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Preparation of (η^5-cyclopentadienyl) and (η^5-methylcyclopentadienyl)Fe(CO)$_2$Me cyclodextrin inclusion compounds and their subsequent ligand substitution reactions. Attempts at cyclodextrin mediated enantioselective ligand substitution

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Abstract

Two iron complexes, (η^5-Cyclopentadienyl)Fe(CO)$_2$Me and (η^5-Methylcyclopentadienyl)Fe(CO)$_2$Me, were prepared followed by their α, β, and γ cyclodextrin inclusion compounds. The included iron complexes participate in phosphine induced ligand substitution reactions under both thermal and photochemical conditions with no CO insertion/alkyl migration products observed in either case. © 1997 Elsevier Science S.A.

1. Introduction

Since the mid-1950s the interest in the chemistry of cyclodextrins and their inclusion compounds has grown rapidly [1]. Cyclodextrins (CDs) are cyclic oligomers of α-D-glucopyranose consisting of six (α-CD), seven (β-CD), or eight (γ-CD) units. The cyclic array of the sugar units produces a 'torus' shaped structure that encloses a chiral hydrophobic cavity (Fig. 1) [1]. As a result, cyclodextrins have the ability to form non-covalent inclusion compounds with a variety of compatible hydrophobic molecules. Numerous applications of practical importance for cyclodextrins and their modified derivatives have been discovered (for recent reviews see [2]). Cyclodextrin bonded stationary phases are also well known for their efficiency in the separation of chiral compounds [3].

Recently, there have been reports on the formation of adducts between cyclodextrins and transition metal complexes (for a review see [4]). Several groups have been successful in synthesizing inclusion compounds of ferrocenyl complexes as well as arene complexes [5]. Most reported subsequent reaction chemistry involves reactions of ferrocenyl substituent functional groups (for some examples of cyclopentadienyl and arene complex cyclodextrin inclusion compounds see [5]). In addition to this chemistry, molecular modelling studies of ferrocene inclusion compounds with α, β, and γ cyclodextrins have also been reported [6]. In chemistry most closely related to our current study, Shimada, Harada, and Takahashi communicated the preparation of cyclodextrin inclusion compounds of (η^5-cyclopentadienyl)iron(dicarbonyl)(CH_3) complexes in 1991 (η^5-cyclopentadienyl = Cp) [7]. These authors reported that the included complexes insert carbon monoxide and sulfur dioxide into the Fe–R bond in the solid state [7].

We recently reported a synthesis of CpFe(CO)$_2$ substituted 1,3-dienyl complexes and were interested in converting these achiral dienyl complexes into optically active CpFe(CO)(PR$_3$) substituted dienes for use in asymmetric Diels–Alder reactions [8]. We envisioned that CpFe(CO)(PR$_3$)R complexes might be prepared in optically active form by carrying out a ligand substitution reaction on CpFe(CO)$_2$R cyclodextrin inclusion compounds. Is asymmetric induction possible by carrying out a ligand substitution reaction on a prochiral

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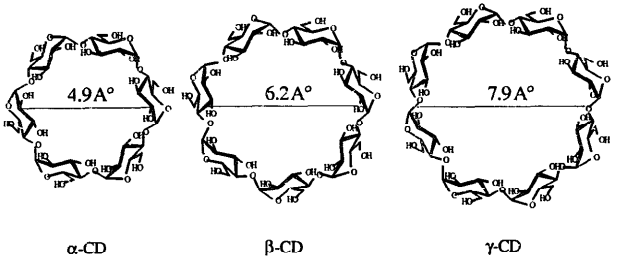


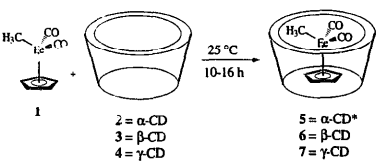
Fig. 1. Cyclodextrin structures.

organometallic complex which is inside, or at least close to, a chiral cyclodextrin cavity? (Fig. 2). We report here our initial attempts to answer this question about ligand substitution reactions using $CpRFe(CO)_2Me$ (R = H, Me) cyclodextrin inclusion compounds.

2. Results and discussion

2.1. Preparation of inclusion compounds

The inclusion compounds of (η^5-cyclopentadienyl)iron(dicarbonyl)(methyl)[9] (**1**) with α, β, and γ-CD were readily prepared using a procedure analogous to one recently reported to work for alkyne dicobalt hexacarbonyl complexes [10]. The preparation of these compounds (**5–7**) has been communicated previously [7]. At room temperature, the iron complex **1** was added to a saturated aqueous solution of the appropriate cyclodextrin and stirred vigorously for 16 h. During this period, a yellow solid gradually separated out. The solid was collected by filtration, washed thoroughly with water and with tetrahydrofuran to remove any non-included iron complex **1**. (Note: In the case of γ-cyclodextrin, washing with THF led to instantaneous deinclusion of the iron complex **1**.) Finally, drying of the solid in vacuo gave the inclusion compounds (**5–7**) as pale yellow solids. The inclusion compounds thus obtained are thermally stable up to 170°C.



* forms a 2:1 α-CD:**1** compound.

