ELSEVIER

Journal of Organometallic Chemistry 533 (1997) 131–141

Journal of Organometallic Chemistry

Optically active transition-metal complexes VII [1]
Iron and ruthenium complexes with the optically active cyclopentadienyl ligand PCp: syntheses and ligand exchange reactions

Bernhard Pfister [b], Ruedi Stauber [a], Albrecht Salzer [b,*]

[a] *Institut für Anorganische Chemie, Universität Zürich, Zürich, Switzerland*
[b] *Institut für Anorganische Chemie, RWTH Aachen, D 52056 Aachen, Germany*

Received 26 August 1996

Abstract

The optically active complexes [PCpFe(CO)$_2$]$_2$ and [PCpRu(CO)$_2$]$_2$ (PCp = pinene-fused cyclopentadiene) have been converted into half-sandwich complexes PCpM(CO)$_2$X (X = Cl, Br, I, CH$_3$, COMe, COPh, COMes) by either oxidative or reductive methods. Ligand exchange of one of the diastereotopic carbonyl ligands for a Lewis base L (L = tertiary phosphine or phosphite) generates diastereomeric complexes PCpML(CO)X with pseudo-tetrahedral chirality at the metal centre. Diastereomeric ratios increase with increasing steric bulk of the new ligand, with upper limits of 64% *de*. With M = Ru, both photochemical and thermal methods of ligand exchange are possible for X = halogen, giving rise not only to different but also reverse ratios of diastereomers. Optical inductions by thermal ligand exchange are significantly higher and are shown to be of thermodynamic origin.

Keywords: Optically active ligands; Iron; Ruthenium; Cyclopentadienyl; Asymmetric induction

1. Introduction

The use of organometallic compounds in organic synthesis as well as homogeneous catalysis remains a subject of topical interest. This is due to the unique properties of transition metal complexes to catalyse a multitude of chemical transformations, some of which, like hydroformylation, polymerization and hydrogenation, are processes of major industrial importance.

This interest extends into the field of enantioselective catalysis, where major advances are expected from the application of optically active transition metal complexes. It is now widely accepted that stereogenic metal centres play a dominant role in influencing the stereocontrol of catalytic and stoichiometric reactions. The most common ligands used in enantioselective catalysis are chiral Lewis bases such as chelating phosphines [1], amines [2] and alcohols [3].

One of the most important and ubiquitous ligands in organometallic chemistry is the cyclopentadienyl anion and its derivatives. Metal–π-complexes have, however, until recently not played an important role in homogeneous catalysis. This has drastically changed since chiral catalysts such as the Brintzinger–Kaminsky *ansa*-metallocenes have been introduced into stereospecific polymerization processes [4]. The same complexes, in optically active form, are also now recognized as important catalysts for a number of organic transformations [5]. Chelating phosphines with a ferrocene backbone have found applications in enantioselective catalysis, the important difference between these and other phosphines being the planar chirality generated by the π-complexation of the aromatic ring ligand and the stereochemical environment created by the coplanar arrangement of the two cyclopentadienyl rings attached to iron [6].

There have been numerous other attempts to synthesize optically active cyclopentadienyl ligands and the subject has recently been reviewed by Halterman [7]. Apart from the examples cited above, there are few examples of sandwich or half-sandwich complexes used

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* Corresponding author.

[1] For Part VI, see Ref. [29]. Dedicated to Professor G.E. Herberich on the occasion of his 60th birthday.

PII S0022-328X(96)06849-0

in enantioselective catalysis, where the cyclopentadienyl ligand is the only source of chirality [7].

Cyclopentadienyl complexes, with or without other ligands, have, however, found a number of general catalytic applications for isomerizations, cycloadditions and oligomerizations [8–10]. They play, for instance, an important role in Trost's strategy of 'atom-efficient' transformations [11]. Generally, only simple non-chiral ligands such as C_5H_5 or C_5Me_5 have been used. These ligands also occur in complexes successfully used for enantioselective transformations, but only in combination with optically active ligands such as chelating phosphines or phosphites [12,13]. Cyclopentadienyl ligands also play a dominant role in complexes with stereogenic metal centres, where they impart thermodynamic as well as kinetic stability to complexes with tetrahedral or square-pyramidal chirality [14–16].

In extension of our studies on rhenium complexes with the optically active cyclopentadienyl ligand (1*R*,8*R*-(–)-9,9-dimethyltricyclo[6.1.1.$0^{2,6}$]deca-2,5-dienyl, Pcp, 'pinene-fused cyclopentadienyl') [17,18], we have also investigated half-sandwich complexes of iron and ruthenium. The aim of our research was to define the role that an optically active cyclopentadienyl ligand could play in the asymmetric induction of a new chiral centre at the metal.

2. Results and discussion

Paquette et al. have already described the synthesis of the dimeric iron precursor $[PCpFe(CO)_2]_2$ (1) and its solid state structure [19]. While our investigations were in progress, there was also a report by some American workers [20] on substitution reactions of 1 and its ruthenium analogue 2, which had also been prepared by us independently [21]. The dimeric complexes had been oxidized by iodine and the monomeric half-sandwich complexes $PCpM(CO)_2I$ (M = Fe, Ru) were reacted with several vinylphosphines to generate diastereomeric mixtures of complexes $PCpM(CO)I(PR_3)$ with diastereomeric ratios ranging from 3:2 to 5:1, corresponding to *de* values of 20–66%. The authors also reported the crystal structures for the dimer $[PCpRu(CO)_2]_2$ and the monomeric iodide $PCpRu(CO)_2I$, confirming that the optically active cyclopentadienyl ligand was exclusively coordinated from the sterically less hindered *exo*-side and that both dimeric complexes in the solid state adopted the less common *cis*-geometry (Scheme 1).

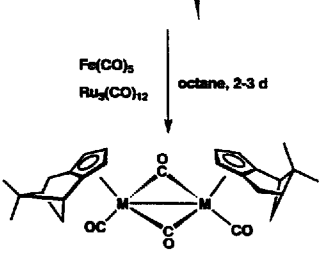
This result is in contrast to our previous observation that syntheses with the lithium or thallium salt of PCp invariably led to diastereomeric mixtures of *exo*- and *endo*-isomers under kinetic control [17,18]. The chemistry of PCp therefore resembles that of its diolefin analogue nopadiene, which under conditions of thermodynamic ligand exchange invariably led to the formation of only one optically active *exo*-diolefin complex, while ligand exchange under kinetic control gave rise to two isomeric *exo*- and *endo*-products [21,22].

