

## PHOTOPOLYMERIZATION WITH TRANSITION METAL COMPLEXES

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### Abstract

This paper gives an introduction to photopolymerchemistry with special emphasis to photopolymerizations using organometallic initiators. Photopolymers are used in various processes for the manufacturing of printed circuit boards (PCBs) and for integrated circuits in microelectronic applications.

Organometallic compounds have a great potential as photoinitiators for free-radical initiated (vinyl-group-bearing compounds, i.e. acrylates) and cation initiated (epoxides or vinyl ethers) polymerizations.

Two new photoinitiators from our research laboratories, titanocenes and iron arenes, shall demonstrate the usefulness of organometallic chemistry for imaging systems.

The bis-cyclopentadienyl-titanium-bis-pentafluorophenyl shows high sensitivity in radical initiated processes and has exceptional stability in acrylic resist formulations. Trapping experiments of the titanocene under exposure with the stable radical TMPO gave a  $\text{Cp}(\text{C}_6\text{F}_5)\text{Ti}(\text{TMPO})_2$  and a pentafluorophenyl-cyclopentadienyl. The observed primary photoproduct is assigned to a mono-hapto-cyclopentadienyl derivative which has free coordination sites for the addition of i.e. acrylates.

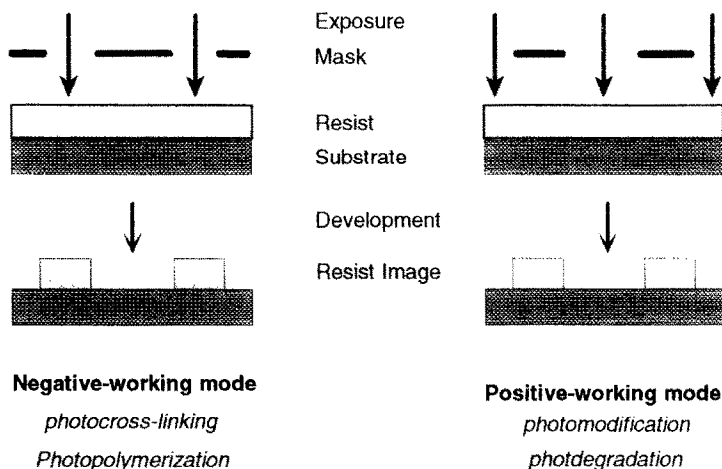
From  $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-benzene})\text{Fe}(\text{II})\text{hexafluorophosphate}$  a Lewis acid is generated under exposure with the loss of the benzene ligand. The free coordination sites can be captured by nucleophiles, i.e. epoxides, which react to cyclic polyethers. With ethylene oxide, bis-[12]crown-4-iron-bis-hexafluorophosphate is formed.

Two new preparation procedures are described for the synthesis of iron arene complexes. Starting from ferrocene, iron arene complexes can be synthesized in the presence of an aromatic compound,  $\text{AlCl}_3$  and  $\text{TiCl}_4$  in high yields. Beside the iron sandwich compound, also titanocene-dichloride is formed. Thermal ligand exchange reactions with thermally labile iron arene complexes allow to synthesize new derivatives with heterocyclic ligands or functionalized aromatics.

## 1. PHOTOREACTIVE POLYMERS

The physical properties of photoresist coatings change when the coatings are exposed to light. The change usually is one of solubility and results in solvent discrimination between exposed and unexposed areas. Photocross-linking and photoinitiated polymerization decrease solubility, whereas photomodification of functionality and photodegradation increase it. Exposure of coatings to light through a pattern results in solubility changes and, therefore, image boundaries that can be used to form resist images. Images can be produced by solvent development in either negative- or positive-working modes, as depicted in Fig. 1.