α-Cyclodextrin (**2**) forms 2:1 inclusion complexes with **1** (2:1 α-cyclodextrin:iron complex) as judged by comparison of the Cp (δ4.97, 5H, d_6-DMSO) to H_1 (4.80, 12H) ^{1}H-NMR integrals [7] whereas β and γ-cyclodextrins form 1:1 inclusion complexes as judged by similar integration comparisons (βCp, 4.97, 5H:H_1, 4.82, 7H) and (γCp, 4.96, 5H:H_1, 4.87, 8H). Iron complex (**1**) appears to be moving freely within the cavity in **5** since we only see 6 ^{13}C resonances for the cyclodextrin. 1:1 complexes **6** and **7** likewise show 6 ^{13}C resonances for the cyclodextrin. Highest yields for the inclusion compounds were obtained when β-cyclodextrin was the host molecule. Some analytical data for these complexes is presented in Table 1. Aside from the carbonyl stretching frequencies, there is no major differ-

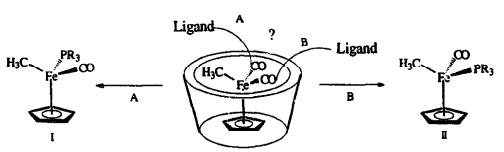


Fig. 2. Ligand exchange on cyclodextrin inclusion complexes.

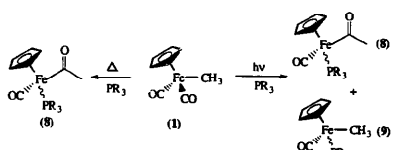
Table 1
Spectral comparison of the cyclodextrin inclusion compounds (5, 6, and 7)

Complex	Cyclodextrin	Me, Cp-^{1}H NMR[a]	CO-^{13}C NMR	IR (cm^{-1})[b]	% Yield
1	–	0.06, 4.97	218.1	2016, 1925	–
5	α	0.04, 4.97	218.3	2008, 1953	33
6	β	0.05, 4.96	218.2	1999, 1949	84
7	γ	0.05, 4.96	218.2	2004, 1943	65

[a] Residual protonated solvent in DMSO-d_6 was used as an internal reference.
[b] IR spectra were obtained as a nujol mull.

ence in the ^{1}H-NMR and ^{13}C-NMR spectra of these inclusion compounds. The inclusion compounds are insoluble in most common organic solvents, dissolve completely only at elevated temperatures (> 75°C) in water, but are readily soluble in DMSO at room temperature.

It has been well documented that the product of the reaction of (η^5-cyclopentadienyl)iron (dicarbonyl)(methyl) (1) with various phosphine and phosphite ligands depends on the reaction conditions [11]. Thermal reaction of 1 with phosphines, in a coordinating solvent such as tetrahydrofuran, produced only the CO inserted iron–acyl complex (8); whereas under photolytic conditions, a 2:1 mixture of 8 and the phosphine substituted iron–methyl (9) was obtained (Scheme 2) [11].



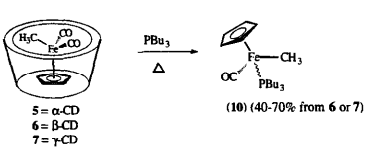
We first examined the effect of cyclodextrin inclusion on phosphine ligand substitution reactions of iron methyl inclusion compounds (5–7) under thermal and photochemical conditions.

2.2. Ligand substitution under thermal conditions

To have any chance of ultimately doing enantioselective ligand substitution reactions, it is absolutely essential that the prochiral iron complex (1 in this case) remains included within the cyclodextrin cavity during the ligand substitution reaction. To be enantioselective, the ligand substitution would also have to take place associatively through a 'slipped' (η^3-C_5H_5)Fe(CO)$_2$(PR_3)Me intermediate or dissociatively produce a 16e CpFe(CO)Me fragment that would retain its pyramidal character in the cyclodextrin long enough for the substitution to occur stereoselectively [12]. Since organic solvents were most likely to cause deinclusion, we carried out our initial reactions of inclusion compounds (5–7) in water using a hydrophobic liquid phosphine, tri-*n*-butylphosphine. We chose tri-*n*-butylphosphine for these initial studies thinking that the butyl groups would provide access to the hydrophobic interior of the cyclodextrin. We first performed control reactions in water and observed by ^{1}H-NMR that the iron complex (1) remains included even after heating an aqueous suspension of 6 at 60°C for 10 h or an aqueous suspension of 7 at 45°C for 4 h.

An aqueous suspension of β-cyclodextrin inclusion compound (6) was then heated in the presence of excess of tri-*n*-butylphosphine at 60°C for 5 h. Over this time, the phosphine droplets gradually turned orange. The reaction mixture was cooled and filtered. Analysis of the recovered β-cyclodextrin (3) by ^{1}H-NMR revealed complete deinclusion of iron methyl (1) from within its cavity and the phosphine substituted iron methyl complex (10) [13] (65%) was recovered following extraction of the filtrate. Similar results were obtained when the corresponding γ-cyclodextrin inclusion compound (7) was used (45°C, 5 h); however, when the α-cyclodextrin inclusion compound (5) was heated in water (60°C, 5 h) with PBu_3, the inclusion compound (5) was recovered unreacted (80%). This result may not be surprising since the α-inclusion compound (5) appears to be a 2:1 (cyclodextrin:iron) complex by ^{1}H-NMR and phosphine access to the metal center may be completely blocked. In the β- and γ-cyclodextrin cases (1:1 adducts), the phosphine substituted complex (10) (ligand substitution rather than CO insertion) was the only product of the reactions of 6 or 7, so cyclodextrin inclusion has drastically altered the thermal reaction chemistry of 1 with phosphines. These complexes (6 and 7) participated in ligand substitution reactions presumably because ligand/cyclodextrin steric interactions slow down the rates of alkyl migration. During the course of the ligand substitution reaction, the guest molecule is expelled from the cavity after ligand substitution presumably due to its increased steric bulk as a result of replacing a CO ligand with PBu_3. We know that the phosphine is not simply acting as a solvent to extract 1 from the cyclodextrin so that the ligand substitution can occur in phosphine/water since a control experiment where 1 was heated at 60°C for 5 h with

