

Cyclopentadienylmetal Complexes Bearing Pendant Phosphorus, Arsenic, and Sulfur Ligands[†]

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I. Introduction

Bidentate ligands have proven important in a variety of complexes and are invaluable in a number of catalytic processes. While ligands of this type usually have two identical ligand fragments (homobidentate ligands), heterobidentate ligands allow for a differentiation of the ligands and therefore are prone to selective reactions. This is especially interesting in cases where the ligands are rather different from one another. Phosphane and cyclopentadienyl ligands are among the most commonly used in organometallic chemistry, and they are quite different in nature: Whereas a phosphane is electroneutral and often subjected to ligand exchange processes, the cyclopentadienyl ligand is normally considered to be negatively charged and rather tightly bound to a metal.

Reviewing the literature in the field of cyclopentadienylmetal complexes bearing pendant phosphorus, arsenic, and sulfur ligands is timely given that the number of publications of relevance to this topic is growing exponentially as can easily be seen from the list of references in this review: the number of references since 1993 clearly exceeds that of all years before. The reason for this development may be that cyclopentadienylmetal complexes bearing pendant



Holger Butenschön was born and raised in Hamburg, Germany. After his army service he studied chemistry at the University of Hamburg and obtained his Dr. rer. nat. degree in 1983 with Professor Armin de Meijere as a fellow of the Studienstiftung des Deutschen Volkes. From 1983 to 1984 he spent a postdoctoral year with Professor K. Peter C. Vollhardt at the University of California at Berkeley as a NATO fellow. Having returned to Germany, he joined the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr as a Liebig fellow to do preparative organometallic work in the fields of anellated arenachromium complexes and cyclopentadienyl cobalt complexes with pendant phosphane ligands. After his habilitation in 1991 (University of Hamburg), he became a Heisenberg fellow of the DFG at the University of Wuppertal from 1992 to 1993. Since 1993 he has been a professor of organic chemistry at the University of Hannover. In 1999 he was a foreign visiting professor at Kyushu University in Fukuoka, Japan. Holger Butenschön is the editor of the German translation of Peter Vollhardt's and Neil Schore's textbook *Organic Chemistry* as well as a coauthor of the *Memofix OC*. He currently serves as the chairman of the Hannover district of the German Chemical Society (GDCh). His spare time is occupied by the female part of his family, his wife Bettina and their four daughters Lisa, Nora, Inga, and Lara.

phosphorus, arsenic, and sulfur ligands are expected to perform chemistry different from that of usual cyclopentadienyl complexes. Indeed this has often been the case. Complexes discussed in this review facilitate the complexation of sensitive ligands, offer new aspects concerning chirality, allow novel reactions, and are beginning to be applied to transition metal catalysis. It is therefore hoped that this review will contribute to these developments by offering state of the art information for those active in the field and, even more important, for those who join in the future.

This review covers the chemistry of cyclopentadienylmetal complexes, in which the cyclopentadienyl ligand bears a sidearm which includes a phosphorus, arsenic, or sulfur ligand. The pendant ligand has to be separated from the cyclopentadienyl part, that is,

[†] Dedicated to Professor Günther Wilke on the occasion of his 75th birthday.

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cyclopentadienylphosphane complexes are not included. Only those papers are relevant here in which such a sidearm coordinates to the metal with chelate formation. This means, e.g., that ferrocene catalysts with a phosphane sidearm not coordinating to the ferrocene iron atom are usually excluded. Compounds which do not form chelates are included only if they are relevant to the chemistry covered here. A few of the compounds reviewed here were mentioned in earlier reviews; however, these were not comprehensive and are now out of date.^{1,2} Literature has been reviewed up to 1999. A review by Siemeling covering cyclopentadienyl chelate complexes with pending oxygen ligands appears in this issue.³

Unless otherwise indicated, the representation of chiral compounds refers to racemic material.

II. (Phosphanylalkyl)cyclopentadienyl Complexes

The characteristic feature of (phosphanylalkyl)cyclopentadienyl complexes is a combination of a cyclopentadienyl and a phosphane ligand being connected to one another by an alkyl chain or a similar spacer. After a description of the syntheses of such ligands, their complexes will be reviewed according to the metal. Because according to our own experience ³¹P NMR is especially diagnostic and of much help for those active in the field, the available data are collected in Tables 1–4. For quick reference, complexes which have been characterized by X-ray crystallography are listed in Table 5.