Figure 1:

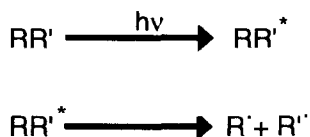


The negative-working mode depends on a light-induced decrease in solubility of polymer molecules. Virtually all polymers undergo chemical changes in one way or another as a result of their exposure to sufficiently energetic light. The documented first use of photoresistlike materials was in 1823 when coatings of a natural bituminous material, bitumen of Judea, were prepared and applied to metal that was exposed by means of a camera to a landscape scene [1]. A visible image formed after the coated metal was washed in a natural oil and the resulting relief image was chemically etched to produce an image of the landscape on the surface of metal. In the 1930s, the photohardening of unsaturated ketones and acids was utilized to provide etchable images for watchcase engraving [2]. The need for photoresists became great in the late 1940s with the development of the printed circuit industry. Development of photocross-linkable polymers, designed for use in the graphics arts, particularly, lithography, began in 1947 [3,4].

Photocross-linking, photomodification of functionality and photodegradation involve preformed, high molecular weight, photosensitive polymers. In photopolymerization, the result of photoreaction is the polymerization of a low molecular weight

monomeric material to form a high molecular weight polymer. In general, the net effect of the light energy in photopolymerization is the production of some kind of initiating species. Thus, a photopolymerizable system usually consists primarily of mono- or multifunctional polymerizable monomers, depending on whether cross-linking is desired; a photoinitiating system; and a preformed polymeric binder that can be used or omitted, according to the particular application.

The photoinitiator is responsible for producing initiating species by the action of light energy. Depending on the type of polymerization, the photoinitiator system can be free-radical or ionic. The two types of free-radical photoinitiator systems are those in which the mechanism of radical production is intramolecular photocleavage and those involving intermolecular proton abstraction. The first system, in which a compound absorbs light and is photocleaved, is the simplest:



Ionic photoinitiator systems can be either anionic or cationic. Much less is known about the ionic systems than about the free-radical systems. However, numerous publications deal mainly with the cationic type which polymerizes a variety of monomers [5]. The anionic systems tend to be more specific. The known cationic photoinitiators include the aryldiazonium salts ( $\text{ArN}^+\text{X}^-$ ), the diaryliodonium salts ( $\text{ArAr}'\text{I}^+\text{MX}^-$ ) and the triarylsulfonium salts ( $\text{ArAr}'\text{Ar}''\text{S}^+\text{X}^-$ ) [6].

Organometallics are known to undergo light induced processes in which radicals or cations are formed [7]. If they absorb light of the desired wavelength they can be suitable photoinitiators. However, a few basic requirements have to be met:

- 1.) The complexes themselves and their mixtures with the polymerizable materials must be thermally stable.
- 2.) They must absorb strongly in the UV/visible region of the spectrum.
- 3.) Upon irradiation they should undergo efficient processes yielding an anion, a radical or cation capable of starting polymerization.

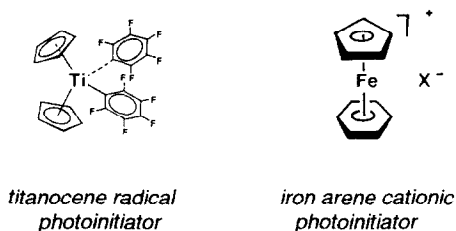
To date the vast majority of polymerization processes is achieved by free radical polymerization.

This is especially true for manufacture of integrated circuits.

An effort has been made over the last ten years to find initiators for cationic polymerization [5,6,8,9]. The so formed polymers generally have a number of advantages over radically initiated systems. Up until now there is no system known in which anionic polymerization can be brought about by light.

This paper will present an overview over two new organometallic photoinitiators, shown in fig. 2, for radical and cationic photopolymerization processes.

Figure 2:



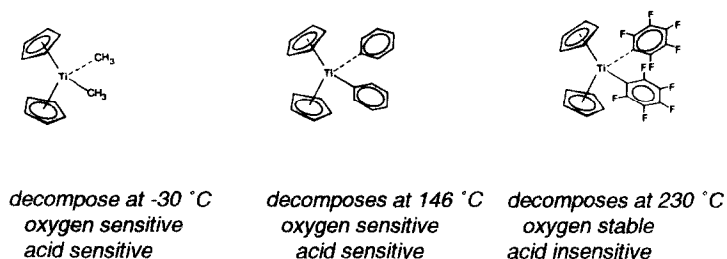
## 2. TITANOCENE PHOTOINITIATORS

A number of titanium(IV)-complexes have been described as light sensitive and some have been claimed as photoinitiators [10]. The photochemistry of bis-cyclopentadienyl-titanium-diphenyl has been extensively studied [11].