PBu_3 in water in the absence of cyclodextrin produced a 5:1 mixture of $CpFe(CO)(PBu_3)(C(O)CH_3)$ (**8**, R = Bu) (the expected thermal CO insertion product) and **10**. Phosphine containing CpFe complexes are apparently incapable of cyclodextrin inclusion regardless of phosphine used since we saw no evidence for cyclodextrin inclusion when racemic $CpFe(CO)(PPh_3)(C(O)CH_3)$ [11] (**8**, R = Ph) was stirred with β- or γ-cyclodextrin in H_2O over 24 h. This outcome would appear to preclude any hope of using cyclodextrin inclusion as a method of kinetic resolution for racemic iron acyls (for recent classical resolution procedures for $CpFe(CO)(PR_3)(C(O)CH_3)$ complexes see [14,15]). We also do not believe alkyl migration/CO insertion occurs in the cyclodextrin cavity to produce **8** (R = Bu) followed by cyclodextrin assisted decarbonylation of an included iron acyl to produce **10**, since heating a β-cyclodextrin inclusion complex of an iron acyl ($CpFe(CO)_2COCH_3$) with PPh_3 in water (65°C, 5 h) yielded no decarbonylation product or ligand substitution product. Instead included acyl was recovered almost quantitatively.



Thermal reactions of cyclodextrin inclusion compounds were next investigated in a polar aprotic solvent where we suspected deinclusion might be competitive with ligand substitution or insertion reactions. We again first performed control experiments: (1) heating **1** with phosphine in CH_3CN in the absence of cyclodextrin produced a 5:1 mixture of CO insertion product (**8**, R = Bu) to ligand substitution product (**10**) as expected; (2) heating inclusion compound (**6**) at 60°C for 4 h in CH_3CN in the absence of phosphine we observed 30% deinclusion of **1**; (3) likewise heating **7** at 45–50°C for 2 h in CH_3CN also resulted in 30% deinclusion and recovery of **1**. Next, the reaction of **6** with PBu_3 was carried out thermally in acetonitrile at 60°C (the phosphine in this case is in solution). The organometallic product is again slowly expelled from the cavity and dissolves in the surrounding acetonitrile (the solution turns orange during the reaction). The recovered cyclodextrins may be reused after recrystallization from water. This is particularly useful when using the more expensive γ-cyclodextrin. Again, as in the case of the results from H_2O, only the ligand substitution product (**10**) was observed. We conclude from this result that ligand substitution is faster than complex deinclusion since we would have expected to see some **8** (R = Bu) if deincluded **10** was heated in the presence of phosphine in CH_3CN.

2.3. Ligand substitution under photolytic conditions

Ligand substitution could also be accomplished under photolytic conditions [11]. As expected, photolysis of **1** (150-W flood lamp, 15 min) in CH_3CN with PBu_3 resulted in the production of **10** with no **8** (R = Bu) observed. Additional control experiments involving photolysis of **5–7** in water or CH_3CN in the absence of phosphine result in the decomposition of **1** and are not particularly meaningful other than they tell us that cyclodextrin inclusion does not protect **1** from photochemical decomposition [9]. Photolysis of an aqueous suspension of β–CD complex (**6**) and tri-*n*-butylphosphine, using a 150-W flood lamp, also led to decomposition of **1** and no recovered **8** (R = Bu) or **10**. The ^{1}H-NMR of the recovered β-cyclodextrin showed that it was free of the iron methyl complex (**1**). Similarly photolysis of **5** with PBu_3 in CH_3CN also led to the decomposition of **1**. On the other hand, when acetonitrile suspensions of cyclodextrin inclusion compounds (**6–7**) were photolyzed in the presence of tri-*n*-butylphosphine, after 4–5 h, the phosphine substituted complex (**10**) was isolated.

2.4. Determination of enantiomeric excess of substitution products (10)

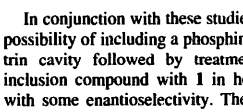
The enantiomeric ratio of the ligand substitution products (**10**) formed (from the thermal and photochemical ligand substitution experiments described above) was determined by the method of Flood et al. [16]. Flood and co-workers have shown that sulfur dioxide insertion at low temperatures into optically active $CpFe(CO)(PR_3)(R)$ complexes occurs with retention of configuration at the iron center [16]. We first prepared a racemic sample of **11** and found the methyl groups of the two enantiomers of **11** were readily observable by ^{1}H-NMR using (s)-tri-fluoroethanol-9-anthryl [15] as a chiral shift reagent. This SO_2 insertion method had to be used here since a variety of commercially available chiral shift reagents failed to resolve the methyl or cyclopentadienyl resonances of **10**. Exposure of **10** (obtained from the aqueous reaction of inclusion complex **6** with PBu_3) to liquid sulfur dioxide at −10°C produced the SO_2 inserted iron–sulfinate complex (**11**) (41% overall yield for the 2 steps from **6**). ^{1}H-NMR in C_6D_6, using (s)-tri-fluoroethanol-9-anthryl as a chiral shift reagent, resolved the *S*-methyl resonance into two peaks of near equal intensities at 2.93 and 2.90 ppm (54:46). Similarly, sulfinate complex (**11**) obtained from the ligand substitution of inclusion complex **6** performed in CH_3CN showed an enantiomeric ratio of 52:48 (67% isolated yield from **6**). The enantiomeric ratios, as observed by chiral shift reagent studies, obtained for ther-

Table 2
Summary of reactions of inclusion complexes 5, 6 and 7 with PBu_3

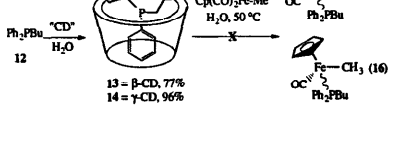
Entry	Complex	Reaction conditions	% 11[a]	Enant. ratio[b]
1	5	PBu_3, H_2O, 60°C, 5 h	[c]	
2	5	PBu_3, CH_3CN, hν, 4h	[d]	
3	6	PBu_3, H_2O, 60°C, 5 h	41	54:46
4	6	PBu_3, CH_3CN, hν, 4 h	67	52:48
5	7	PBu_3, H_2O, 60°C, 5 h	[e]	52:48
6	7	PBu_3, CH_3CN, hν, 4 h	[e]	54:46

[a] Yield reported is for two steps, 5 or 6 or 7 to 10 to 11.
[b] (s)-tri-fluoroethanol-9-anthryl as a chiral shift reagent.
[c] 5 Was recovered unreacted (80%).
[d] Cyclodextrin 2 was recovered but no iron complex.
[e] Excess phosphine was not removed from 11 following SO_2 insertion.