The dynamic behaviour and geometry of complexes $[CpM(CO)_2]_2$ [M = Fe, Ru, Os] have been the subject of many detailed spectroscopic investigations, which confirm that the carbonyl-bridged and non-bridged isomers exist in dynamic equilibrium of *cis* and *trans* forms, the ratios being solvent- and temperature-dependent. These equilibria are also influenced by the bulk of the cyclopentadienyl ligand, very bulky ligands even leading to a predominance of a monomeric 17 e^--radical $C_5R_5Fe(CO)_2$ [23] in solution.

The temperature-dependent dynamic behaviour of 1 in solution has not been investigated [24] although it is reported that 2 gives one signal in the ^{13}C-NMR (224.5 ppm) for the carbonyl carbons, believed to be the averaged value between terminal and bridging carbonyl chemical shifts [20].

Our own investigations confirm that 1 and 2 show dynamic behaviour in solution. In the ^{13}C-NMR of 1, five signals appear for the cyclopentadienyl ring carbons at 50 °C, which broaden and disappear below 20 °C. At –15 °C, all lines are doubled in an approximate ratio of 6:4, two signals being almost isochronous (Fig. 1).

In the carbonyl region, there is no resonance visible at 20 °C, while at –20 °C, two sharp signals emerge at 212.5 ppm (terminal CO) and at 276.0 ppm (bridging CO) and a broad signal at 244 ppm. This signal disappeared again on cooling to –60 °C, the lowest temperature we could reach for solubility reasons, while the other signals remained sharp. The corresponding ruthenium complex 2 shows similar behaviour, with one carbonyl resonance visible at 225 ppm. This signal disappears at –40 °C and no new resonances appear until



(1) M = Fe (2) M = Ru

Scheme 1.

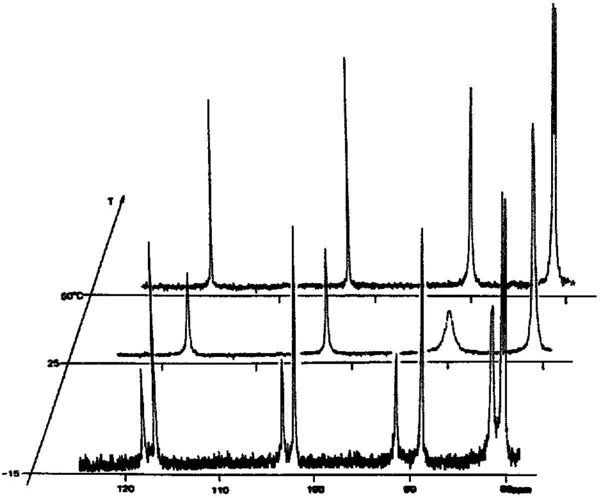


Fig. 1. ^{13}C-NMR ($CDCl_3$) of the cyclopentadienyl carbon atoms of **1** at −15, 25 and 50°C (from bottom).

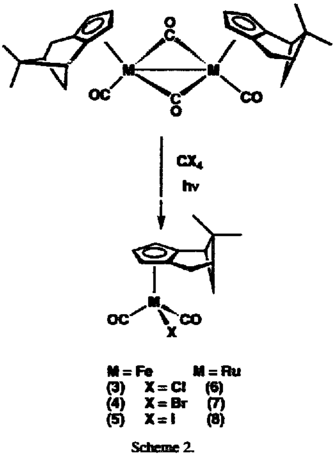
−60°C. These results indicate that **1** and **2** undergo rapid carbonyl scrambling and exist as carbonyl-bridged *cis–trans* isomers in dynamic equilibrium in solution.

The dimers $[PCpM(CO)_2]_2$ can be converted into monomeric half-sandwich complexes by either oxidative or reductive routes. Oxidative routes most often involve the cleavage of the metal–metal bond with elemental halogens. The oxidation of **1** and **2** with iodine had already been described by Bhaduri et al. [20]. An alternate method is the photochemical reaction of the dimers with CX_4 (X = Cl, Br, I) and this proved more efficient in our hands. Irradiation of **1** in CCl_4 generated the complex $PCpFe(CO)_2Cl$ (**3**) in almost quantitative yield. Likewise, irradiation of **1** with CBr_4 and CI_4 in benzene led to the formation of $PCpFe(CO)_2Br$ (**4**) and $PCpFe(CO)_2I$ (**5**) in very good yields. The progress of the reaction is conveniently monitored by IR spectroscopy. These complexes are red to black solids which exhibit two resonances in the IR for the carbonyl groups and two resonances in the ^{13}C-NMR for the two diastereotopic CO carbons.

Similar reactions with **2** allowed the synthesis of $PCpRu(CO)_2Cl$ (**6**), $PCpRu(CO)_2Br$ (**7**) and $PCpRu(CO)_2I$ (**8**) as yellow to brown crystalline powders, again in excellent yields (Scheme 2).

Bhaduri et al. [20] had studied the exchange reactions of **5** and **8** with several vinylphosphines. Prolonged thermal reaction (44 h) of **5** with the corresponding phosphine in refluxing benzene gave the monomeric chiral-at-iron complexes $PCpFe(CO)I(PR_3)$. They obtained a mixture of two inseparable diastereomers with moderate to good diastereomeric excess of one diastereomer.

According to our investigation, this reaction is invariably accompanied by considerable decomposition as well as the formation of an ionic species $[PCpFe(CO)_2(PR_3)]I$. We have therefore chosen a pho-



Scheme 2.