Photoinitiators however must be thermally stable and offer advantages over conventional radical UV-initiators.

During our work with titanium complexes we discovered enhanced thermal and oxidative stability as well as a very efficient curing rate when a fluorinated aryl ligand is introduced into the complex [12, 13].

Figure 3:



The synthesis of these complexes was easily achieved according to the literature procedure by reacting lithium pentafluorophenyl with titanocene dichloride at low temperature [14].

The photochemistry of the fluorinated compounds however proved to be totally different from what was known about the phenyl derivative.

Rausch (1978) had found that benzene and diphenyl were formed as the major products when the complex was irradiated in solution.

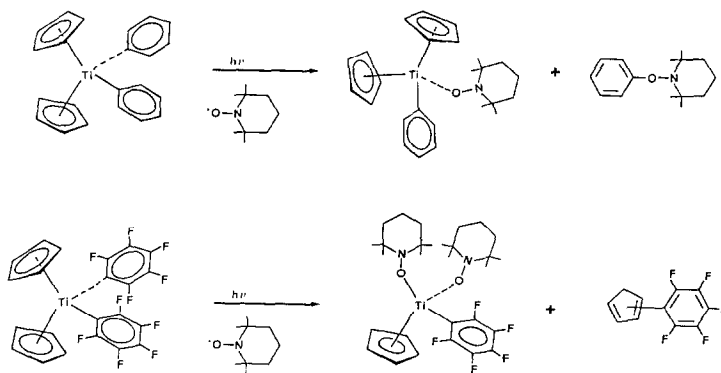
We were able to trap the radicals formed by homolysis of the Ti-aryl bond with the aid of a radical scavenger (TMPO) [14].

From the photoreaction of the fluorinated compound however no organic radicals could be trapped. Pentafluorophenyl substituted cyclopentadienes were observed as the main organic products and a titanium fragment which had reacted with two radical scavengers was isolated (see fig.4).

Urwyler and Wirz [15] have applied flash photolysis on the fluorinated titanocene at ambient temperature and lowtemperature matrices to study the photochemistry.

The primary photoproduct they observed in dry, degassed benzene solution at room temperature ( $k=5 \times 10^9 \text{s}^{-1}$ ) was a blue isomer which was formed with unit quantum yield. Its structure was assigned to a monohapto cyclopenta-dienyl derivative. Such a phototransformation generates the coordinatively unsaturated titanocene ( $\eta^1$ -cyclopentadienyl)( $\eta^5$ -cyclopentadienyl)Ti(IV)-bis-pentafluorophenyl.

Figure 4:



Photolysis in the presence of radical trap TMPO

The absolute rate constants for trapping this coordinatively unsaturated isomer by water, methanol, acetone, acetonitrile, nitromethane, 1,4-butane-diol bisacrylate, TMPO, carbon monoxide, molecular oxygen, and molecular nitrogen are in the range of  $10^6$  to  $10^9 \text{M}^{-1}\text{s}^{-1}$ .

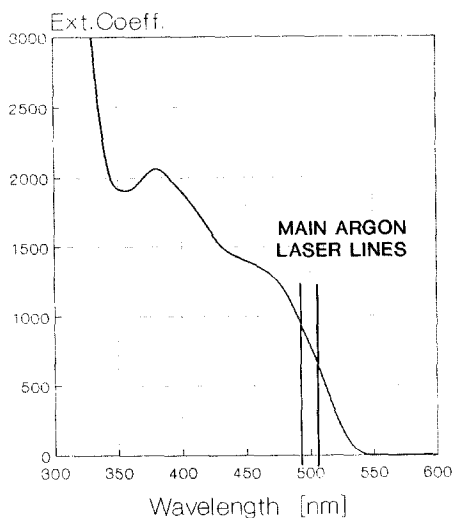
The absorbance difference spectrum generated by 530-nm laser flash photolysis in dry benzene solution at ambient temperature is comparable to the difference spectrum resulting from photolysis in an argon matrix at 14 K, indicating that the