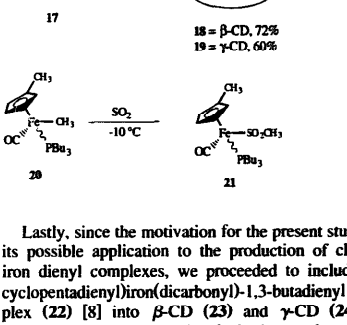
mal and photochemical reactions between the inclusion compounds (6 and 7) and PBu_3 in H_2O and CH_3CN are presented in Table 2. These results might not be surprising since the metal carbonyls of 5 (218.2), 6 (218.1), and 7 (218.3) were not diastereotopic by ^{13}C-NMR (d_6-DMSO). Docking calculations on ferrocene complexation with β and γ cyclodextrins indicated that axial or tilted and equatorial complexation geometries have almost identical energies so it is difficult to make predictions about what geometries might be preferred for these related CpFe containing complexes [6].



In conjunction with these studies we also checked the possibility of including a phosphine inside the cyclodextrin cavity followed by treatment of the phosphine inclusion compound with 1 in hopes of producing 10 with some enantioselectivity. The inclusion complexes for diphenylbutylphosphine with β- and γ-CD (13 and 14) were synthesized in a manner analogous to complex 6, in 77% and 96% yields respectively. However, phosphine to phosphine oxide oxidation was rapid for these inclusion complexes and when aqueous or acetonitrile suspensions of phosphine inclusion complexes 13 and 14 were heated with 1 we only saw traces of ligand substitution product (16) by ^1H-NMR. By far the major iron-containing product recovered was unreacted 1.



In an effort to change the orientation of the cyclopentadienyl ligand inside the cyclodextrin cavity, thus possibly affecting the accessibility of the carbonyl ligands, $CpMeFe(CO)_2Me$ (17) and its β and γ-cyclodextrin inclusion compounds were also synthesized. Starting from 1-methyl-2,4-cyclopentadiene, $CpMeFe(CO)_2Me$ (17) [9,17] was obtained in 65% overall yield. The corresponding β- and γ-cyclodextrin inclusion compounds 18 and 19 were easily prepared as described above for 6 and 7 in 72% and 60% yields, respectively. Control reactions involving heating 18 (55°C, 5 h) and 19 (45°C, 4 h) in H_2O again showed no deinclusion of 17. Inclusion complexes 18 and 19 from the controls were recovered by filtration and ethyl acetate extracts of the water filtrate showed no free 17 by ^1H-NMR. The reactivity of these inclusion compounds 18 and 19 towards PBu_3 ligand substitution under thermal and photolytic conditions was then studied as described above. The results of these ligand substitutions followed by SO_2 insertion and chiral shift reagent analysis are presented in Table 3.



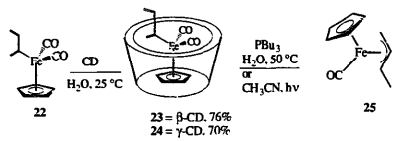
Lastly, since the motivation for the present study was its possible application to the production of chiral at iron dienyl complexes, we proceeded to include (η^5-cyclopentadienyl)iron(dicarbonyl)-1,3-butadienyl complex (22) [8] into β-CD (23) and γ-CD (24). All attempts to effect ligand substitution under thermal

Table 3
Summary of reactions of inclusion complexes 18 and 19 with PBu_3

Entry	Complex	Reaction conditions	% 21[a]	Enant. ratio[b]
1	18	PBu_3, H_2O, 50°C, 4 h	[c]	47:53
2	18	PBu_3, CH_3CN, hν, 4 h	43	51:49
3	19	PBu_3, H_2O, 60°C, 5 h	[c]	52:48
4	19	PBu_3, CH_3CN, hν, 4 h	41	52:48

[a] Yield reported is for two steps; 18 or 19 to 20 to 21.
[b] (s)-tri-fluoroethanol-9-anthryl as a chiral shift reagent.
[c] Excess phosphine was not removed from 21 following SO_2 insertion.

(aqueous) or photochemical (acetonitrile) conditions described above led to the formation of the corresponding monocarbonyl π-allyl complex (**25**) which we had already prepared and characterized in our earlier investigation of the chemistry of **22** in the absence of cyclodextrins [8].



3. Conclusion

In conclusion, we have demonstrated that it is possible to carry out ligand substitution reactions in solution on an organometallic complex included in a cyclodextrin cavity. Whereas $CpRFe(CO)_2R'$ complexes normally participate in CO insertion/alkyl migration reactions when heated with phosphines, the inclusion compounds of these complexes instead participated in ligand substitution reactions presumably because ligand/cyclodextrin steric interactions slow down the rates of alkyl migration. Unfortunately, this ligand substitution reaction did not prove to be enantioselective. This failure could be due to the fact that the cyclopentadienyl ligand does not include into the cyclodextrin far enough to make the metal carbonyl ligands appear diastereotopic [6]. Further modification of the cyclodextrin and/or the organometallic complex or possibly switching to other types of chiral hosts will be necessary (for some recent references to synthetically modified cyclodextrins see [18]; for a review of chemistry of other possible hosts see [19]). Hopefully, observation of diastereotopic metal carbonyls following cyclodextrin inclusion or encapsulation of the cyclopentadienyl ligand into other chiral environments will provide a useful indicator of what future inclusion complexes look to be promising candidates for enantioselective ligand substitutions.