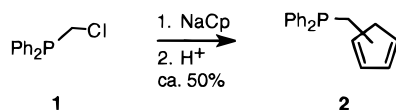
A. Ligand Syntheses

In many cases the complexes are formed by complexation of an appropriate ligand, which had been separately prepared. In other cases, ligands of complexes are formed by a chemical reaction at a complex in the course of which an already present ligand is transformed into the desired one. In this section, ligand syntheses of the first category are reviewed; the latter syntheses are less general in character and are therefore presented in the corresponding metal complex section.

(Phosphanylalkyl)cyclopentadienes and the corresponding cyclopentadienides have been prepared by two main routes, by nucleophilic substitution reactions, in most cases with the cyclopentadienyl (Cp) anion as the nucleophile, and by a nucleophilic addition to fulvenes or to spiroannellated cyclopentadienes.

Reaction of (chloromethyl)diphenylphosphane (**1**) with sodium cyclopentadienide (NaCp) afforded [(diphenylphosphanyl)methyl]cyclopentadiene (**2**) in 50% yield after aqueous workup (Scheme 1). **2** is

Scheme 1



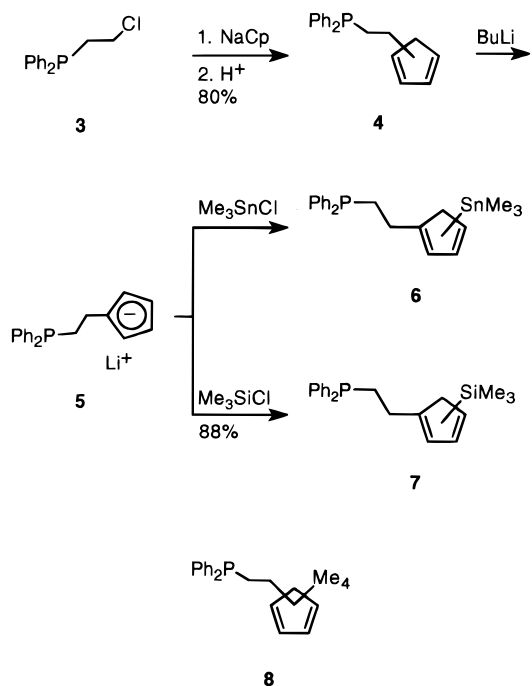
described as a colorless oil which rapidly polymerizes at room temperature.⁴

Some [(phosphanyl)ethyl]cyclopentadienes were prepared by nucleophilic substitution of the respec-

tive 1-chloro-2-phosphanylethanes with cyclopentadienide. Sometimes the cyclopentadienes obtained were immediately deprotonated with base to prevent polymerization, intermolecular Diels–Alder reactions, and formation of mixtures of isomers.

Reaction of NaCp with 1-chloro-2-(diphenylphosphanyl)ethane (**3**) gave [(diphenylphosphanyl)ethyl]cyclopentadiene (**4**) in 80% yield (Scheme 2). Depro-

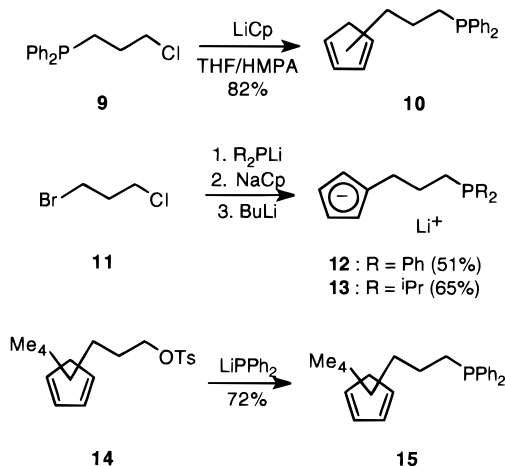
Scheme 2



tonation with butyllithium afforded cyclopentadienide **5**; subsequent quench with chlorotrimethylstannane resulted in a mixture of isomeric [(diphenylphosphanyl)ethyl](trimethylstannyl)cyclopentadienes **6**.^{5,6} The corresponding reaction with chlorotrimethylsilane gave cyclopentadienes **7** in 88% yield.⁷ In a similar way, tetramethyl derivative **8** was prepared from 1-chloro-2-tosylethane by treatment with the tetramethylcyclopentadienyl anion followed by lithium diphenylphosphide.⁸ However, Jutzi reported the reaction to give almost exclusively isomeric geminal disubstituted cyclopentadiene derivatives when the tetramethylcyclopentadienyl anion was treated with 1-chloro-2-tosylethane.⁹