same primary photoproduct is formed under both conditions. The photolysis of it in low-temperature CO and N<sub>2</sub> matrices gave rise to different photoproducts due to the addition of CO or N<sub>2</sub>, respectively. Irradiation with light in the visible region leads, in the CO matrix, to the formation of a strong band at 2040cm<sup>-1</sup> attributed to CO stretching of a metal-bound carbonyl group and, in the N<sub>2</sub> matrix, to a weak double band at 2282 cm<sup>-1</sup> and 2288 cm<sup>-1</sup>, attributed to a nitrogen complex [16].

Based on these experiments one can speculate that also an addition of an acrylic monomer occurs to the unsaturated monohapto-titanium intermediate which starts then the polymerization reaction.

These titanium based photoinitiators are among those with the greatest curing speed for vinyl polymerization. They are applicable in the manufacture of permanent coatings and integrated circuits [17]. Due to their absorption in the visible and the bleaching of it during exposure (the photoproducts don't absorb in the visible region) they can be applied in the curing of thicker layers as they are required for the application as planarising dielectrics between metal layers. Their pronounced absorption in the region between 400 and 600 nm opens an opportunity to use these photoinitiators in laser direct imaging (LDI) [18]. The main emissions of an argon laser are exactly in the region of the charge-transfer band of our titanium photoinitiators (see fig.5)

Figure 5:



UV/VIS -spectra of bis-pentafluorophenyl  
titanocene in CH<sub>2</sub>Cl<sub>2</sub>

One of the major advantages of LDI is the elimination of the photomask from the imaging process. Instead of using design data to produce artwork, and then use this

artwork in contact printing to transfer an image to a printed circuit board (PCB), laser direct imaging allows one to go directly from computer generated design data to imaged boards. Basically the computer is switching a laser beam on and off which is scanning over the hole board field.

It is acknowledged that many of the board defects seen in manufacturing of printed circuit boards are caused by problems in the image transfer process. By eliminating the phototool, and thus reducing the amount of operator handling, LDI has the ability to greatly improve overall yield.

A second advantage of LDI is the increase accuracy of image placement on the board. While phototool dimensions shift due to changes in temperature and humidity, an LDI system can write the image onto the panel with an accuracy of better than  $\pm 15$  microns over the entire board of 50 x 60 cm.

This practical example of LDI for the industrial production of printed circuit boards shows clearly the advantage of an organometallic photoinitiator. No organic type of molecule has a fair chance to match the three basic requirements for this application which are:

1. high sensitivity at 488 nm wavelength,
2. high quantum yield to form an active intermediate and
3. photobleaching which allows to cure thick resist layers.

### 3. IRON-ARENE PHOTOINITIATORS

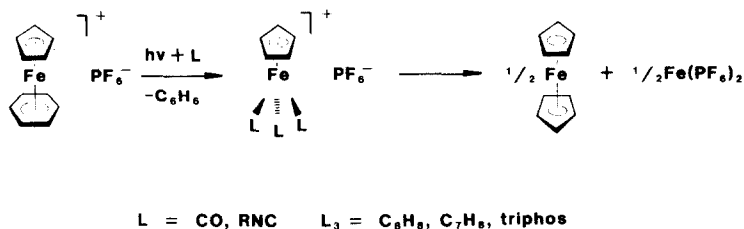
In recent years the photocrosslinking of epoxides has become a field of increasing interest. Crosslinked polyethers with their favourable properties such as thermal stability, mechanical strength, and chemical resistance thus became available for coating and imaging applications. In contrast to free radical polymerization of vinylic substrates the cationic polymerization of epoxy resins is not inhibited by oxygen. Several types of cationic photoinitiators have been described in the literature [7]. A number of organometallic compounds have also been tested for this purpose [8,9,19-24]. So far most of the cationic photoinitiators have had certain drawbacks which withheld them from achieving a major break-through. In many cases there is a lack in thermal stability.