4. Experimental section

4.1. General methods

For a description of instrumentation and chromatographic adsorbents used see ref. [20]. Cyclopentadienylirondicarbonyl dimer was purchased from Strem Chemicals and used as received. α-Cyclodextrin was purchased from TCI America and used as received. β-cyclodextrin and tri-*n*-butylphosphine were purchased from Aldrich Chemical and used as received. γ-Cyclodextrin was generously donated by American Maize and used as received. Iron complexes **1** [9] and **17** [17] were prepared according to previously published methods. Authentic racemic $CpFe(PBu_3)(CO)Me$ (**10**) was prepared as previously described [13]. Cyclodextrin inclusion compounds are invariably obtained as hydrates. All inclusion compounds reported here were vacuum dried at 1 mmHg overnight prior to obtaining elemental analysis data.

4.1.1. General procedure 1: synthesis of inclusion compounds

To a saturated aqueous solution of the appropriate cyclodextrin (1.5 eq) was added the iron-complex (1.0 eq). The mixture was stirred at ambient temperatures for 16 h. A pale yellow solid gradually precipitated out. The solid was collected by suction filtration and washed with copious amounts of water to remove any nonincluded cyclodextrin. Next, the solid was washed with THF 3×5 ml (unless specified otherwise). The pale yellow solids thus obtained were then dried in vacuo at room temperature overnight.

4.1.2. General procedure 2: thermal reactions of inclusion complexes with PBu_3 in water

A 50-ml round-bottomed flask equipped with a magnetic stir bar was charged with water (15 ml). The solution was degassed and the appropriate cyclodextrin inclusion compound was added. Excess (5 to 10 eq) tri-*n*-butylphosphine was added and the resulting suspension was heated at 50°C for 4–5 h with stirring. During this time, the phosphine droplets gradually take on an orange/amber color. After this heating period, the mixture was allowed to cool to 25°C and the suspension was extracted with ethyl acetate (2×15 ml). The organic extracts were combined and dried over anhydrous Na_2SO_4. Removal of the volatiles on a rotary evaporator afforded an amber colored oil. The crude product was directly converted to the SO_2 insertion product without purification as follows. (Caution: The SO_2 insertion reaction should be performed in a well ventilated hood.) The amber oil was redissolved in freshly distilled CH_2Cl_2 (15 ml) and cooled to -10°C. The solution was degassed then sulfur dioxide gas was bubbled through the solution for 2 min. Stirring was continued for 30 min then the reaction mixture was allowed to warm to 25°C. Removal of the volatiles via rotary evaporation left an amber colored viscous oil. Purification was achieved by chromatography on alumina. The excess phosphine was eluted with hexane. The iron sulfinate was then obtained as an amber oil following elution with $CHCl_3$ and solvent removal via rotary evaporation and high vacuum.

4.1.3. General procedure 3: photochemical reaction of inclusion compounds with PBu_3 in acetonitrile

A 50-ml round-bottomed flask equipped with a magnetic stir bar was charged with acetonitrile (20 ml). The solution was degassed and the appropriate cyclodextrin inclusion compound was added. Tri-*n*-butylphosphine (1.1 eq) was added along with a reflux condenser. The mixture was irradiated for 4 h while stirring using a 150-W flood lamp at a distance of 20 cm. As the reaction progresses, the acetonitrile solution slowly turns an orange/amber color. After cooling the mixture, the suspension was filtered. Concentration of the filtrate resulted in an amber oil which by ^{1}H-NMR in all cases showed near quantitative conversion to the corresponding phosphine substituted iron complex. The iron complex was promptly submitted to the sulfur dioxide insertion/purification sequence as described in Section 4.1.2 above.

4.2. (η^5-Cyclopentadienyl)iron(dicarbonyl)(methyl)-α-cyclodextrin complex (5)

The procedure of Section 4.1.1 was followed using α-cyclodextrin (2.0 g, 2.05 mmol) and η^5-cyclopentadienyl)iron–methyl complex (**5**) (0.263 g, 1.37 mmol). The corresponding inclusion compound (**5**) was obtained as a pale yellow solid (0.72 g, 0.34 mmol, 33%): m.p. 182–187°C (dec). IR (nujol): 3323 (OH, vs), 2008 (CO, vs) 1953 (CO, vs) 1156 (s), 1079 (s), 1029 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 5.57–5.41 (m, 24H), 4.97 (s, 5H), 4.79 (d, 12H, J = 3.2 Hz), 4.56–4.43 (m, 12H), 3.86–3.50 (m, 36H), 3.47–3.20 (m, 36H), 0.04 (s, 3H). ^{13}C-NMR (DMSO-d_6): 218.3, 102.0, 85.9, 82.0, 73.3, 72.1, 72.0, 60.0, −23.2. Anal. Calcd for $C_{44}H_{68}FeO_{32}\cdot 6H_2O$: C, 41.52; H, 6.33. Found: C, 41.11; H, 6.24. LRMS (FAB) m/z Calcd for $C_{43}H_{68}FeO_{31}$ $(M-CO)^+$ 1136.3, found: 1135.7, found $(M-CO+Na)^+$: 1157.6.