[3-(Diphenylphosphanylpropyl)]cyclopentadienes **10** were prepared as a mixture of two isomers by reaction of 3-chloropropyl diphenylphosphane (**9**) with lithium cyclopentadienide in 82% yield¹¹ (Scheme 3). The use of HMPA was mandatory for the success of the synthesis. Alternatively, (3-phosphanylpropyl)cyclopentadienyl anions **12** and **13** were prepared in 51% and 65% yield in a sequence of nucleophilic substitution reactions starting from 1-bromo-3-chloropropane (**11**) by treatment with lithium phosphides¹⁰ and then with NaCp in THF, followed by hydrolysis and deprotonation with butyllithium.^{11–13} In a similar way tetramethyl derivative **15** was obtained by reaction of separately prepared (3-tosylpropyl)tetramethylcyclopentadienes **14** with lithium diphenylphosphide in 72% yield.¹⁴

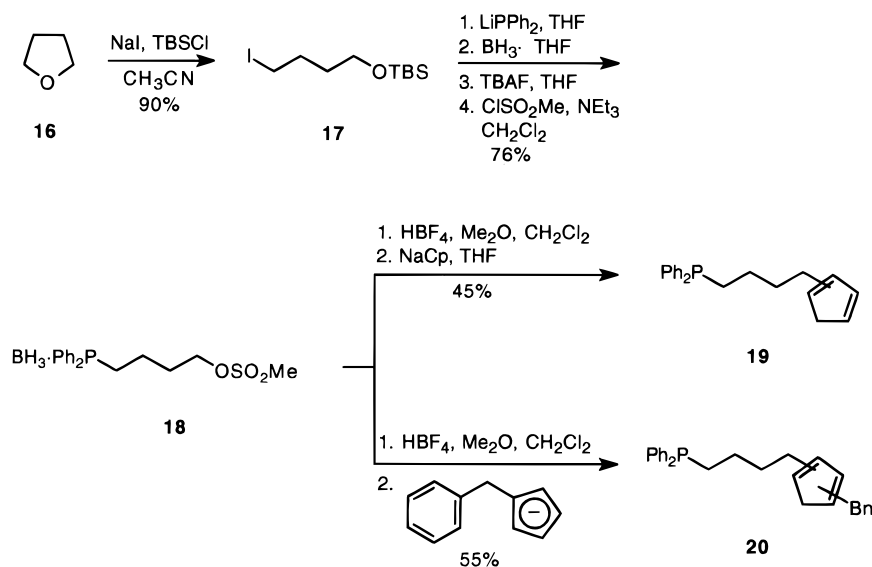
Scheme 3



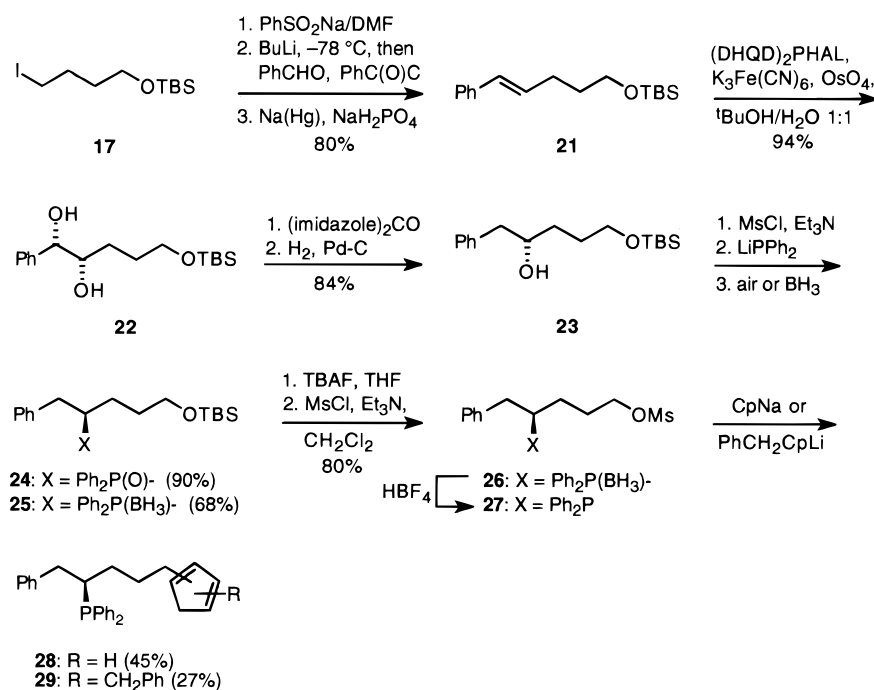
Ligands with a C₄ spacer were prepared by ring opening of THF (**16**) followed by substitution to **17** and **18** and subsequently to **19** as well as **20**, which were obtained as mixtures of isomers in moderate yields¹⁵ (Scheme 4).