Our new iron-arene photoinitiators can overcome most of these shortcomings [25].

Photolysis of the arene complexes in the presence of monodentate ligands, i.e. carbon monoxide, leads to new complexes of the type  $\text{CpFe}(\text{L})_3^+$ , where-as in pure nonprotic solvents, ferrocene and iron salts are formed (Fig. 6) [26,27].

Investigations in our laboratories showed that photolysis in methylene chloride solution in the presence of ethylene oxide also yielded ferrocene and iron salt complexes [28]. The main fraction of these salts comprised a white crystalline crown ether complex, whose structure was determined by x-ray analysis (Fig. 7). Beside [12]crown-4-complexes, small amounts of [15]crown-5-complexes were also formed.

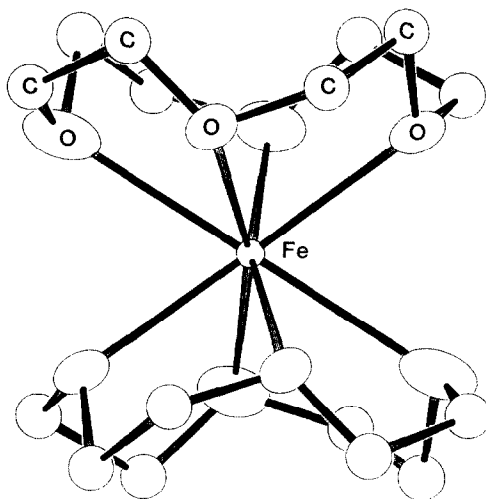
Figure 6:



*Photochemical ligand exchange reactions on iron arene complexes*

Photolysis of iron-arene complexes in solutions of more reactive epoxides than ethylene oxide or in epoxide solutions of high viscosity (which disfavour bimolecular reactions of the photogenerated iron species) also gave colourless iron polyether complexes and only traces of ferrocene. In view of these results, it appears likely that a ligand-exchanged iron complex is also formed with technical epoxy resins during exposure which contains three coordinated epoxide functions. Ring opening and polymerization could then start in the ligand sphere of the iron cation leading to cyclic polyethers.

Figure 7:



*X-ray crystal structure of bis [12]crown-4 iron  
bishexafluorophosphate*

Iron-arene photoinitiators have excellent light absorption properties in the ultraviolet and visible regions of the spectrum. As shown in fig. 8, absorption can be varied over



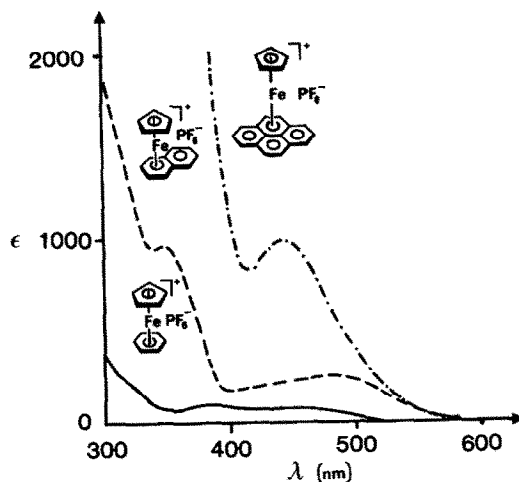
a wide range by structural changes in the ligands. If desirable, the photolysis of these iron salts can be sensitized, i.e. with anthracene derivatives.

The relative effectiveness of the three iron arene derivatives shown in figure 7 in a 30  $\mu\text{m}$  thick epoxy resist layer, containing 2.5 weight percent iron arene, varies from 1, for the benzene complex, over 6, for the naphthalene complex, to 30 for the pyrene complex [29].