4.3. (η^5-Cyclopentadienyl)iron(dicarbonyl)(methyl)-β-cyclodextrin complex (6)

The procedure of Section 4.1.1 was followed using β-cyclodextrin (3.55 g, 3.12 mmol) and iron complex (**1**) (0.600 g, 3.12 mmol). The corresponding inclusion compound (**6**) was obtained as a pale yellow solid (3.48 g, 2.62 mmol, 84%): m.p. 175–180°C (dec). IR (nujol): 3336 (OH, vs), 1999 (CO, vs) 1949 (CO, vs) 1156 (s), 1081 (s), 1031 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 5.73–5.66 (m, 14H), 4.97 (s, 5H), 4.82 (d, 7H, J = 3.2 Hz), 4.50 (t, 7H, J = 3.2 Hz), 3.71–3.52 (m, 21H), 3.40–3.23 (m, 21H), 0.05 (s, 3H). ^{13}C-NMR (DMSO-d_6): 218.2, 102.0, 85.6, 80.1, 73.1, 72.4, 72.0, 60.0, −23.3. Anal. Calcd for $C_{50}H_{78}FeO_{37}\cdot 2H_2O$: C, 44.06; H, 6.06. Found: C, 43.67; H, 6.11. LRMS (FAB) m/z Calcd for $C_{50}H_{78}FeO_{37}Na$ $(M+Na)^+$ 1349.3, found: 1348.5.

4.4. (η^5-Cyclopentadienyl)iron(dicarbonyl)(methyl)-γ-cyclodextrin complex (7)

The procedure of Section 4.1.1 was followed using γ-cyclodextrin (2.0 g, 1.61 mmol) and η^5-cyclopentadienyl)iron–methyl complex (**1**) (0.296 g, 1.07 mmol). The corresponding inclusion compound (**7**) was obtained as a pale yellow solid (1.03 g, 0.70 mmol, 65%): m.p. 185–190°C (dec). IR (nujol): 3348 (OH, vs), 2004 (CO, vs) 1943 (CO, vs) 1642 (s), 1157(s), 1081 (s), 1028 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 5.80–5.66 (m, 16H), 4.96(s, 5H), 4.87 (d, 8H, J = 3.3 Hz), 4.54 (t, 8H, J = 5.2 Hz), 3.71–3.50 (m, 24H), 3.40–3.23 (m, 24H), 0.05 (s, 3H). ^{13}C-NMR (DMSO-d_6): 218.2, 101.7, 85.8, 80.1, 72.9, 72.6, 72.2, 60.0, −23.4. Anal. Calcd for $C_{56}H_{88}FeO_{42}\cdot 4H_2O$: C, 43.08; H, 6.20. Found: C, 43.21; H, 6.28. LRMS (FAB) m/z Calcd for $C_{55}H_{85}FeO_{42}Na$ $(M-Me+Na)^+$ 1497.1, found: 1497.2.

4.5. (η^5-Cyclopentadienyl)Fe(CO)(PBu_3)(SO_2Me) (11)

Iron complex (**1**) (0.50 g, 2.60 mmol) and tri-*n*-butylphosphine (0.526 g, 0.647 ml, 2.60 mmol) were dissolved in freshly distilled, degassed heptane (100 ml). The yellow solution was irradiated using a 150-W flood lamp for 15 h. As the reaction progressed, the yellow solution gradually turned red. The heptane was removed via rotary evaporation and the crude product was purified by chromatography on alumina (1:1 benzene/$CHCl_3$). Removal of the volatiles afforded **10** as a dark oil (0.68 g, 1.78 mmol, 68%). Complex **10** (0.50 g, 1.30 mmol) was cooled to −10°C and liquid SO_2 (~25 ml) was allowed to condense onto the complex. After 10 min, CH_2Cl_2 was added (5 ml) to the flask and the resulting dark green solution was stirred at −10°C for 2 h. The flask was then removed from the ice bath and excess SO_2 allowed to evaporate. Solvent was removed via rotary evaporation and the oil thus obtained was purified by chromatography on alumina ($CHCl_3$) to yield **11** as an amber oil following solvent removal (0.370 g, 0.81 mmol, 63%). IR (C_6D_6): 2966 (s), 2931 (s), 1960 (vs), 1155 (s), 1032 (s) cm^{-1}. ^{1}H-NMR (C_6D_6): 4.24 (d, 5H, J = 1.2 Hz), 2.98 (s, 3H), 2.17–1.68 (m, 6H), 1.62–1.27 (m, 12H), 0.85 (t, 9H, J = 7.0 Hz). ^{13}C-NMR (C_6D_6): 219.0(d, J = 28.0 Hz), 84.4, 61.2, 27.0 (d, J = 25.8 Hz), 26.0, 24.5 (d, J = 13.2 Hz), 13.9. Anal. Calcd for $C_{19}H_{35}FePO_3S$: C, 53.03; H, 8.20. Found: C, 52.76; H, 8.13. HRMS Calcd. for $C_{18}H_{35}FePO_2S$ 402.1444. Found (M^+-CO) 402.1426.

4.6. Diphenylbutylphosphine β-cyclodextrin Complex (13)

The procedure of Section 4.1.1 was followed using β-cyclodextrin (2.0 g, 1.76 mmol) and diphenyl-

butylphosphine (0.260 g, 1.17 mmol). The corresponding inclusion compound (**13**) was obtained as an off white solid (1.22 g, 0.90 mmol, 77%): m.p. 235–240°C (dec). IR (nujol): 3332 (vs), 1652 (w) 1409 (m), 1332 (m), 1159 (s), 1029 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 7.85–7.70 (m, 4H), 7.57–7.28 (m, 6H), 5.82–5.61 (m, 14H), 4.65 (d, 7H, J = 3.2 Hz), 4.50 (t, 7H, J = 3.2 Hz), 3.75–3.46 (m, 21H), 3.38–3.25 (m, 21H), 2.33–2.03 (m, 2H), 1.36 (m, 4H), 0.82 (t, 3H, J = 6.0 Hz) ^{13}C-NMR (DMSO-d_6):138.7 (d, J = 14.0 Hz), 132.4 (d, J = 18.5 Hz), 128.6, 128.5, 102.0, 81.6, 73.1, 72.7, 72.1, 60.0, 27.8 (d, J = 15.5 Hz), 26.5 (d, J = 11.0 Hz), 23.6 (d, J = 13.2 Hz), 13.7. Anal. Calcd for $C_{58}H_{89}PO_{35} \cdot 7H_2O$: C, 46.34; H, 6.91. Found: C, 46.05; H, 6.78. LRMS (FAB) m/z Calcd for $C_{58}H_{89}PO_{36}$ $(M + H + O)^+$ (the included phosphine oxide) 1393.3, found: 1393.4.

