBr in THF at 0°C led to two kinds of compound, **3** and **4**. Compound **3** is produced by addition of the methyl group exclusively to the α position in **1**. Compound **4** is derived from direct attack of the methyl group at the carbonyl carbon. Acyl manganese complexes are not rare. Pauson reported [7] the formation of acyl manganese complex by the reaction of $(C_6Me_6)Mn(CO)_3^+$ with MeLi and Brookhart also published [8] the formation of acyl manganese complex by reaction between $(C_6H_6)Mn(CO)_3^+$ and Me_2CuLi in diethyl ether at −78°C. Suitable crystals for X-ray analysis were grown from the hexane solution of compound **4**. An ORTEP diagram of the molecule is shown in Fig. 1. The single-crystal X-ray structure of **4** confirms formation of the acyl compound. The manganese acyl bond distance (Mn–C(O)Me, 2.023(7) Å) is close to the value (2.04(1) Å) found in the manganese formyl complex *trans*-$Mn(CHO)(CO)_2\{P(OPh)_3\}_2$ [9], but is somewhat short compared with the manganese alkyl bond length observed in $MnMe(CO)_4PPh_3$ (2.30(6) Å) [10] and $(OC)_4MnPPh_2(CH_2)_5CO$(2.202(5) Å) [11]. The Mn, C1, O1, and C14 atoms define a plane (maximum deviation 0.019 Å). Thus the observed bond distance and the planarity of the manganese acyl group may be related to the d_π–p_π back-donation from a transition metal to an acyl group as previously suggested by Churchill for the *trans*-$CpMo(CO)_2(PPh_3)COCH_3$ system [12]. The angles about the acyl carbon (C1) range from 117.3(7)° to 124.5(6)° (av. 120°) [13] and the bond distance (1.210(8) Å) of the C=O double bond of an acyl group is similar to the value of 1.21(1) Å found in *trans*-$Mn(CHO)(CO)_2\{P(OPh)_3\}_2$ [9]. The Mn atom is located 1.676(1) Å below the plane of the arene ring.

Addition of PhMgBr to **1** was found to be directed exclusively to the α position. Addition of RMgX to **1** favours the α position similar to that reported for RMgX addition to (toluene)Mn(CO)$_3^+$ [14]. When the $(CH_3C_6H_5)Mn(CO)_3^+$ cation was treated with RMgX, a mixture of *meta*- and *ortho*- adduct was obtained the ratio of which was found to be 2 : 1 (R = Me) and 4 : 1 (R = Ph). By varying the reaction conditions, we tried to find acyl complex in the addition of PhMgBr to **1**. However, we could find no evidence for the presence of acyl complexes in the PhMgBr addition reaction. Addition of $NaP(O)(OMe)_2$ to **1** was also found to be directed exclusively to the α position. Treatment of **1** with $LiCH_2CN$ resulted in the production of compound **7**. Compared to other reactions, the yield of the reaction was rather low because of decomposition of **7** in the work-up. However, after isolation as solids, **7** is stable in air. Due to the different chemical environment, the methylene protons appear at δ 1.89 and 1.73 ppm as two doublet of doublets in the ^1H NMR spectrum.

In conclusion, it has been demonstrated that the nucleophilic addition to **1** is very regioselective to give a α-position adduct. Thus we expect that this reaction can be used to functionalize the α position of tetralin and the resulting cyclohexadienyl complexes via activation and nucleophilic addition can ultimately yield cyclohexadiene [15].

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