Table 1
Ligand exchange of 3 with $P(i\text{-}Pr)_3$ at different stoichiometric ratios and temperatures

Equiv. $P(i\text{-}Pr)_3$	Temperature (°C)	Irradiation time (min)	Yield (%)	*de* (%)
1.3	+8	70	64	52
1.7	+8	40	84	64
3.0	+8	30	86	61
1.7	+20	60	45	34
1.7	−20	40	—	—

tochemical route for ligand substitution instead, which allows much lower reaction temperatures and shorter reaction times, therefore minimizing decomposition. We have tried to optimize reaction conditions by varying stoichiometry, reaction time and temperature. As the model reaction for these studies, we chose the reaction of 3 with tris(isopropyl)phosphine, as preliminary studies had shown (vide infra) that this ligand gave one of the highest diastereomeric ratios. The results are summarized in Table 1. The optimal reaction conditions require the use of 1.7 equiv. of phosphine in toluene solution at a temperature of 8 °C and a reaction time of 40 min. The progress of ligand exchange was again monitored by IR control (Fig. 2). Diastereomeric ratios were determined by integration of the $^{31}P\{^1H\}$-resonances of the two diastereomers formed (Fig. 3).

At higher temperatures, yields decreased considerably due to decomposition, but we also observed lower diastereoselectivities. This is also true for prolonged irradiation times which are required when less than 1.7 equiv. of ligand were used. At lower temperatures, no ligand exchange was observed, the photochemical decomposition of the coordinatively unsaturated intermediate apparently being faster. The mechanism of ligand exchange is quite evidently dissociative and kinetically controlled (vide infra).

Next, we investigated the influence of the stereochemical bulk of the phosphine or phosphite ligand on the diastereomeric ratios obtained in these ligand exchange reactions. Table 2 shows the results of these experiments, where diastereomeric ratios are correlated with the Tolman cone angle of the phosphorus ligand.

The results can be summarized as follows. The diastereomeric ratios increase with increasing bulk of the phosphine or phosphite ligand. Best results are obtained with tris(isopropyl)phosphine and tris(cyclohexyl)phosphine, which also react with very high product yields. This is in agreement with the results by Bhaduri et al. [20], who observed the same trend of increasing diastereomeric ratios with increasing bulk of the phosphine. Their results, were, however, obtained by thermal ligand exchange and thus presumably under thermodynamic control, while our ligand exchange reactions were performed under kinetic control.

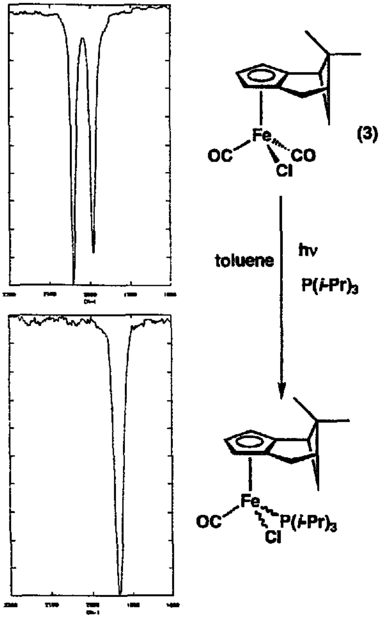


Fig. 2. IR spectra of 3 and $R_{Fe}S_{Fe}$-*exo*-PCpFe(CO)Cl(P(*i*-Pr)$_3$) in toluene.

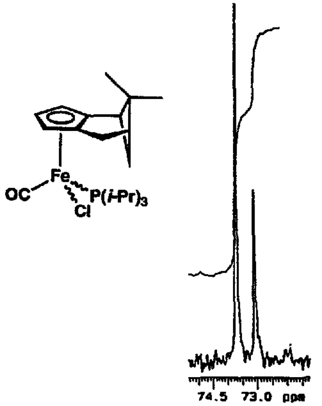


Fig. 3. ^{31}P NMR of the diastereomeric mixture of $R_{Fe}S_{Fe}$-*exo*-PCpFe(CO)Cl(P(*i*-Pr)$_3$).

Table 2
Ligand-exchange reactions (photochemical at +8°C) of *exo*-(η^5-PCp)Fe(CO)$_2$X with monodentate phosphines or phosphites

X	PR$_3$	Tolman cone angle Θ of PR$_3$ (deg)	Yield (%)	*de* (%)
Cl	PMe$_3$	118	74	12
Cl	PEt$_3$	132	79	28
Cl	P(*i*-Pr)$_3$	160	84	64
Cl	PCy$_3$	170	84	63
Cl	PMe$_2$Ph	122	82	6
Cl	PMePh$_2$	136	79	30
Cl	PPh$_3$	145	64	50
Cl	P(*o*-Tol)$_2$Ph	—	41	46
Cl	P(*o*-Tol)$_3$	194	25	18
Cl	P(OMe)$_3$	107	59	10
Cl	P(OEt)$_3$	109	69	10
Cl	P(OPh)$_3$	128	74	10
I	PPh$_3$	145	96	16
I	P(OMe)$_3$	107	36	8
I	P(OEt)$_3$	109	99	24

No complete conversion is observed for even bulkier phosphines such as tris(*o*-tolyl)phosphine, where the reaction rate decreases and therefore decomposition rivals ligand exchange. There is no clear trend for the different halide ligands; but, in general, the diastereomeric ratios are highest for X = Cl. A similar observation was also made for the corresponding ruthenium complexes (vide infra).

Unfortunately, all complexes PCpFe(CO)X(PR$_3$) appear to be relatively unstable and begin to decompose even on storage at −30°C after a few days. They also decompose slowly in solution, so that we were unable to separate the diastereomers by chromatographic methods. Brunner et al. have investigated the thermal epimerization of optically active complexes CpFeCO(CH$_3$)L, where L was an optically active phosphine. They were able to increase the rate of this reaction by electron transfer catalysis [25]. We were unable to epimerize our complexes or to effect ligand exchange under similar conditions, as addition of either [FeCp$_2$]PF$_6$ or Na/Hg to our complexes led to considerable decomposition, so that the results obtained are not conclusive enough.

Fortunately, reactions on the corresponding ruthenium complexes allowed one to perform ligand exchange reactions under both kinetic as well as thermodynamic control. Complexes **6–8** were amenable to photochemical ligand exchange at ambient temperature as well as thermal ligand exchange in boiling xylene. This is in agreement with similar reactions performed by Cesarotti et al. [26] on (neomenthylC$_5$H$_4$)Ru(CO)$_2$I, but in contrast to Bhaduri et al. [20], who have stated that thermal ligand exchange on PCpRu(CO)$_2$I was not possible.

The results of ligand exchange reactions on ruthenium complexes **6–8** are summarized in Table 3.

