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Synthesis of planar chiral tricarbonylcyclopentadienylmanganese complexes using a $Mn(CO)_3^+$ transfer reaction†

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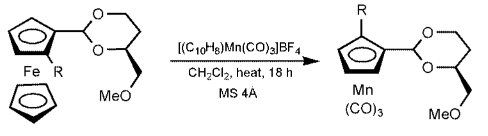
Planar chiral ligand transfer reactions can be carried out by the reaction of [(naphthalene)$Mn(CO)_3$]BF_4 with planar chiral ferrocene derivatives.

Ligand transfer from one metal to another is a useful reaction when the complex cannot be easily prepared by conventional methods and is popular in organometallic chemistry.[1] Among these, cyclopentadienyl transfer reactions may be of synthetic interest,[2,3] in particular if cheap substrates such as commercially available ferrocene derivatives can be used as starting materials. However, there have been no reports of ligand transfer reactions from ferrocene derivatives to a manganese moiety to prepare cyclopentadienyl manganese complexes. Such complexes have many notable features such as high thermal stability, lack of substantial air or water sensitivity, kinetic inertness toward substitution reactions, and stereochemical robustness. These characteristics will be useful properties when manganese complexes are used as auxiliaries in other reactions.

Herein we report the synthesis of planar chiral cyclopentadienyltricarbonylmanganese complexes from the reaction of planar chiral ferrocenes with [(η^6-naphthalene)$Mn(CO)_3$]BF_4[4] and their application in asymmetric reactions. Planar chiral chelates of $CpMn(CO)_3$ derivatives are quite rare and hence their use in asymmetric reactions has not been developed. There has been a report[5] of enantioselective allylic substitution of cyclic substrates by catalysis with palladium complexes of *P*,*N*-chelate ligands attached to a $CpMn(CO)_3$ unit.

Refluxing equimolar amounts of a planar chiral ferrocene derivative **1a** and [(η^6-naphthalene)$Mn(CO)_3$]BF_4 in the presence of 4 Å molecular sieves in CH_2Cl_2, followed by standard work-up procedures, led to a 46% yield of the air-stable, planar chiral tricarbonylcyclopentadienylmanganese complex **2a** [eqn. (1)].‡

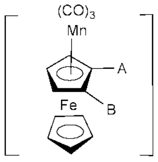


(1)

1a-c

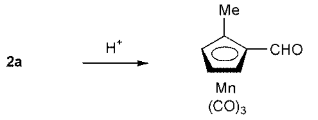
2a R = Me
2b R = $SiMe_3$
2c R = $SiMe_2(CH{=}CH_2)$

As far as we are aware, this is the first use of a ligand transfer reaction in the synthesis of a planar chiral tricarbonylcyclopentadienylmanganese complex. Interestingly, formation of $CpMn(CO)_3$ was not observed in the reaction products. Birch *et al.*[6] first tested the idea of chirality transfer in the reaction between a chiral donor complex and an unsymmetrical diene ligand. Since then, there have been many reports on the synthesis of chiral organometallic compounds.[7] However, there have been no known reactions on the synthesis of tricarbonylcyclopentadienylmanganese derivatives. Surprisingly, during the transfer reaction, a *complete inversion* of the absolute configuration occurred [eqn. (1)]. This suggests that a bimetallic species [Cp–Fe–Cp–$Mn(CO)_3$]$^+$ **A**, in which one of the Cp rings is coordinated to both metals, occurs as an intermediate in this reaction especially given the recent isolation and characterization of bimetallic complexes [Cp*–M–Cp*–$Mn(CO)_3$]$^+$ (M = Fe, Ru, Os).[8] In the same way, compounds **2b**,**c** were synthesized from the corresponding mixed ferrocenes **1b**,**c**. According to the study of Herberich *et al.*,[9] the migrating Cp is always the unsubstituted ligand. They explained this observation based upon on the electronic structural differences between Cp^- and Cp^{*-}. However, in our case, the substituted cyclopentadienyl ligand always migrated.



A

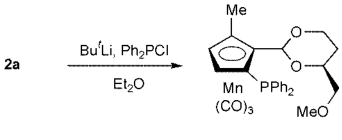
Acid hydrolysis of **2a** yielded the known compound **3** [eqn. (2)];[10] according to the ^1H NMR spectrum of **2a** and the optical rotation of **3**, compound **3** is optically pure.



(2)

3

We investigated whether the triol group in **2** could be used as a directing group in the functionalization of the cyclopentadienyl ring. Deprotonation of **2a** by Bu^{t}Li followed by the addition of PPh_2Cl yielded **4** in 67% yield [eqn. (3)].



(3)

4

The structure of **4** was confirmed by an X-ray crystal structure determination (Fig. 1).[11] Thus, the diphenylphosphino group was successfully introduced with the aid of the triol group.

