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Synthesis of planar chiral (1,3-disubstituted arene)$Mn(CO)_3^+$ cations *via* addition of nucleophiles to (oxocyclohexadienyl)$Mn(CO)_3$ in the presence of chiral ligands†

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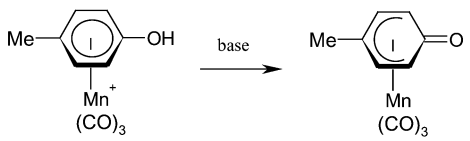
The first example of the synthesis of planar chiral (1,3-disubstituted arene)$Mn(CO)_3^+$ cations (3) has been demonstrated by a reaction of (*p*-cresol)$Mn(CO)_3^+$ with $KOBu^t$ followed by addition of nucleophiles and subsequent quenching with electrophiles in the presence of (*S*)-binaphthol in CH_2Cl_2.

Planar chiral transition-metal π-complexes of *ortho*- and *meta*-disubstituted arenes have emerged as useful starting materials in organic synthesis and as potential ligands for asymmetric catalysis. The planar chirality enables new stereogenic centers to be formed with high stereoselectivity.[1] In this regard, tricarbonylchromium(0) complexes of aromatic compounds have received much attention.[2] Optically active arene chromium complexes have been obtained through resolution *via* diastereoselective synthesis and by enantioselective methods.[3–7]

The reaction of organotransition metal complexes with nucleophiles offers a powerful method in the formation of carbon–carbon bonds. When an arene is bound to the cationic $Mn(CO)_3^+$ fragment, it becomes substantially more electrophilic than in the neutral (arene)$Cr(CO)_3$ complexes.[8] However, in spite of their potential usefulness, there have been no reports on the synthetic methods of planar chiral (arene)$Mn(CO)_3^+$ complexes from achiral arenes, even though the respective groups of Pearson and Miles[9] reported the synthesis of chiral η^5-dienyl manganese complexes by a chiral auxiliary-directed asymmetric additions to arene–manganese tricarbonyl complexes. Herein we describe our initial study of the synthesis of planar chiral manganese complexes of 1,3-disubstitued arenes from a readily available *p*-cresol manganese complex. To the best of our knowledge, this is the first synthesis of planar chiral 1,3-disubstituted arene manganesetricarbonyl complexes.

Treatment of (*p*-cresol)$Mn(CO)_3^+$ with $KOBu^t$ in THF afforded oxocyclohexadienyl manganese complex **1** [eqn. (1)].

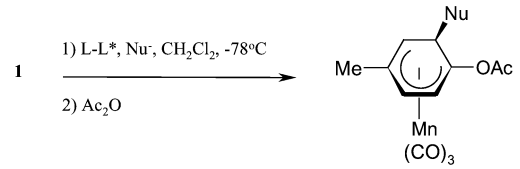


(1)

1

Complex **1** was easily attacked by nucleophiles such as Grignard reagents and alkyllithium.[10] Nucleophiles exclusively attacked the terminal positions of the cyclohexadienyl ring.

The external ligand-controlled enantioselective addition of organometallic reagents to prochiral molecules is a powerful tool in asymmetric methodology. Thus, it was expected that the nucleophile addition to a prochiral manganese complex **1** in the presence of external chiral ligand would induce asymmetry in the sequential nucleophile/electrophile addition to **1** [eqn. (2)].



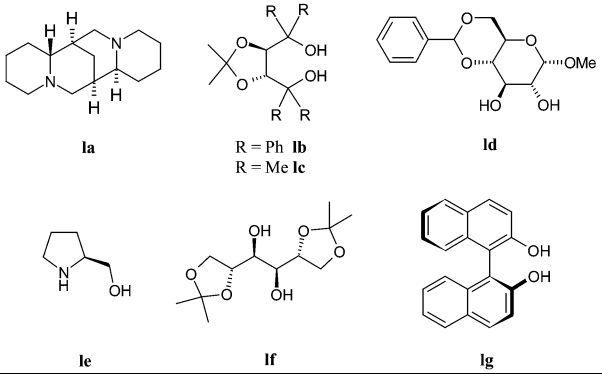
(2)

2

Thus, we screened several chiral ligands in the nucleophile addition reaction to **1** (Table 1). As we expected, planar chiral (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes **2** were obtained in reasonable to high yields. The yields were sensitive to the chiral ligand and reaction medium, the ee values were highly dependent upon them, and the *S* or *R* configuration was also dependent upon the chiral ligand. Generally, chiral diol ligands were superior to chiral N,O- and N,N-chelating ligands. The best result was obtained when the reaction was conducted in the presence of (*S*)-binaphthol in CH_2Cl_2.

Next we investigated the reaction with various nucleophiles (Table 2). When an electron-withdrawing group such as *p*-CF_3 was introduced to a phenyl ring, no reaction was observed, presumably due to the low nucleophilicity of the resulting

Table 1 The results of chiral induction with various ligands[a]



la R = Ph **lb** R = Me **lc** **ld** **le** **lf** **lg**

Entry	Ligand	Solvent	Yield[b] (%)	Ee[c] (%)	Config.[d]
1[e]	**la**	THF	85	7	*R*
2	**lb**	THF	61	24	*R*
3	**lc**	THF	95	35	*S*
4	**lg**	THF	82	54	*S*
5	**lc**	CH_2Cl_2	51	50	*R*
6	**ld**	CH_2Cl_2	67	35	*S*
7	**le**	CH_2Cl_2	65	13	*R*
8	**lf**	CH_2Cl_2	70	9	*R*
9	**lg**	CH_2Cl_2	78	95	*S*

[a] *Reaction conditions*: 1.5 equiv. ligand and 4.5 equiv. PhMgBr, −78 °C, 18 h. [b] Isolated yields. [c] Determined by HPLC using a Chiralcel OD column. [d] The absolute configuration was determined by X-ray analyses of **3a** and **3b**. [e] 1.5 equiv. ligand and 1.5 equiv. PhMgBr used.