Yields are excellent by both methods and complexes are much more stable than the corresponding iron analogues. There is the same overall trend in the diastereomeric ratios increase with increasing bulk of the phosphine, but generally with lower values for ruthenium than for iron. Diastereomeric ratios are consistently higher for thermal ligand exchange, so that these reactions were studied in more detail and with more examples. The highest values of ca. 50% were again obtained with tris(isopropyl)phosphine and tris(cyclohexyl)phosphine. No complete conversion was observed for bulkier phosphines.

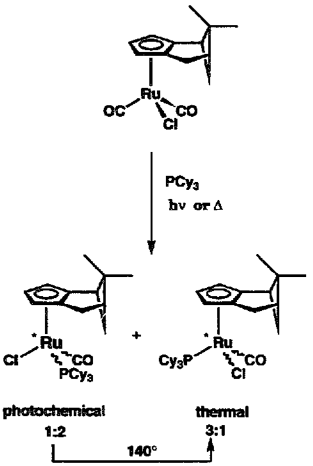
Surprisingly, the major isomer obtained under photochemical conditions becomes the minor isomer under thermal conditions. Thus, while with tris(isopropylphosphine) under photochemical conditions a ratio of 1:2 was obtained, the ratio under thermal conditions was 3:1 (from ^{31}P{^{1}H} NMR spectra). The photochemical product mixture can be cleanly converted to the thermal product mixture by prolonged heating in refluxing xylene. The mechanism of this epimerization is most likely dissociative with the fission of the Ru–P bond as the rate-determining step.

The thermal mixture, on the other hand, remains unchanged when subjected to UV irradiation (Scheme 3).

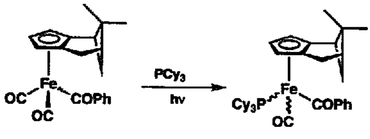
We conclude from these results that the optically active PCp ligand is capable of inducing a new chiral centre at the transition metal under both kinetic and thermodynamic control. To our knowledge, this is the

Table 3
Ligand-exchange reactions ($h\nu$ = photochemical at +8°C, Δ = thermally in boiling xylene) of *exo*-(η^5-PCp)Ru(CO)$_2$X with monodentate phosphines or phosphites

X	PR$_3$	Θ (deg)	Yield ($h\nu$) (%)	*de* (%)	Yield (Δ) (%)	*de* (%)
Cl	PMe$_3$	118			88	20
Cl	PEt$_3$	132			72	40
Cl	P(*i*-Pr)$_3$	160	87	35	81	50
Cl	PCy$_3$	170	85	33	71	48
Cl	PMe$_2$Ph	122			90	20
Cl	PMePh$_2$	136			79	30
Cl	PPh$_3$	145	91	12	89	40
Cl	P(OEt)$_3$	109			94	25
Cl	P(OPh)$_3$	128			65	24
Br	PPh$_3$	145			88	18
I	PPh$_3$	145	97	18	98	23
I	P(OMe)$_3$	107			98	26
I	P(OEt)$_3$	109			88	6



Scheme 3.



(11)

Scheme 4.

first instance where such a pronounced differentiation between kinetic and thermodynamic control has been established for complexes with an optically active cyclopentadienyl ligand. Surprisingly, no such induction has been observed by us on similar ligand exchange reactions performed on $[PCpRe(CO)_2NO]^+$ [17].

We are currently trying to separate the ruthenium diastereomers by medium-pressure chromatography to obtain separate isomers and to grow single crystals of some compounds in order to determine the absolute configuration of the major isomers. All attempts to separate the diastereomers by crystallization have failed so far. It is interesting to note that $PCpRe(CH_3)NO(PPh_3)$, a diastereomeric mixture in an exact 1:1 ratio, crystallized in one single crystal [17]. Both isomers have very similar structures, the overall geometry being largely governed by the two bulky ligands PPh_3 and PCp, with PPh_3 orientated as far away as possible from the sterically demanding pinene part of the cyclopentadienyl ligand. This probably is also the case in all $PCpM(CO)X(PR_3)$ complexes, as only the two quaternary carbons of the cyclopentadienyl ring show $^{31}P-^{13}C$ coupling constants between 2 and 11 Hz, while coupling constants between the three other carbon atoms and phosphorus are too small to be resolved.

We were also able to obtain optically active half-sandwich iron complexes by the reductive route. On treating **2** with Na/Hg amalgam, we were able to generate $Na[PCpFe(CO)_2]$ in solution. This reacted readily with methyliodide to give an almost quantitative yield of $[PCpFe(CO)_2CH_3]$ (**9**). Similar treatment of the sodium metallate with acetylchloride, benzoylchloride and 2,4,6-trimethyl-benzoylchloride gave $[PCpFe(CO)_2COCH_3]$ (**10**) $[PCpFe(CO)_2COC_6H_5]$ (**11**) and $[PCpFe(CO)_2COC_6H_2(CH_3)_3]$ (**12**).

The complex $CpFe(CO)_2CH_3$ is well known to undergo migratory CO insertion when treated with a Lewis-base. We have not been able to observe this reaction with $PCpFe(CO)_2CH_3$, as prolonged treatment of **9** with PPh_3 in boiling acetonitrile gave virtually unchanged starting material after 3 days. Photochemical ligand exchange of one CO ligand for a tertiary phosphine, on the other hand, is possible. Initial experiments with **9** and **10** showed only very low diastereomeric ratios of the two possible isomers. We therefore studied the reaction with the benzoyl complex **11** in more detail, using PCy_3 as the ligand. We believed that with a bulkier ligand such as the benzoyl group the diastereoselectivity on creating a new chiral centre would be greater and this was indeed so (Scheme 4).

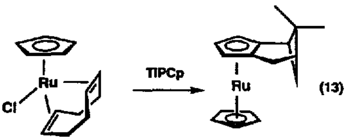
Again, we tried to optimize reaction conditions by variation of temperature, stoichiometry and solvent. The results are summarized in Table 4.

Under optimal conditions, diastereomeric ratios of > 50% could be obtained by reaction of the benzoyl complex with the bulky phosphine PCy_3.