The absorption spectrum of the initial organometallic photoinitiator changes with prolonged exposure time. This exemplifies also a photo-bleachable system as it is described above for the titanocene photoinitiators, which permits light penetration through thick layers as photolysis proceeds.

From the spectral changes measured in technical epoxy resins, the quantum yield of the photoinduced ligand exchange reaction was found to be close to one.

Figure 8:



UV/VIS-spectra of iron arene complexes in  $\text{CH}_2\text{Cl}_2$

The structure of the counter ion of the iron-arene complex influences the reaction rate and the degree of polymerization of the polyethers. The polymerization rate decreases according to the following order:  $\text{SbF}_6^- > \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^-$ . Replacing the  $\text{CpFe}(\text{benzene})$ -hexafluorophosphate by the hexafluoroantimonate derivative in the epoxy resist described above allows to use a 30 times lower exposure energy to cure the layer.

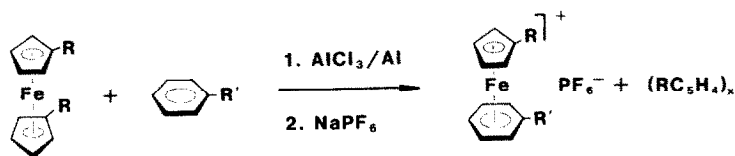
On the other hand, with the  $\text{BF}_4^-$ -complex, the most selective reaction of ethylene oxide was observed yielding 90 percent [12]crown-4 and 10 percent [15]crown-5, whereas with the  $\text{SbF}_6^-$ -complex, the two cyclic ethers were formed in the ratio of 3:2.

#### 4. PREPARATION OF CYCLOPENTADIENYL IRON ARENE SALTS

In 1957 Coffield, Sandal, and Clossen [30] reported the first preparation starting from  $(\eta^5\text{-cyclopentadienyl})\text{iron dicarbonyl dichloride}$  with aluminium chloride in refluxing mesitylene to the mesitylene derivative.

In 1963 Nesmeyanov and coworkers [31] reported that it was possible to prepare the  $(\eta^6\text{-benzene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}$  tetraphenylborate by the reaction of ferrocene and aluminium chloride in the presence of aluminium powder and refluxing benzene. Since the paper from Nesmeyanov this procedure has been the preferred synthetic route with well over 100 new  $\pi\text{-arene-}\pi\text{-cyclopentadienyl-iron(II)}$  salts reported [32]. The general procedure to form the hexafluorophosphate complexes is shown in figure 9:

Figure 9:



*Synthesis of iron arene complexes starting from ferrocene*

$\pi$ -complexes with substituted benzenes, phenol, thiophenol as well as some heterocycles like i.e. carbazole became available [33,34].

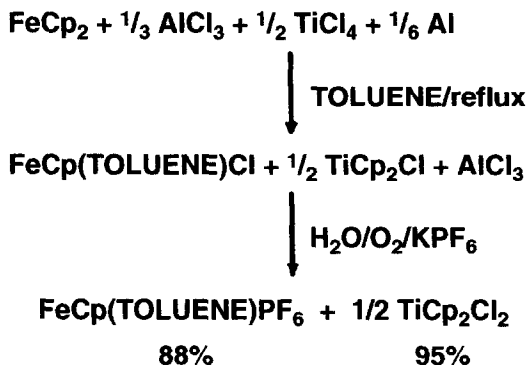
The yields of products obtained according to the Nesmeyanov procedure are moderate to small, generally between 10 and 40 % and therefore not sufficient for an industrial use.

A slightly different procedure was found in our laboratories [35] in which stoichiometric amounts of aluminium chloride, aluminium powder and additionally titanium tetrachloride were used.

When these components are mixed with ferrocene in refluxing toluene the yield of the corresponding  $\pi$ -complex was close to 90%.

Fortunately, the replaced cyclopentadienyl moiety get trapped by the titanium tetrachloride and gives titanocene monochloride which can be oxidised by air to titanocene dichloride, the starting material for the titanocene photoinitiators. In the work up procedure after air flushing through the hydrolysed the titanocene dichloride precipitates out and can be separated. The toluene  $\pi$ -complex is obtained in crystalline pure form from the aqueous solution after adding a hexafluorophosphate salt. Fig.10 shows all the equations and yields.