Starting from **17** a similar, chiral ligand system was prepared by Trost. Reaction with PhSO₂Na in DMF, followed by BuLi, benzaldehyde, and benzoyl chloride, and then Na/Hg gave Julia olefination product **21** (*E:Z* = 98:2) (Scheme 5). An asymmetric dihydroxylation provided the diol **22** (94%, ee = 97%). The corresponding carbonate allowed hydrogenolysis to give alcohol **23**, which after mesylation was treated with LiPPh₂ under S_N2 conditions to give the phosphane, which was oxidized with air to phosphane oxide **24** or protected with borane to give adduct **25**. Protecting group exchange afforded mesylate **26**,

Scheme 4



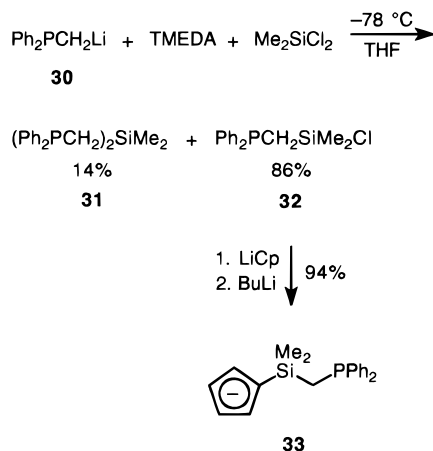
Scheme 5



from which the phosphane **27** was liberated. Final substitution with NaCp or PhCH₂CpLi resulted in ligand **28** or **29** with 97% ee.¹⁵

Ligand **33** with a silicon atom incorporated in the spacer was made by Schore¹⁶ in 94% yield by treatment of (diphenylphosphanyl)methylithium (**30**) with dichlorodimethylsilane followed by substitution of **32** with lithium cyclopentadienide and deprotonation with butyllithium (Scheme 6). More recently, Jones

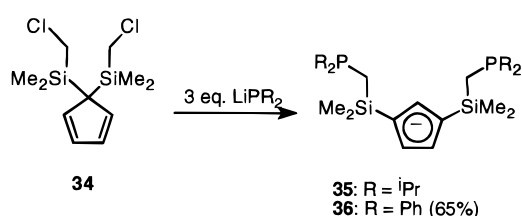
Scheme 6



published a modification which avoids formation of side product **31**.¹⁷

Ligands **35** and **36** with two phosphane sidearms were prepared by Fryzuk upon treatment of 5,5-bis-(2-chloroethyl)cyclopentadiene (**34**) with 3 equiv of lithium diisopropylphosphide or lithium diphenylphosphide^{18,19} (Scheme 7).

