

Template synthesis and cocatalytic behavior of phosphorus donor containing *trans*-Fe(0) metallacrown ethers

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Some new phosphorus donors containing *trans*-Fe(0) metallacrown ethers were obtained by template synthesis. The cocatalytic properties of these complexes and the X-ray diffraction structure of complex **1** were discussed.

Keywords Phosphorus donor, metallacrown ethers, synthesis, cocatalytic properties

Introduction

Recently, there is an increasing interest in phosphorus donor containing metallacrown ethers because of their ability to bind metal cation and small molecules and to develop some catalytic systems with enzyme like activities and selectivities.¹

But, adopting mixed solvents (C₂H₅OH/THF) instead of ethanol under non-high dilution conditions we have obtained *trans*-Fe(0) metallacrown ethers without polymeric products in a fair isolated yield (45—65%) (see Scheme 1).

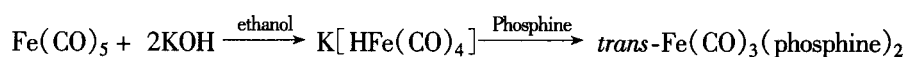
A plausible mechanism is the template action of the potassium cation, which would make the cyclization reaction easily occur (see Fig. 1).

All products were air-stable pale-yellow microcrystals. The ³¹P NMR spectra gave single resonance at from δ 50.77 to 75.86. The IR spectra are typical for *trans*-Fe(CO)₃L₂ and exhibit two or three ν(CO) vibrations

Most of the reported complexes have a *cis*-phosphorus donor group. Up to now only a few *trans*-metallacrown ethers have been obtained.² Both *cis*- and *trans*-complexes were usually prepared by high dilution technique. Here we report some new phosphorus donors containing *trans*-Fe(0) metallacrown ethers and their behavior as co-catalysts.

Results and discussion

In our laboratory a series of *trans*-Fe(CO)₃(phosphine)₂ have been synthesized³ by Brunet's method.⁴ Using the same procedure we failed to get the aimed compounds because of the formation of polymers.



depending on the local symmetry of the carbonyl groups at the iron atoms (*D*_{3h} or *C*_s) for complexes **1—4**, and the diiron compound **5** gives five ν(CO) vibrations due to its low symmetry.

The X-ray structural data of complex **1** presented in Fig. 2 show that the iron atom possesses a trigonal bipyramidal configuration. The P-Fe-P unit (174.6°) is some deviation from linearity. The iron atom and the three carbonyl groups are in the same plane, which is perpendicular to the 11-membered ferramacrocyclic. The angle C(1)-Fe-C(2) (125.1°) is larger than angles C(2)-Fe-C(3) (119.4°) and C(1)-Fe-C(3)

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(115.5°) and bisects the ferramacrocycle.

Scheme 1

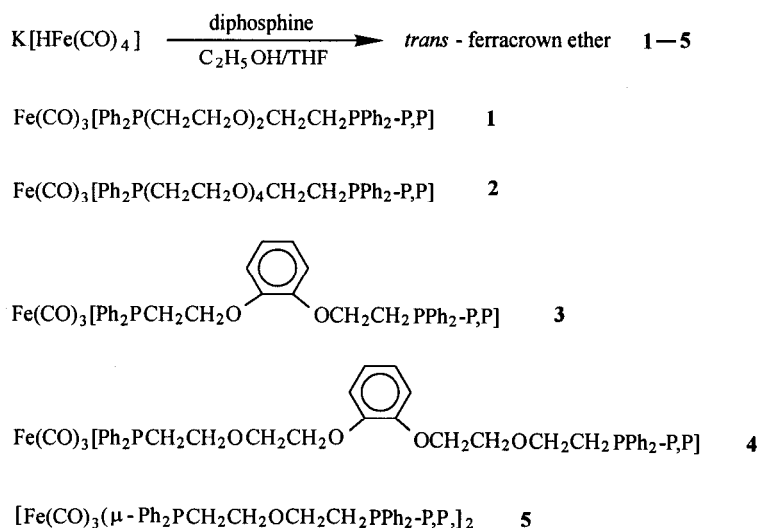


Table 1 Catalytic behavior of KI-ferracrown ethers 1–5^a

Catalytic system and amount (mmol)	EO conversion (%)	EC selectivity (%)
KI (1.2)	33.09	100
KI – Ph ₂ P(CH ₂ CH ₂ O) ₂ (CH ₂ CH ₂)PPh ₂ (1.2) (0.38)	61.30	100
KI — 1 (1.2) (0.38)	87.03	100
KI — 2 (1.2) (0.38)	87.08	100
KI — 3 (1.2) (0.38)	88.25	100
KI — 4 (1.2) (0.38)	89.24	100
KI — 5 (1.2) (0.38)	90.63	100

^aEO = ethylene oxide; EC = ethylene carbonate.

Reaction conditions: EO, 10 mL; THF, 90 mL; CO₂ pressure, 4 MPa; temperature, 120°C; time, 3 h.

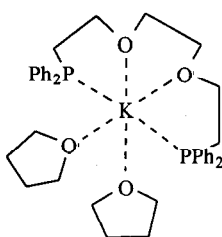
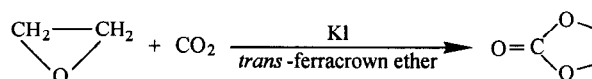


Fig. 1 A plausible mechanism.

We use these ferracrown ethers as co-catalysts to evaluate their function in the reaction of ethylene oxide

with carbon dioxide in the presence of potassium iodide to form ethylene carbonate. The results are given in Table 1.