The highest yields are obtained at +8 °C, a temperature where the $16e^-$ intermediate formed by photochemical ligand dissociation rapidly reacts with the new ligand PCy_3. In more dilute solutions ($2.25\,mmol\,l^{-1}$), we see only decomposition. At lower temperatures, diastereomeric ratios are slightly better, but yields decrease due to decomposition. The weakly coordinating

Table 4
Photochemical ligand exchange reactions of $PCpFe(CO)_2(COC_6H_5)$ (**11**) ($6.75\,mmol\,l^{-1}$) with PCy_3

Equiv. PCy_3	Temperature (°C)	Reaction time (min)	Solvent	Yield (%)	*de* (%)
1	+8	60	toluene	65	55
2	+8	40	toluene	93	52
2	−2	40	toluene	87	56
2	−12	45	toluene	81	57
2	−2	15	THF	77	44
2	−12	30	THF	30	50
1	−2	30	THF	70	46



Scheme 5.

solvent THF does not offer any improvement, as both yield and *de* values are lower than with toluene. Possibly, a relatively stable THF solvate is formed, which under photochemical reaction conditions tends to decompose with a similar rate as it undergoes ligand exchange. THF also lowers the diastereomeric ratios.

As yet, we have not been able to separate the diastereomers PCpFeCO(COC$_6$H$_5$)(PCy$_3$) by crystallization or chromatographic methods, so that we have been unable to gain more structural information on these complexes or study their reactivity. The corresponding trimethylbenzoyl complex **12** shows only decomposition when irradiated in the presence of tris(cyclohexyl)phosphine.

In final experiments we have also been able to prepare diastereomerically pure ruthenocenes with the PCp-ligand. We chose CpRuCODCl and Cp*RuCODCl as suitable precursors.

These, on reaction with TlPCp yielded the metallocenes PCpRuCp and PCpRuCp* in very good yields as yellow to orange oils. The π-facial selectivity in this synthesis is excellent, giving exclusively a single *exo*-PCp-isomer (Scheme 5).

This result is in contrast to studies by Paquette et al. [24], who prepared various ruthenium and iron sandwich complexes with the PCp ligand, but invariably as diastereomeric mixtures of *exo*- and *endo*-isomers. The diastereomeric ratio is possibly influenced by the bulky COD ligand, which in the ligand exchange process allows the PCp ligand to approach only with its sterically less hindered face. We have found a similar trend in the synthesis of various PCpRh(diolefin) complexes, where only with the COD ligand the *exo*-isomer is exclusively formed, while smaller diolefins give mixtures of diastereomers [21]. A similar trend has also been identified by Bhaduri in the synthesis of PCpRu(arene) cations [20].

3. Summary

We have been able to establish that iron and ruthenium half-sandwich complexes with the optically active cyclopentadienyl ligand PCp show moderate to good diastereoselectivities when subjected to ligand exchange reactions in which a new chiral centre at the metal is introduced. These results are in contrast to similar reactions performed on rhenium complexes of PCp, where no diastereoselectivities were observed. These diastereoselectivities are both kinetic and thermodynamic in origin. A future goal of our research is a variation of the PCp-ligand so that even higher *de*-values can be obtained, the ultimate target being a cyclopentadienyl ligand that completely controls the stereochemistry at the metal centre.

Preliminary results on analogous reactions with modified PCp ligands confirm that higher *de* values can indeed be reached with ruthenium and that these diastereomeric phosphine complexes can be conveniently separated by high-performance medium-pressure chromatography. In this way, we hope that structural information will soon become available on these complexes and we will be better able to understand the influence that a chiral cyclopentadienyl ligand exerts on the stereochemistry at a pseudo-tetrahedral metal centre.

4. Experimental

4.1. General

All reactions and manipulations were performed under nitrogen by use of standard vacuum line and Schlenk tube techniques. All solvents were degassed before use. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Dichloromethane and chloroform were distilled from calcium hydride. Toluene, *p*-xylene, *n*-hexane and *n*-octane were dried over molecular sieves. Unless otherwise indicated, all commercially available reagents were used as-received. Column chromatography was performed using either silica gel (70–230 mesh ASTM, Merck Kieselgel 60) or neutral alumina (grade III, Merck Aluminiumoxid 90). For organometallic complexes, all chromatography was carried out under nitrogen. PCpH [24], TlPCp [17], CpRuCODCl [27], Cp*RuCODCl [28], [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ [19], *exo*-(η^5-PCp)Fe(CO)$_2$I, [*exo*-(η^5-PCp)Ru(CO)$_2$]$_2$ and *exo*-(η^5-PCp)Ru(CO)$_2$I [20] were prepared as described in the literature. Infrared spectra were recorded on a Perkin–Elmer 1750 Fourier Transform spectrophotometer as solutions in *n*-hexane, toluene or dichloromethane using NaCl cells. Photochemical reactions were performed in a Mangels reaction vessel with a Philips 150 W high-pressure mercury lamp with quartz immersion wells. NMR spectra were recorded on either a Varian VXR 300 or a Varian Unity 500 spectrometer in CDCl$_3$ or C$_6$D$_6$ solutions. ^{1}H- and ^{13}C-NMR spectra were referenced to tetramethylsilane (TMS) using internal solvent peaks; ^{31}P-NMR spectra were referenced to H$_3$PO$_4$ (external). In Section 4, ^{13}C- and ^{31}P-NMR data are given in terms of the proton decoupled (broad band) spectra.

4.2. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$Cl (3)

A solution containing 1.0 g (1.8 mmol) of [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ in 140 ml CCl$_4$ was photolysed under N$_2$ for 1 h at 20 °C. The progress of the reaction was monitored by IR spectroscopy. Evaporation of the solvent and column chromatography over neutral alumina (1.5 × 20 cm) in CH$_2$Cl$_2$ afforded the product as a light red solid; yield of **3**, 1.1 g (97%). IR (CCl$_4$, cm^{-1}): ν(CO) = 2044 s, 1999 s. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 213.2, 212.8, 115.7, 109.3, 85.4, 74.7, 71.1, 41.1, 40.5, 40.4, 40.1, 34.0, 25.8, 25.0, 21.1. Anal. Found: C, 54.91, H, 4.96%. C$_{14}$H$_{15}$ClFeO$_2$ (306.6) calcd.: C, 54.85, H, 4.93%.

4.3. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$Br (4)

2.50 g (4.6 mmol) of [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ were dissolved in 50 ml of chloroform and cooled to −5 °C. While stirring, 0.47 ml (1.46 g, 9.2 mmol) bromine were added slowly. The solution was stirred for 2 h while gradually being brought to ambient temperature. The solvent was then removed and the residue was taken up in *n*-hexane. Spontaneous precipitation afforded a dark-brown solid; yield of 1, 2.5 g (77%).