Figure 10:



The above described reaction sequence works well with simple aromatic compounds, i.e. alkylated benzene derivatives, and condensed polyaromatics. But, when heteroaromatics or aromatics are used with substituents containing complexation sites for the strong Lewis acids  $\text{AlCl}_3$  and  $\text{TiCl}_4$ , yields get drastically smaller or no product is formed. Failures of complexation were reported with i.e. thiophene, indole, acetophenone and benzonitrile [36].

Alternative methods without using the Lewis acid have been studied including photochemical ligand exchange [37], thermolysis in the presence of excess  $\text{P}(\text{OEt})_3$  [38] and ligand exchange reactions after reduction to the 19-electron complexes [39]. However, it can be limited to the liberation of the arene in the presence of a two-electron ligand like CO.

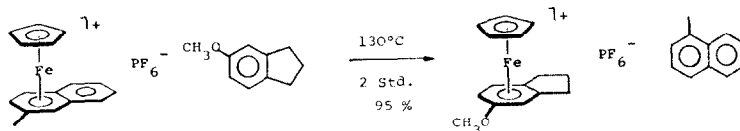
None of these procedures deliver the desired functionalized complexed, aromatics in good yields or could be applied in a industrial scale production.

We have found a new and simple method [40] to the iron arene complexes after studying the thermal stability of various derivatives. Simple  $\pi$ -complexes with arenes like benzene toluene or chlorobenzene decompose in the solid state or solvents above 200 °C, whereas those with condensed polyaromatics like naphthalene, pyrene or perylene decompose already around 150 °C.

This observation led us to try an experiment where the  $(\eta^5\text{-cyclopenta-dienyl})(\eta^6\text{-naphthalene})\text{Fe(II)-hexafluorophosphate}$  was refluxed in anisole for three hours. A colour change was observed from red to yellow-brown and after precipitation with ether, pure anisole complex was isolated in 95% yield.

A similar reaction is shown on fig. 11 in which a 1:1 mixture of methyl-naphthalene complex with methoxy-indane was heated for two hours at 130 °C. Again a clean reaction with high yield was observed.

Figure 11:

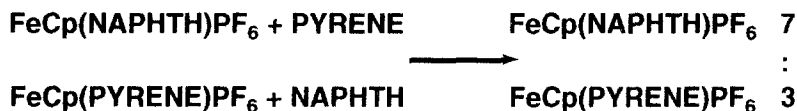


*Thermal ligand exchange reaction on thermally labile  
methyl naphthalene iron complex*

The Nesmeyanov or our  $\text{TiCl}_4$  modified procedure gave zero percent yield of the desired methoxy-indane  $\pi$ -complex.

Several new complexes could be synthesized by this thermal ligand exchange method including thiophene, hydroxy-indane, stylobene, 2-phenyl-acetic acid ethyl ester and different beta-estradiol-derivatives.

An other nice prove of thermal ligand exchange is exemplified with the reaction shown below:



When either a 1:1 mixture of the naphthalene complex was heated with pyrene or the pyrene complex with naphthalene, the same product ratio was obtained. By adding more of the free aromatic the equilibrium ratio was influenced as expected. These reactions were performed in 1,2-dichloro-ethane in a pressure tube at 130 °C. Also this method has its limitations. Heteroaromatics with stronger nucleophilic centres, i.e. pyridine and pyrazole, and aromatics with strong electron withdrawing substituents, i.e. trifluoromethyl benzene, acetophenone and benzoic acid ethyl ester cannot be used under this conditions.

## 5. CONCLUSION

Organometallic photochemistry has practically not been used in industrial processes so far. The two examples of using organometallic photochemistry for polymerization initiation seem only the beginning of exploiting a so far unused field. The better access to iron arenes allows to exploit the activating effect of the  $\text{FeCp}^+$  group for synthetic applications similar to chromium tricarbonyl complexation.

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