4.7. Diphenylbutylphosphine γ-cyclodextrin Complex (14)

The procedure of Section 4.1.1 was followed using γ-cyclodextrin (2.0 g, 1.54 mmol) and diphenylbutylphosphine (0.228 g, 1.03 mmol). The corresponding inclusion compound (**14**) was obtained as a white solid (1.50 g, 0.98 mmol, 96%): m.p. 240–245°C (dec). IR (nujol): 3361 (vs), 1642 (w), 1157 (s), 1079 (s), 1029 (s), 940 (m), 863 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 7.36 (bs, 10H), 5.74–5.65 (m, 16H), 4.82 (d, 8H, J = 3.3 Hz), 4.44 (t, 8H, J = 7.0 Hz), 3.74–3.47 (m, 24H), 3.44–3.18 (m, 24H), 2.04 (t, 2H, J = 7.4 Hz), 1.35 (m, 4H), 0.82 (t, J = 6.1 Hz, 3H). ^{13}C-NMR (DMSO-d_6): 138.7 (d, J = 13.6 Hz), 132.4 (d, J = 18.3 Hz), 128.7, 128.5, 102.0, 81.6, 73.1, 72.5, 72.1, 60.0, 27.5 (d, J = 15.9 Hz), 26.8 (d, J = 11.0 Hz), 23.6 (d, J = 13.4 Hz), 13.8. Anal. Calcd for $C_{64}H_{99}PO_{30}$: C, 49.93 H, 6.48. Found: C, 49.79; H, 6.53. LRMS (FAB) m/z Calcd for $C_{64}H_{100}PO_{31}$ $(M + H + O)^+$ (the included phosphine oxide) 1556.4, found: 1555.8. LRMS (ESI) m/z Calcd for $C_{64}H_{100}PO_{30}$ $(M + H)^+$ 1539.5, found: 1539.5.

4.8. (η^5-Methylcyclopentadienyl)iron(dicarbonyl)(methyl)-β-cyclodextrin complex (18)

The procedure of Section 4.1.1 was followed using β-cyclodextrin (2.0 g, 1.76 mmol) and iron complex (**17**) (0.240 g, 1.17 mmol). The corresponding inclusion compound (**18**) was obtained as a pale yellow solid (1.13 g, 0.84 mmol, 72%): m.p. 190–195°C (dec). IR (nujol): 3354 (vs), 1999 (vs) 1944 (vs) 1157 (s), 1081 (s), 1030 (s), 944 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 5.75–5.68 (m, 14H), 4.85–4.75 (m, 11H), 4.50 (t, 7H, J = 3.2 Hz), 3.72–3.50 (m, 21H), 3.40–3.20 (m, 21H), 1.80 (s, 3H), 0.0 (s, 3H). ^{13}C-NMR (DMSO-d_6): 218.4, 103.3, 102.0, 85.3, 83.9, 81.6, 73.0, 72.5, 72.0, 60.0, 12.3, −19.8. Anal. Calcd for $C_{51}H_{80}FeO_{37} \cdot 2H_2O$: C, 44.46; H, 6.15. Found: C, 43.38; H, 6.21. LRMS (FAB) m/z Calcd for $C_{50}H_{78}FeO_{37}Na$ $(M–Me + Na + H)^+$ 1349.4, found: 1349.6.

4.9. (η^5-Methylcyclopentadienyl)iron(dicarbonyl)(methyl)-γ-cyclodextrin complex (19)

The procedure of Section 4.1.1 was followed using γ-cyclodextrin (2.0 g, 1.54 mmol) and iron complex (**17**) (0.221 g, 1.07 mmol). The corresponding inclusion compound (**19**) was obtained as a pale yellow solid (0.96 g, 0.64 mmol, 60%): m.p. 185–190°C (dec). IR (nujol): 3330 (vs), 2001 (vs) 1943 (vs) 1157 (s), 1078 (s), 1027 (s), 940 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 5.81–5.70 (m, 16H), 4.87–4.76 (m, 12H), 4.54 (t, 8H, J = 5.2 Hz), 3.70–3.50 (m, 24H), 3.45–3.23 (m, 24H), 1.80 (s, 3H), 0.0 (s, 3H). ^{13}C-NMR (DMSO-d_6): 218.5, 103.3, 101.8, 85.4, 83.9, 81.0, 73.0, 72.7, 72.3, 60.0, 12.4, −19.8. Anal. Calcd for $C_{57}H_{90}FeO_{42} \cdot 2H_2O$: C, 44.48; H, 6.16. Found: C, 43.30; H, 6.16. LRMS (FAB) m/z Calcd for $C_{56}H_{90}FeO_{41}K$ $(M–CO + K)^+$ 1481, found: 1481.