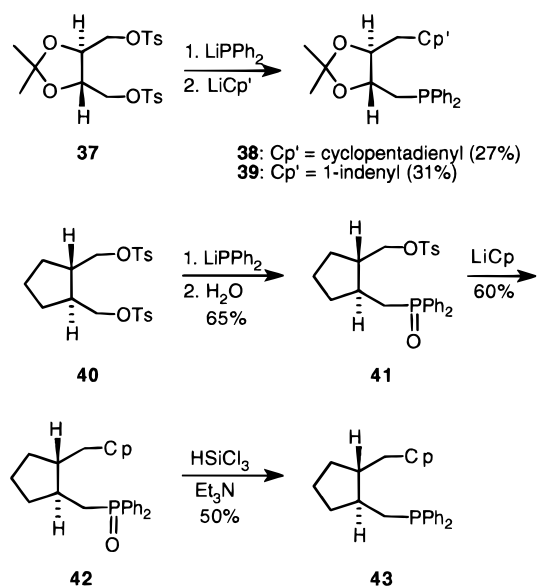
Scheme 7



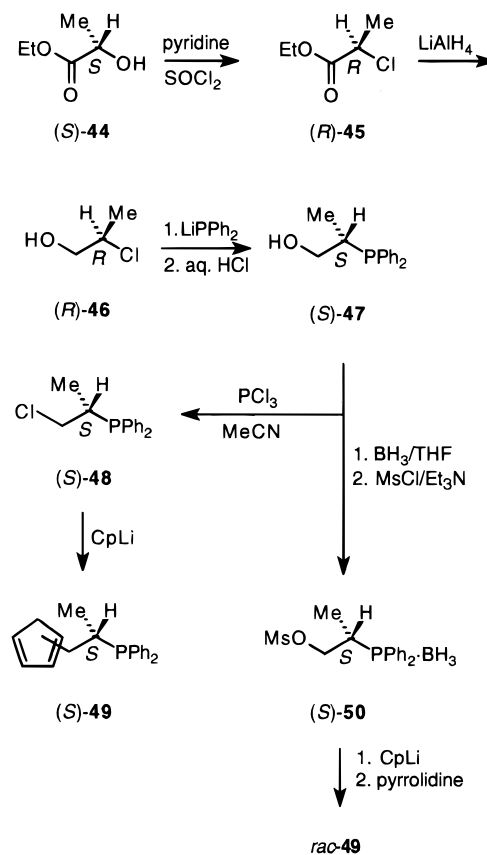
The first enantiomerically pure chiral representatives of this class of ligands were published by Tani in 1995.^{20,21} Enantiomerically pure ditosylate **37**, derived from L-threitol, was treated stepwise with lithium diphenylphosphide and with cyclopentadienyllithium or indenyllithium to give ligands **38** and **39** in 27% and 31% yield, respectively (Scheme 8). In addition, enantiomerically pure ditosylate **40** was treated with lithium diphenylphosphide, followed by oxidative aqueous workup. Phosphorane **41** was obtained in 65% yield, and subsequent substitution of the second tosyl group by lithium cyclopentadienide gave **42** (60% yield), which was reduced to the desired ligand **43** with trichlorosilane in 50% yield. **43** is described as an air-sensitive colorless oil, which was characterized as its oxide **42**.

Recently the synthesis of chiral ligand **49** was reported by van der Zeijden. The synthesis starts from ethyl (1*S*)-lactate (**44**), which reacts with thionyl chloride to give **45**, which is reduced to **46** (Scheme

Scheme 8



Scheme 9

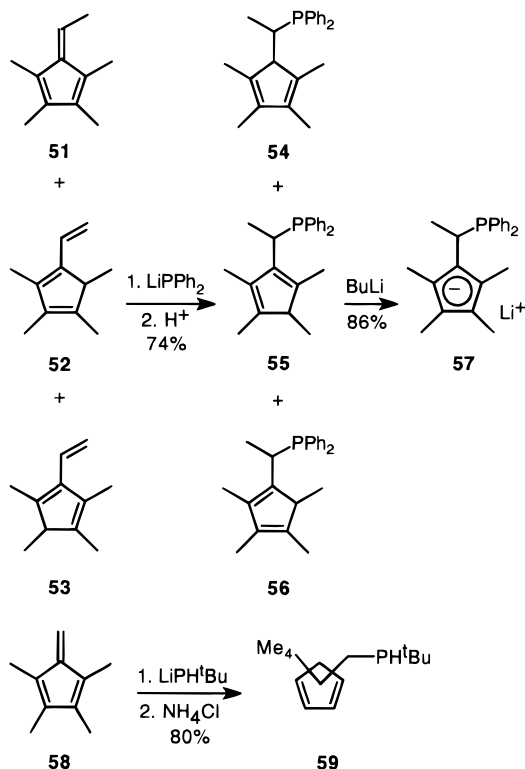


9). Treatment with LiPPh₂ gave phosphanyl alcohol **47**, and chlorination with PCl₃ to **48** followed by a nucleophilic substitution with CpLi afforded (*S*)-**49** in high yield with 66% ee. Protection of the phosphane moiety in **47** with borane, mesylation, substitution with CpLi, and deprotection with pyrrolidine (via **50**) gave **49** as a racemate. It is remarkable that the substitution with CpLi was successful whereas elimination occurred when CpNa was used.²²