The same product can also be prepared by irradiation of 1.0 g of **1** and 2.5 g of CBr$_4$ in 300 ml of benzene at 7 °C. The reaction is complete after 1 h.

IR (CHCl$_3$, cm^{-1}): ν(CO) = 2040 s, 1994 s. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 211.4, 211.0, 113.6, 104.0, 86.6, 73.9, 71.8, 39.0, 38.7, 38.3, 32.7, 27.1, 24.6, 20.4. Anal. Found: C, 47.12, H, 4.05%. C$_{14}$H$_{15}$BrFeO$_2$ (351.0) calcd.: C, 47.91, H, 4.31%.

4.4. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$(CH$_3$) (9)

To a solution of Na[*exo*-(η^5-PCp)Fe(CO)$_2$], prepared from 4.0 g (7.4 mmol) [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ and 80 g sodium amalgam (containing 1% of mercury) in 120 ml tetrahydrofuran 1.7 ml (3.88 g, 27.3 mmol) of methyliodide were dropped slowly by syringe at ambient temperature. The solution was stirred for a further 12 h to the exclusion of light. Evaporation of the solvent and column chromatography over neutral alumina (1.5 × 25 cm) in *n*-hexane afforded an orange oil; yield of **9**, 4.10 g (97%).

IR (*n*-hexane, cm^{-1}): ν(CO) = 1997 s, 1937 s. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 219.0, 218.8, 115.2, 101.6, 86.2, 77.7, 75.8, 41.3, 41.0, 40.2, 35.0, 26.2, 24.9, 21.0, −18.4. Anal. Found: C, 62.83, H, 6.45%. C$_{15}$H$_{18}$FeO$_2$ (286.2) calcd.: C, 62.95, H, 6.34%.

4.5. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$(COCH$_3$) (10)

To a solution of Na[*exo*-(η^5-PCp)Fe(CO)$_2$], prepared of 1.50 g (2.8 mmol) [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ and 25 g sodium amalgam (containing 1% of mercury), in 30 ml tetrahydrofuran, 0.5 ml (0.55 g, 7.0 mmol) of acetylchloride were dropped slowly by syringe at −80 °C. The solution was stirred overnight in the dark while gradually being brought to room temperature. Evaporation of the solvent and column chromatography over neutral alumina (1.5 × 25 cm) in *n*-hexane afforded an orange oil; yield of **10**, 1.57 g (90%).

IR (*n*-hexane, cm^{-1}): ν(CO) = 2010 s, 1955 s, 1660 w. ^{13}C-NMR (125 MHz, C$_6$D$_6$): δ = 252.2, 216.5, 118.4, 103.7, 88.0, 79.3, 77.6, 51.2, 41.1, 40.8, 40.2, 35.9, 26.2, 25.4, 21.0. Anal. Found: C, 60.94, H, 5.82%. C$_{16}$H$_{18}$FeO$_3$ (314.2) calcd.: C, 61.16, H, 5.77%.

4.6. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$(COPh) (11)

11.55 ml (99.45 mmol) of benzoylchloride were added to a suspension of 19.5 g (66.3 mmol) Na[*exo*-(η^5-PCp)Fe(CO)$_2$] in 300 ml of toluene at ambient temperature. The suspension was stirred for 3 days in the dark. After removal of the solvent in vacuo, the resulting red-brown residue was extracted with *n*-hexane (3 × 25 ml), and the extracts were filtered over Celite. The red filtrate was taken to dryness under reduced pressure and purified by column chromatography over silica gel (1.5 × 40 cm). Elution with 4:1 (v/v) *n*-hexane–Et$_2$O gave two bands. The first red band contained [*exo*-(η^5-PCp)Fe(CO)$_2$]$_2$ as a by-product, the second yellow band afforded the crude product. Recrystallization from *n*-hexane at −30 °C gave a light yellow solid; yield of **11**, 18.7 g (75%).

IR (*n*-hexane, cm^{-1}): ν(CO) = 2015 s, 1962 s, 1625 w. ^{1}H-NMR (500 MHz, C$_6$D$_6$): δ = 7.68 (m, 2H, Ph), 7.16 (m, 2H, Ph), 7.09 (m, 1H, Ph), 4.32 (t, J = 2.7 Hz, 1H), 4.04 (dd, J = 2.7, 1.7 Hz, 1H), 3.95 (br, 1H), 2.48–2.36 (m, 2H), 2.11 (t, J = 5.4 Hz, 1H), 1.98 (dd, J = 16.5, 2.4 Hz, 1H), 1.74 (d, J = 10.4 Hz, 1H), 1.70 (m, 1H), 1.03 (s, 3H, CH$_3$), 0.38 (s, 3H, CH$_3$). ^{13}C-NMR (125 MHz, C$_6$D$_6$): δ = 260.0, 216.3, 216.1, 145.3, 130.0, 128.2, 126.4, 118.5, 103.4, 88.3, 79.5, 78.3, 41.5, 41.1, 40.5, 36.2, 26.5, 25.9, 21.4. Anal. Found: C, 66.60, H, 5.28%. C$_{21}$H$_{20}$FeO$_3$ (376.2) calcd.: C, 67.04, H, 5.36%.

4.7. Preparation of *exo*-(η^5-PCp)Fe(CO)$_2$(COMes) (12)

3.80 g (20.8 mmol) of 2,4,6-trimethylbenzoyl chloride were added to a suspension of 2.04 g (6.94 mmol) Na[*exo*-(η^5-PCp)Fe(CO)$_2$] in 40 ml of toluene at ambient temperature. The suspension was stirred for 3 days in the dark. After removal of the solvent in vacuo, the resulting red-brown residue was extracted with *n*-hexane (3 × 15 ml), and the extracts were filtered over Celite. The red filtrate was taken to dryness under reduced pressure and purified by column chromatography over silica gel (1.5 × 40 cm). Elution with 2:1 (v/v) *n*-

hexane–Et_2O gave two bands. The first red band contained [*exo*-(η^5-PCp)Fe$(CO)_2$]$_2$ as the main product, the second yellow band afforded the desired product as a yellow oil; yield of **12**, 0.96 g (32%).