We next investigated the use of the ligand transfer reaction in the synthesis of *P*,*N*-ligands and studied palladium-catalyzed asymmetric allylic alkylation. The use of ligands derived from (arene)$Cr(CO)_3$ as a chiral chelating ligand is quite popular.[12] However, the use of $CpMn(CO)_3$ as a chiral chelating ligand is quite rare.[5]

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† Electronic supplementary information (ESI) available: characterization of **2b**, **2c**, **4**, **6**, **7**, **8** and **9**, and a typical procedure for Pd-catalyzed allylic alkylation. See http://www.rsc.org/suppdata/cc/b1/b102693n/

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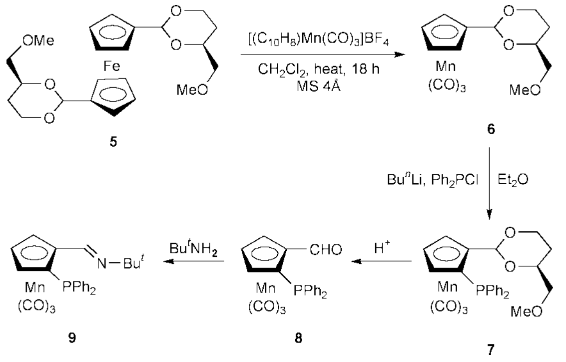
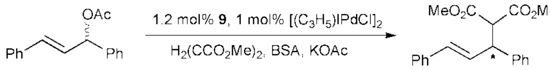
The planar chiral *P,N*-ligands **9** were synthesized from **5** [eqn. (4)].



(4)

Ligand transfer reaction of **5** afforded **6** in 74% yield. Deprotonation of **6** followed by the addition of PPh_2Cl and subsequent reaction with acid gave **8** in 75% yield. The condensation reaction of **8** with *tert*-butyl amine gave a *P,N*-ligand **9a** in 96% yield. The de of **7** prepared from **6** was 75%. However, after recrystallization, the de of **7** was $>99.5\%$.

The palladium-catalyzed asymmetric allylic alkylation of *rac*-1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate was successfully carried out [eqn. (5)].



(5)

Reaction of *rac*-1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate in the presence of 1 mol% Pd catalyst at 15 °C for 4 h gave the allylic alkylation product methyl-2-carbomethoxy-3,5-diphenylpent-4-enolate in high yields and high ee values (95% yield and 89% ee in CH_2Cl_2; 96% yield and 92% ee in DMSO). Lowering the reaction temperature to -20 °C in CH_2Cl_2 led to an increase of the ee value to 94% with a 74% yield.

In conclusion, we have conducted the first demonstration that a planar chiral ligand transfer reaction can be carried out by the reaction of $[(naphthalene)Mn(CO)_3]BF_4$ with planar chiral ferrocene derivatives and we have shown that the *P,N*-ligand prepared in this study can be employed in palladium-catalyzed asymmetric allylic alkylation.

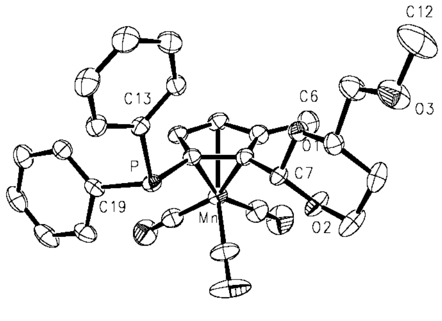


Fig. 1 X-Ray structure of **4**.

Notes and references

‡ Compounds $(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]BF_4$, **1** and **5** were synthesized as previously described.[4a,13,14]

Synthesis of **2a**: a Schlenk flask containing 0.50 g of molecular sieves was flame-dried. After the flask was cooled to r.t., **1a** (0.35 g, 1.06 mmol), $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]BF_4$ (0.40 g, 1.13 mmol), and 15 mL of CH_2Cl_2 were added to the flask. The resulting solution was heated at reflux for 18 h. After the solution was cooled to r.t., the solution was filtered over a pad of Celite. The filtrate was evaporated to dryness and chromatographed on a silica gel column eluting with hexane and diethyl ether (10 : 1 v/v). Removal of the solvent gave **2a** (oil, 46%, 0.17 g). IR ν(CO) 2012, 1920 cm^{-1}; δ_H(300 MHz, d_6-benzene, TMS) 5.21 (br s, 1 H), 5.03 (br s, 1 H), 4.15 (br s, 1 H), 4.07 (dd, 3.7, 11.0 Hz, 1 H), 3.85 (m, 1 H), 3.60 (m, 2 H), 3.56 (m, 1 H), 3.55 (s, 3 H), 2.05 (s. 3 H), 1.87 (m, 1 H), 1.26 (d, 13.0 Hz, 1 H); δ_C(75 MHz, d_6-benzene) 225.7, 102.8, 99.5, 96.4, 82.6, 81.1, 79.8, 76.1, 75.3, 66.6, 59.1, 28.0, 12.1; HRMS calc. for $C_{15}H_{16}MnO_6$: *m/z* 349.0484; obs: 349.0483. $[\alpha]_D^{21} = -36$ (*c* 0.42 in CH_2Cl_2).

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11 *Crystal data*: for **4**: monoclinic, space group $P2_1$; $a = 8.0816(7)$, $b = 15.0390(4)$, $c = 10.9049(9)$ Å, $\beta = 90.422(3)°$, $V = 1325.34(16)$ Å^3, $Z = 2$, $D_c = 1.334$ Mg m^{-3}; $-10 < h < 10$, $-17 < k < 17$, $-14 < l < 13$, $R1 = 0.0379$, $wR2 = 0.10791$. For **7**: orthorhombic, space group $P2_12_12_1$; $a = 7.6659(2)$, $b = 17.7774(8)$, $c = 18.6479(10)$ Å; $V = 2541.33(19)$ Å^3, $Z = 4$; $D_c = 1.355$ Mg m^{-3}; $-9 < h < 9$, $-23 < k < 22$, $-24 < l < 24$; $R1 = 0.0526$, $wR2 = 0.1398$. CCDC reference numbers 157495 and 157496. See http://www.rsc.org/suppdata/cc/b1/b102693n/ for crystallographic data in CIF or other electronic format.
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