The reaction gave low conversion (33%) when KI alone was used as the catalyst. By the addition of the diphosphine Ph₂P(CH₂CH₂O)₂CH₂CH₂PPh₂ to the catalytic system the conversion was increased to 61%.

Using ferramacrocrown ethers **1**–**5** as cocatalysts, much higher conversions (87–90%) may be realized. Their coordination action to potassium cation and the activation by I^- ion would be responsible for this increase. Because these crown ethers are 11–17 membered cycles, the potassium cation might form a 1:2 sandwich structure with them or binds over the rings. It is possible that the iron(0) atom which is a Lewis base center shows a weak interaction with the K^+ cation.

The complexes **3** and **4** including phenyl group in

the cycle linkage have better cocatalytic behavior than the corresponding complexes **1** and **2**, respectively. The 16-membered diferracrown ether **5** displays more efficient action, which may imply the importance of the interaction between $Fe(0)$ and K^+ ion.

It is worthy of notice that these crown ethers exhibit co-catalytic activity comparable to 18-membered DB18C6 in the reaction, and it is predicted that they will display better co-catalytic properties if their cavity fit to the relative cation.

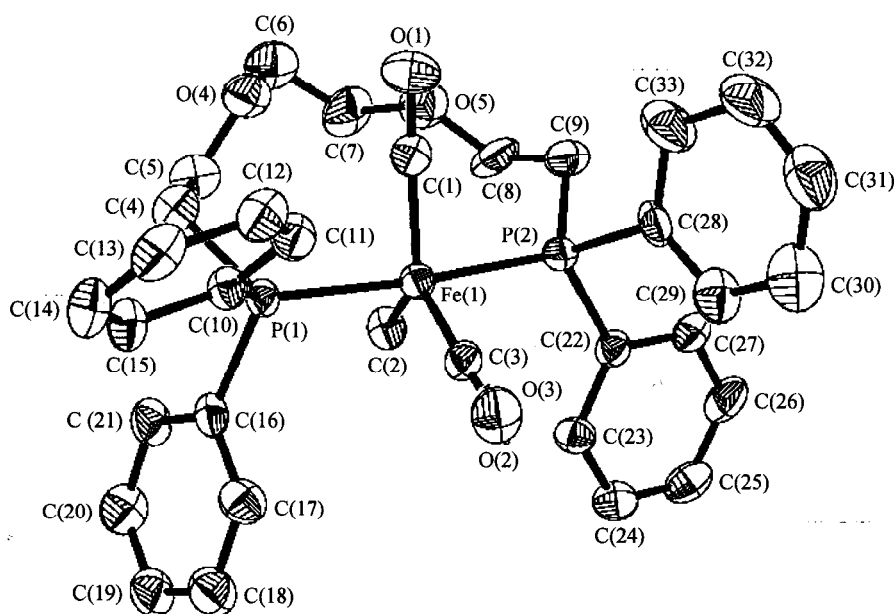


Fig. 2 Molecular structure of **1** (C–H hydrogen atoms are not shown).

Experimental

All the manipulations were carried out on a standard high-vacuum line under an inert gas atmosphere. All the solvents were purified by standard procedure.

Preparation of *trans*-Fe(0) metallacrown ethers

In a Schlenk flask $Fe(CO)_5$ (4.5 mmol) was added to a solution of potassium hydroxide (9 mmol) in ethanol (100 mL). After the mixture was stirred for 30 min at ambient temperature a solution of diphosphine (4.5 mmol) in THF (20 mL) was added. The mixture was refluxed for 24 h. After cooling to room temperature the yellow solid was filtered. The work up procedure of the product is similar to the method described.⁴
 δ_P : **1**, 75.86; **2**, 71.76; **3**, 68.12; **4**, 69.39; **5**,

71.76. $\nu(CO)$: **1**, 1970w, 1882s; **2**, 1970w, 1880s; **3**, 1975w, 1875s; **4**, 1975w, 1880s; **5**, 1980w, 1905s, 1885s, 1880s, 1850m cm^{-1} . **1**, Calcd: C, 62.23; H, 5.15; Found: C, 62.53; H, 5.14. **2**, Calcd: C, 62.18, H, 5.60; Found: C, 61.72; H, 5.35. **3**, Calcd: C, 62.87; H, 4.81; Found: C, 62.18; H, 4.68. **4**, Calcd: C, 62.96; H, 5.13; Found: C, 62.66; H, 5.14. **5**, Calcd: C, 63.92; H, 4.81; Found: C, 63.92; H, 4.68.

Crystal structure determination

Complex **1** $C_{33}H_{22}FeO_5P_2$. $M = 626.4$. orthorhombic, $a = 1.2393(1)$, $b = 1.4805(1)$, $c = 1.6925(1)$ nm; $V = 3.080(1)$ nm³, $T = 294$ K, space group $p2_12_12_1$, $Z = 4$, $\mu(Mo K_\alpha) = 0.633$ mm⁻¹, 6030 reflections measured, 5392 unique ($R_{int} = 0.024$)

which were used in all calculations. The formal wR (F^2) was 0.044, $R1 = 0.051$, Siemens PA/Pc four-circle diffractometer was used.

Catalytic reaction

In a 170 mL autoclave with a magnetic stirring bar were placed a certain quantity of THF, ethylene oxide, KI and co-catalyst. The autoclave is purged with CO_2 three times, then filled with CO_2 to the specified pressure. The mixture was stirred and heated to the reaction temperature. After the reaction the autoclave is quickly cooled to room temperature. The reaction mixture was analyzed by GC (see Table 1).

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