IR (*n*-hexane, cm^{-1}): ν(CO) = 2024 m, 2010 s, 1973 m, 1958 s, 1650 w, 1613 w. ^{1}H-NMR (500 MHz, C_6D_6): δ = 6.68 (s, 2H, Ph), 4.31 (dd, J = 2.75, 2.44 Hz, 1H), 4.29 (dd, J = 2.75, 1.53 Hz, 1H), 4.15 (br, 1H), 2.44 (dd, J = 16.8, 2.75 Hz, 1H), 2.38 (m, 1H), 2.34 (d, J = 2.75 Hz, 6H, 2 × CH_3), 2.12 (s, 3H, CH_3), 2.09 (t, J = 5.5 Hz, 1H), 1.98 (dd, J = 16.8, 2.75 Hz, 1H), 1.71 (m, 1H), 1.52 (d, J = 10.1 Hz, 1H), 1.04 (s, 3H, CH_3), 0.39 (s, 3H, CH_3). ^{13}C-NMR (125 MHz, C_6D_6): δ = 259.0, 216.8, 216.3, 155.4, 135.9, 129.1, 117.4, 102.5, 93.2, 80.8, 78.4, 41.5, 40.8, 40.2, 36.5, 26.4, 25.6, 21.3, 21.0, 19.4. Anal. Found: C, 68.42, H, 6.41%. $C_{24}H_{26}FeO_3$ (418.3) calcd.: C, 68.91, H, 6.27%.

4.8. General procedure for the photochemical reaction of exo-(η^5-PCp)Fe$(CO)_2$X (X = Cl, I and COPh) with monodentate phosphines and phosphites

A solution containing 0.55 mmol of *exo*-(η^5-PCp)Fe$(CO)_2$X and 0.93 mmol (1.7 equiv.) of phosphine or phosphite in 140 ml of toluene was photolysed for about 30 min at +8 °C, while a continuous gentle stream of nitrogen was bubbled through the reaction mixture. The progress of the reaction was monitored by IR spectroscopy. At the end of the reaction, then solvent was removed by vacuum distillation at ambient temperature, and the crude product was analysed by ^{31}P NMR spectroscopy to determine the ratio of diastereomers. Purification by column chromatography over silica gel (1.5 × 40 cm) in dichloromethane and evaporation of the solvent afforded the pure product; for yields see Tables 1, 2 and 4.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PMe_3)Cl, green solid. IR (*n*-hexane, cm^{-1}): 1947. ^{31}P-NMR (202 MHz $CDCl_3$): δ = 34.1, 32.5.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PEt_3)Cl, green oil. IR (*n*-hexane, cm^{-1}): 1946. ^{31}P-NMR (202 MHz $CDCl_3$): δ = 57.8, 56.8.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)($PPhMe_2$)Cl, green oil. IR (*n*-hexane, cm^{-1}): 1948. ^{31}P-NMR (202 MHz $CDCl_3$): δ = 42.1, 40.7.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PPh_2Me)Cl, green solid. IR (*n*-hexane, cm^{-1}): 1950. ^{31}P-NMR (202 MHz $CDCl_3$): δ = 54.1, 53.3.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PPh_3)Cl, green solid. IR (*n*-hexane, cm^{-1}): 1953. ^{31}P-NMR (202 MHz $CDCl_3$): δ = 65.5, 63.8.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P{*i*-Pr}$_3$)Cl, green oil. IR (*n*-hexane, cm^{-1}): 1945. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 73.8, 73.1.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PCy_3)Cl, green solid. IR (toluene, cm^{-1}): 1933. ^{31}P-NMR (202 MHz, C_6D_6): δ = 67.0, 66.7.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P{*o*-Tol}$_2$Ph)Cl, green solid. IR (toluene, cm^{-1}): 1944. ^{31}P-NMR (202 MHz, C_6D_6): δ = 69.8, 69.2.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P(*o*-Tol)$_3$)Cl, green solid. IR (toluene, cm^{-1}): 1945. ^{31}P-NMR (202 MHz, C_6D_6): δ = 20.8, 19.9.

S_{Fe},R_{Fe}-*exo*-(η^5 -PCp)Fe(CO)(P{OMe}$_3$)Cl, red-brown oil. IR (n-hexane, cm^{-1}): 1962, ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 179.7, 177.9.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P{OEt}$_3$)Cl, red-brown oil. IR (*n*-hexane, cm^{-1}): 1959. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 186.0, 183.8.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P(OPh)$_3$)Cl, red-brown oil. IR (*n*-hexane, cm^{-1}): 1982. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 170.1, 168.7.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(PPh_3)I, black solid. IR (*n*-hexane, cm^{-1}): 1950. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 69.6, 67.2.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)Fe(CO)(P{OMe}$_3$)I, brown oil. IR (*n*-hexane, cm^{-1}): 1960. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 186.0, 183.8.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)FeCO(P(OEt)$_3$)I, brown oil. IR (*n*-hexane, cm^{-1}): 1956. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 178.8, 176.8.

S_{Fe},R_{Fe}-*exo*-(η^5-PCp)FeCO(PCy_3)(COPh), orange solid. IR (*n*-hexane, cm^{-1}): 1908 s, 1564 w. ^{31}P-NMR (202 MHz, $CDCl_3$): δ = 70.1, 69.6.

4.9. Preparation of exo-(η^5-PCp)Ru$(CO)_2$Cl (6)

A solution containing 2.53 g (4.0 mmol) of [*exo*-(η^5-PCp)Ru$(CO)_2$]$_2$ in 140 ml CCl_4 was photolysed under N_2 for 1 h at 20 °C. The progress of the reaction was monitored by IR spectroscopy. Evaporation of the solvent and chromatography over neutral alumina (1.5 × 20 cm) in CH_2Cl_2 afforded the product as a yellow solid; yield of **6**, 2.73 g (97%). IR (CCl_4, cm^{-1}): 2048 s, 1998 s. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 197.4, 197.0, 120.6, 113.8, 86.1, 76.2, 75.2, 40.9, 40.8, 40.3, 35.5, 25.9, 25.1, 21.4. Anal. Found: C, 48.55, H, 4.27%. $C_{14}H_{15}ClO_2Ru$ (351.80) calcd.: C, 47.80, H, 4.30%.

