

## Reactions of Organometallic Complexes included in Cyclodextrins: Reactivity of Alkyldicarbonyl( $\eta^5$ -cyclopentadienyl)iron Complexes towards Carbon Monoxide and Sulphur Dioxide in the Solid State

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Inclusion compounds of alkyldicarbonyl( $\eta^5$ -cyclopentadienyl)iron with cyclodextrins undergo, in the solid state, insertion of carbon monoxide and sulphur dioxide into the Fe-R bond; the effect of inclusion by cyclodextrin towards the insertion reactions strongly depends on the type of cyclodextrins used.

Cyclodextrins (CDs) are cyclic molecules consisting of either six, seven or eight glucose units ( $\alpha$ -,  $\beta$ - and  $\gamma$ -CD, respectively), each having a slightly different cavity diameter:  $\alpha$ -CD with a 4.5 Å cavity,  $\beta$ -CD with a 7.0 Å cavity and  $\gamma$ -CD with a 8.5 Å cavity. They can form inclusion complexes with a wide variety of guest compounds without any covalent bond being formed. Recently we and Stoddart *et al.* have reported the preparation and properties of cyclodextrin inclusion compounds with organotransition metal complexes.<sup>1</sup> However, there have been no reports on the reaction of organometallic complexes within the cyclodextrin cavity.

We have now found that cyclodextrins form inclusion compounds with alkyliron complexes and that the effect of

cyclodextrin inclusion on CO and SO<sub>2</sub> insertion into the Fe-R bond,<sup>2</sup> in the solid state, depends upon the type of cyclodextrins used. Reactions in the solid state are of current interest; Toda *et al.*, for example, have reported interesting differences between some organic reactions in the solid state and those in solution.<sup>3</sup> We report here the preparation of cyclodextrin inclusion compounds of alkyldicarbonyl( $\eta^5$ -cyclopentadienyl)iron and the reaction of these inclusion compounds with CO and SO<sub>2</sub> in the gas-solid system (Fig. 1).

Cyclodextrin inclusion compounds were prepared in high yields by the method reported previously.<sup>1</sup> The host-guest ratio was determined by <sup>1</sup>H NMR in hexadeuteriodimethyl sulphoxide; the molar ratios of the alkyliron complex to

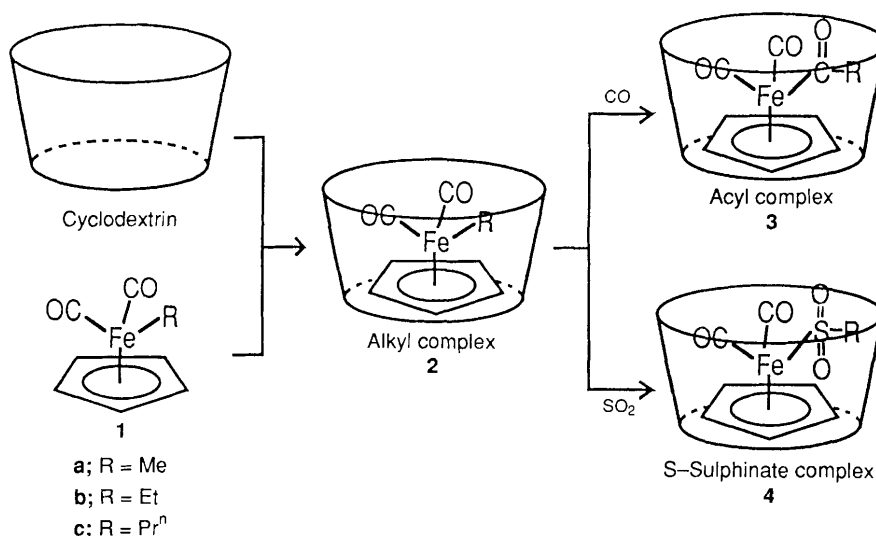


Fig. 1 Preparation of CD-CpFe(CO)<sub>2</sub>R inclusion compounds and reaction with CO and SO<sub>2</sub> in a gas-solid system

**Table 1** Influence of inclusion by CD on CO insertion reactions<sup>a</sup>

Complexes	Conversion (%) of alkyl complex to acyl complex		
	In $\alpha$ -CD	In $\beta$ -CD	In $\gamma$ -CD
Me	0	30	77
Et	10	35	61
Pr <sup>n</sup>	0	20	100

<sup>a</sup> Conditions: temp., 100 °C; CO, 100 atm; reaction time, 3 h.