4.10. (η^5-Methylcyclopentadienyl)Fe(CO)(PBu_3)(SO_2-Me) (21)

General procedures of Section 4.1.2 or Section 4.1.3 were used to prepare this compound as described in Table 3. Yields for obtaining this compound from **18** or **19** are also presented in Table 3. Spectroscopic data for **21**: IR (C_6D_6): 2960 (s), 2932 (s), 1947 (vs), 1465 (m), 1177 (s), 1044 (s) cm^{-1}. ^{1}H-NMR (C_6D_6): 4.84 (bs, 2H), 4.41(bs, 2H), 3.05 (s, 3H), 1.67 (s, 3H), 1.56–1.15 (m, 18H), 0.90 (t, J = 6.6 Hz, 9H). ^{13}C-NMR (C_6D_6): 219.4 (d, J = 28.6 Hz), 99.9, 89.8, 85.3, 84.9, 77.7 61.1, 27.4 (d, J = 25.6 Hz), 26.0, 24.6 (d, J = 13.0 Hz), 13.9.

4.11. 2-(Cyclopentadienylirondicarbonyl)-1,3-butadienyl β-cyclodextrin complex (23)

The procedure of Section 4.1.1 was followed using β-cyclodextrin (2.0 g, 1.76 mmol) and complex **22**[8] (0.270 g, 1.17 mmol). The corresponding inclusion compound (**23**) was obtained as a yellow solid (1.21 g, 0.89 mmol, 76%): m.p.: 185–190°C (dec). IR (nujol): 3344 (vs), 2013 (vs), 1961 (vs), 1642 (w), 1158 (s), 1032 (s), 938 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 6.48 (dd, 1H, J = 17.0, 10.4 Hz), 5.74–5.68 (m, 14H), 5.18 (bs, 1H), 5.03 (s, 5H), 4.93 (bs, 1H), 4.82–4.75 (m, 9H), 4.46 (t, 7H, J = 4.4 Hz), 3.75–3.46 (m, 21H), 3.42–3.20 (m, 21H). ^{13}C-NMR (DMSO-d_6): 216.9, 153.6, 151.5, 129.2, 112.9, 102.0, 86.4, 81.6, 73.1, 72.5, 72.1, 60.0. Anal. Calcd for $C_{53}H_{80}FeO_{37} \cdot 3H_2O$: C, 44.86; H, 6.11. Found: C, 45.07; H, 6.16. LRMS

(FAB) m/z Calcd for $C_{53}H_{81}FeO_{37}$ $(M+H)^+$ 1365.4, found: 1365.5.

4.12. 2-(Cyclopentadienylirondicarbonyl)-1,3-butadienyl γ-cyclodextrin complex (24)

The procedure of Section 4.1.1 was followed using γ-cyclodextrin (2.0 g, 1.54 mmol) and complex **22** [8] (0.246 g, 1.03 mmol). The corresponding inclusion compound (**24**) was obtained as a yellow solid (1.10 g, 0.72 mmol, 70%): m.p. 195–200°C (dec). IR (nujol): 3363 (vs), 2014 (m), 1959 (m), 1644 (m), 1158 (s), 1028 (s), 941 (m), 862 (m) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 6.48 (dd, 1H, $J = 16.6$, 10.0 Hz), 5.75 (m, 16H), 5.18 (bs, 1H), 5.02 (s, 5H), 4.86 (m, 11H), 4.52 (t, 8H, $J = 4.4$ Hz), 3.75–3.46 (m, 24H), 3.42–3.20 (m, 24H). ^{13}C-NMR (DMSO-d_6): 216.7, 153.2, 151.3, 129.1, 112.8, 102.0, 86.4, 81.6, 73.1, 72.5, 72.1, 60.0. Anal. Calcd for $C_{59}H_{90}FeO_{42} \cdot 4H_2O$: C, 44.31; H, 6.18. Found: C, 44.31; H, 6.18. LRMS (FAB) m/z Calcd for $C_{58}H_{90}FeO_{41}$ (M^+-CO) 1498.4, found: 1497.3.

4.13. Thermal reaction of inclusion complex 6

The procedure of Section 4.1.2 was followed using inclusion complex **6** (0.100 g, 0.075 mmol) and tri-*n*-butyl phosphine (0.152 g, 0.187 ml, 0.75 mmol). After chromatographic purification, **11** was isolated as an amber oil (0.013 g, 0.030 mmol, 41%). The ratio of enantiomers was found to be 54:46 using (s)-tri-fluoroethanol-9-anthryl [15] as shift reagent.

4.14. Photolysis of inclusion complex 6

The procedure of Section 4.1.3 was followed using complex **6** (0.100 g, 0.075 mmol) and tri-*n*-butyl phosphine (0.018 g, 22.5 μl, 0.75 mmol). After chromatographic purification, **11** was isolated as an amber oil (0.022 g, 0.049 mmol, 67%). The ratio of enantiomers was found to be 52:48 using (s)-tri-fluoroethanol-9-anthryl [15] as shift reagent.

4.15. Photolysis of inclusion complex 18

The procedure of Section 4.1.3 was followed using complex **18** (0.100 g, 0.075 mmol) and tri-*n*-butyl phosphine (0.023g, 28.0 μl, 0.11 mmol). After chromatographic purification, **21** was isolated as an amber oil (0.014 g, 0.031 mmol, 43%). The ratio of enantiomers was found to be 51:49 using (s)-tri-fluoroethanol-9-anthryl [15] as shift reagent.

4.16. Photolysis of inclusion complex 19

The procedure of Section 4.1.3 was followed using complex **19** (0.100 g, 0.066 mmol) and tri-*n*-butyl phosphine (0.020 g, 24.8 μl, 0.10 mmol). After chromatographic purification, **21** was isolated as an amber oil (0.012 g, 0.027 mmol, 41%). The ratio of enantiomers was found to be 52:48 using (s)-tri-fluoroethanol-9-anthryl [15] as shift reagent.

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