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b201341j/

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Table 2 The results of chiral induction with various nucleophiles[a]

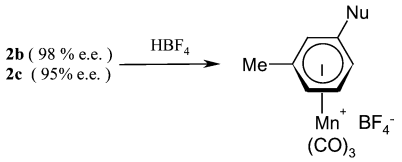
Entry	RMgX	Product	Yield[b] (%)	Ee[c] (%)	Config.
1	4-$CF_3C_6H_4$	**2a**	n.r.	—	—
2	2-Thienyl	**2b**	68	98	*S*
3	Ph	**2c**	78	95	*S*
4	4-MeC_6H_4	**2d**	75	90	*S*
5	4-$MeOC_6H_4$	**2e**	65	76	*S*
6	1-Naphthyl	**2f**	70	66	*S*
7	Bu^n	**2g**	75	67	*S*

[a] *Reaction conditions*: 1.5 equiv. (*S*)-binaphthol, 4.5 equiv. nucleophile, −78 °C, 18 h in CH_2Cl_2 [b] Isolated yields. [c] Ee was determined by HPLC using a Chiralcel OD column.

Grignard reagent. Introduction of an electron-donating group such as *p*-methyl and *p*-methoxy groups to a phenyl ring led to a decrease of the ee value to 90 and 76%, respectively. When a bulky nucleophile such as 2-naphthyl Grignard reagent was used, the ee value fell to 66%. Interestingly, treatment of **1** with 2-thienyl magnesium bromide gave **2b** in 68% yield with a high enantioselectivity 98%.

Other nucleophiles such as PhMgBr/CuI, PhLi and PhLi/CuI were also screened. When PhMgBr/CuI was used as a nucleophile, the ee value was 48%. In the case of phenyllithium, the ee value (14%) was quite poor. When phenyllithium cuprate was used, almost no asymmetric induction occurred. When Et_2Zn was used as a nucleophile, no reaction was observed.

To generate planar chiral (1,3-disubstituted arene)$Mn(CO)_3^+$ cations (**3**) while retaining optical purity (see ESI†), complexes **2** were treated with HBF_4 [eqn. (3)].



(3)

Nu = 2-thienyl **3a** (98 % e.e.)
= Ph **3b** (97 % e.e)

High yields of **3** were obtained with high enantioselectivities. Careful crystallization of **3a** and **3b** from diethyl ether/nitromethane gave single crystals. The molecular structures of **3a** and **3b** were determined by X-ray diffraction. They have very similar unit cell dimensions and the X-Ray crystal structures are quite similar to each other. Thus only the X-ray crystal structure of **3b** is presented in Fig. 1,[11] which clearly shows that nucleophile addition occurs preferentially at the *meta* position of the methyl group and the absolute configuration is *S*.

In general, *ortho* positions are more easily influenced by a nearby chiral auxiliary than *meta* positions. Therefore, most auxilliary-controlled asymmetric reactions provide planar chiral 1,2-disubstituted arene transition-metal complexes, sometimes, with excellent results. In our reactions, chiral induction occurred at one of the two *ortho* positions of the ketone group of (oxocyclohexadienyl)$Mn(CO)_3$ to yield **2** and the acid treatment of **2** generated the planar chiral 1,3-disubstituted arene manganese tricarbonyl cations which could not be obtained by the other methods.

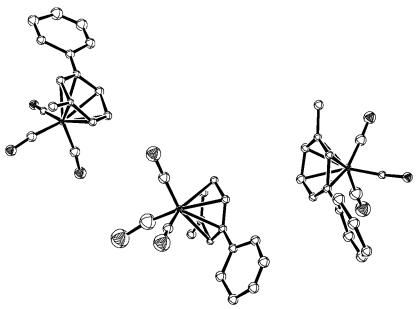


Fig. 1 Crystal structure of **3b**.

In conclusion, we have demonstrated the first synthesis of planar chiral manganesetricarbonyl complexes of 1,3-disubstituted arenes starting from a readily available achiral (*p*-cresol)$Mn(CO)_3^+$ cation. Future work will be directed at applying this chemistry to other transition metal complexes of *p*-substituted phenols as well as studying the synthetic application of this method.

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11 *Crystal data* for **3a**: monoclinic, $P2_1$, a = 14.614(1), b = 10.729(1), c = 17.076(1) Å, β = 114.487(1)°, limiting indices $-17 \leqslant h \leqslant 17$, $-12 \leqslant k \leqslant 11$, $-20 \leqslant l \leqslant 17$, reflections collected/unique 11697/7033 (R_{int} = 0.0500), final R indices [$I > 2\sigma(I)$] $R1$ = 0.0458, $wR2$ = 0.0885. For **3b**: monoclinic, $P2_1$, a = 15.1163(4), b = 10.6658(3), c = 17.0086(6) Å, β = 114.0125(13)°, limiting indices $-18 \leqslant h \leqslant 18$, $-13 \leqslant k \leqslant 10$, $-21 \leqslant l \leqslant 21$, reflections collected/unique 8896/8896 (R_{int} = 0.0000), final R indices [$I > 2\sigma(I)$] $R1$ = 0.0654, $wR2$ = 0.1560. CCDC reference number 182208. See http://www.rsc.org/suppdata/cc/b2/b201341j/ for crystallographic data in CIF or other electronic format.