**Table 2** Influence of inclusion by CD on SO<sub>2</sub> insertion reactions<sup>a</sup>

Complexes	Conversion (%) of alkyl complex to sulphinate complex		
	In $\alpha$ -CD	In $\beta$ -CD	In $\gamma$ -CD
Me	0	0	100
Et	0	0	100
Pr <sup>n</sup>	0	0	100

<sup>a</sup> Conditions: temp., 25 °C; under SO<sub>2</sub> atmosphere; reaction time, 3 h.

cyclodextrin were 0.5 for the  $\alpha$ -cyclodextrin complex and 1.0 for both the  $\beta$ - and  $\gamma$ -cyclodextrin complexes.<sup>†</sup>

Space-filling models based on the result of X-ray analysis<sup>4</sup> of ferrocene-cyclodextrin inclusion compounds imply that the alkyliron complexes appear to fit well in the  $\beta$ -CD cavity. The  $\gamma$ -CD cavity is also large enough to accommodate the alkyliron complexes, whereas the complexes are closely packed in the cavity formed by two molecules of the  $\alpha$ -CD.

The CO insertion reaction was carried out in a stainless-steel autoclave without solvents under 100 atm of carbon monoxide at 100 °C. When SO<sub>2</sub> was used, the solid inclusion compound was exposed to gaseous SO<sub>2</sub> at 25 °C. After 3 h, the product was dissolved in water and extracted with methylene chloride. The conversion of the alkyliron complexes **1a–1c** to the acyl or sulphinate complexes was determined by the <sup>1</sup>H NMR spectra (Tables 1 and 2).<sup>‡</sup>

<sup>†</sup> For example the <sup>1</sup>H NMR spectrum of the inclusion compound of the methyliron complex **1a** with  $\alpha$ -CD shows two singlets at  $\delta$  4.99 (Cp protons) and 0.06 (methyl protons), and a broad resonance at  $\delta$  4.79 due to the <sup>1</sup>H protons of  $\alpha$ -CD. The integrated intensities of these bands, 4.5 : 3 : 12 agreed with those expected, 5 : 3 : 12.

<sup>‡</sup> The amount of product was evaluated by comparison of a <sup>1</sup>H NMR integration ratio of the Cp proton signal (5H) with that of benzene (6H) added as integration standard.

We wondered if the reactivity of the complex would be sensitive to the cavity diameter of the CDs. It may be expected that as the diameter becomes smaller, the conversion of the complex would be diminished owing to steric factors. Indeed, this is precisely what has been observed experimentally. The data listed in the Tables indicate that the different reactivities towards CO or SO<sub>2</sub> strongly depend on the host molecule, *i.e.*, the rate of the insertion reaction decreases sharply with the smaller cavity size of the cyclodextrin ( $\gamma$ -CD >  $\beta$ -CD >  $\alpha$ -CD). Cyclodextrin inclusion is able to control the reactivity of the alkyliron complexes. The alkyliron complexes within the largest cavity ( $\gamma$ -CD) gave the acyl and sulphinate complexes quantitatively, whereas the reaction in the smallest cavity ( $\alpha$ -CD) showed a striking decrease in rate. A plausible interpretation for the difference is that the motion of the guest molecule and the access of CO and SO<sub>2</sub> to the iron are restricted within the cyclodextrin cavity.

The effect of increasing the chain length of the alkyl ligand is not simply predicted because in solution, without CDs, the iron complexes having a longer alkyl group exhibit a higher reactivity towards CO insertion. In the solid state, however, the iron complexes require a larger space for the reaction. Thus among the three kinds of alkyl complexes **1a–c**, the maximum conversion was observed for the ethyl complex **1b**. It is known that in solution the alkyliron complexes are converted to the acyl or sulphinate complexes quantitatively under these conditions.<sup>2</sup>

The present results may demonstrate the delicate geometric requirements to be fulfilled when a macrocycle is used to control the reaction in the cavity.<sup>5</sup>

Received, 30th August 1990; Com. 0/03942J

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