4.10. Preparation of exo-(η^5-PCp)Ru$(CO)_2$Br (7)

1.0 g (1.6 mmol) of [*exo*-(η^5-PCp)Ru$(CO)_2$]$_2$ were dissolved in 25 ml of chloroform and cooled to −5 °C. While stirring, 0.16 ml (0.51 g, 3.2 mmol) bromine were added slowly. The solution was stirred for 3 h while gradually being brought to ambient temperature. The solvent was then removed and the residue was taken up in *n*-hexane. Spontaneous precipitation afforded a dark-brown solid; yield of **7**, 0.8 g (64%).

The same product can also be prepared by irradiation of 1.0 g of **2** and 2.5 g of CBr_4 in 300 ml of benzene at 7 °C. The reaction is complete after 1 h.

IR ($CHCl_3$, cm^{-1}): 2048 s, 2000 s. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 197.0$, 196.6, 120.9, 111.3, 87.4, 76.5, 75.7, 40.8, 40.8, 40.2, 35.9, 25.9, 25.3, 21.3. Anal. Found: C, 42.22, H, 4.05%. $C_{14}H_{15}BrO_2Ru$ (396.3) calcd.: C, 42.43, H, 3.82%.

4.11. General procedure for the thermal reaction of exo-(η^5-PCp)Ru(CO)$_2$X (X = Cl, Br, I) with monodentate phosphines and phosphites

1.0 mmol of *exo*-(η^5-PCp)Ru(CO)$_2$X and 1.1 to 1.5 mmol of phosphine or phosphite were dissolved in 20 ml of *p*-xylene and refluxed for about 2 h. The progress of the reaction was monitored by IR spectroscopy. The solvent was then removed under reduced pressure, and the crude product analysed by ^{31}P-NMR spectroscopy to determine the ratio of diastereomers. Purification by column chromatography over silica gel (1.5 × 40 cm) in dichloromethane and evaporation of the solvent afforded the pure product; for yields see Table 3.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PPhMe$_2$)Cl, yellow oil. IR (xylene, cm^{-1}): 1943. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 23.7$, 23.1.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PPh$_2$Me)Cl, yellow oil. IR (*n*-hexane, cm^{-1}): 1958. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 37.7$, 37.4.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PPh$_3$)Cl, dark-yellow solid. IR (*n*-hexane, cm^{-1}): 1953. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 51.4$, 50.9.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(P{*i*-Pr}$_3$)Cl, orange solid. IR (*n*-hexane, cm^{-1}): 1946. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 72.9$, 67.5.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PCy$_3$)Cl, orange solid. IR (*p*-xylene, cm^{-1}): 1929. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 58.2$, 58.1.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(P{OEt}$_3$)Cl, yellow oil. IR (*n*-hexane, cm^{-1}): 1965. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 149.2$, 146.5.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(P{OPh}$_3$)Cl, yellow solid. IR (*n*-hexane, cm^{-1}): 1987. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 147.8$, 145.3.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PPh$_3$)Br, yellow solid. IR (*n*-hexane, cm^{-1}): 1958. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 51.0$, 50.2.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(PPh$_3$)I, yellow solid. IR (*n*-hexane, cm^{-1}): 1958. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 51.1$, 50.0.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(P{OMe}$_3$)I, yellow solid. IR (*n*-hexane, cm^{-1}): 1969. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 155.1$, 152.5.

S_{Ru},R_{Ru}-*exo*-(η^5-PCp)RuCO(P{OEt}$_3$)I, yellow oil. IR (xylene, cm^{-1}): 1959. ^{31}P-NMR (202 MHz, $CDCl_3$): $\delta = 151.0$, 148.0.

4.12. Synthesis of exo-PCpRuCp (13)

To a solution of 0.25 g (0.80 mmol) of CpRuCODCl in 20 ml of THF at 0 °C a solution of 0.80 mmol of TlPCp in 10 ml of THF is slowly added. TlCl precipitates. After warming to ambient temperatures, the solution is refluxed for 1 h. The cooled solution is then filtered over Celite, the dark-brown filtrate is evaporated in vacuo to dryness and the residue extracted repeatedly with hexane. The collected hexane fractions are evaporated and the light-brown oil is purified by column chromatography over silica gel (1.5 × 20 cm). Elution with 4:1 (v/v) hexane–CH_2Cl_2 gave one single yellow phase, which is collected and gave the desired product as a yellow oil. Yield: 0.2 g (77%).

^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 4.47$ (s, 5H, Cp), 4.41 (m, 2H), 4.27 (t, $J = 2.2$ Hz, 1H), 2.60 (m, 3H), 2.30 (t, $J = 5.6$ Hz, 1H), 2.09 (m, 1H), 1.87 (d, $J = 9.2$ Hz, 1H), 1.33 (s, 3H, CH_3), (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $d = 102.9$, 86.0, 71.6, 70.9, 68.5, 66.7, 42.1, 41.2, 40.8, 37.4, 27.6, 27.0, 21.6. Anal. Found: C, 62.85, H, 6.24%. $C_{17}H_{20}Ru$ (325.4) calcd.: C, 62.74, H, 6.19%.

4.13. Synthesis of exo-PCpRuCp (14)*

This compound is prepared in a similar manner as (**13**), from 1.0 g (2.6 mmol) of Cp*RuCODCl and 2.6 mmol of TlPCp. Yield 0.86 g (84%), orange oil.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.95$ (br, 1H), 3.88 (br, 1H), 3.80 (t, $J = 2.0$ Hz, 1H), 2.60 (m, 3H), 2.38 (d, $J = 2.3$ Hz, 1H), 2.20 (t, $J = 5.7$ Hz, 1H), 2.05 (m, 1H), 1.87 (s, 15H, 5 CH_3), 0.58 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $d = 101.8$, 84.4, 84.3, 71.3, 70.6, 69.7, 42.3, 41.4, 40.2, 35.9, 27.1, 25.8, 21.7, 11.9. Anal. Found: C, 66.69, H, 7.71%. $C_{22}H_{30}Ru$ (395.53) calcd.: C, 66.80, H, 7.64%.

Acknowledgements

We are grateful to the Schweizer Nationalfonds (Grant 20-29821-90), the Deutsche Forschungsgemeinschaft (SFB 380) and the Fonds der Chemischen Industrie for financial support.

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