An alternative route to the (phosphanylalkyl)-cyclopentadienyl ligand system and related ones are nucleophilic additions to fulvenes and to spiroanell-

lated cyclopentadienes. Mintz showed that reaction of lithium diphenylphosphide with an inseparable mixture of 1,2,3,4,6-pentamethylfulvene (**51**) and vinyltetramethylcyclopentadienes **52** and **53** results in the formation of a mixture of double bond isomers of 5-[(2-diphenylphosphanyl)-1-methylethyl]-1,2,3,4-tetramethylcyclopentadienes **54–56** in 74% yield (**55** and **56** as mixtures of two diastereomers each), which can be deprotonated with butyllithium in 86% yield to give 1-[(2-diphenylphosphanyl)-1-methylethyl]-2,3,4,5-tetramethylcyclopentadienide (**57**)^{14,23} (Scheme 10). In a similar way (*tert*-butylphosphanyl)ethyltet-

Scheme 10



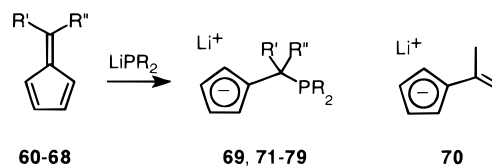
ramethylcyclopentadienes **59** were prepared as a mixture of five isomers from fulvene **58**.²⁴

The additions of lithium phosphides to fulvenes **60–68** gave cyclopentadienides **69** (accompanied by differing amounts of **70**), **71–79** in good yields^{13,25–27} (Scheme 11).

More recently Bergman reported the synthesis of potassium salt **80**, which was obtained by treatment of the corresponding substituted fulvene with $\text{Me}_2\text{PCH}_2\text{Li}$ in 14% yield²⁸ (Chart 1).

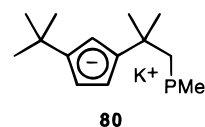
The cyclopropane ring opening of spiro[2.4]hepta-4,6-diene (**81**) by the attack of a nucleophilic anion was first disclosed by Kauffmann.²⁹ In the course of this ring opening, the nucleophile is attached at the end of the ethylene fragment, and the negative charge is implemented in the cyclopentadienyl system with formation of an aromatic cyclopentadienide. The reaction is rather general and can be used to prepare numerous systems in which a cyclopentadienide is connected to a nucleophile by an ethylene spacer. Therefore, it is the method of choice to prepare (2-phosphanylethyl)cyclopentadienides by reaction of **81** with substituted lithium (or potassium³⁰) phosphides. Compounds prepared by this

Scheme 11



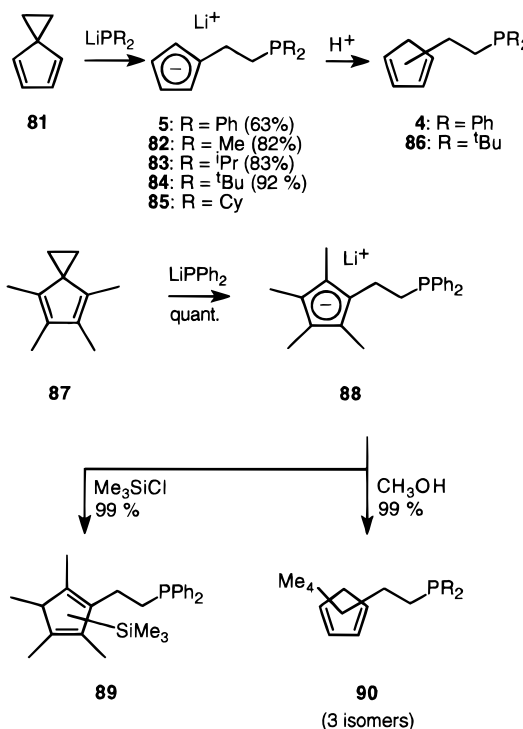
Fulvene	R	R'	R''	Product	Yield (%)
60	Ph	H	H	69	70
60	ⁱ Pr	H	H	71	65
61	Ph	Me	Me	72	75
62	Ph	Me	H	73	81
63	Ph	CMe ₃	H	74	59
64	Ph	Ph	H	75	80
65	Ph	<i>p</i> Tol	H	76	83
66	<i>p</i> Tol	Me	Me	77	85
67	<i>p</i> Tol	Me	H	78	77
68	<i>p</i> Tol	CMe ₃	H	79	80

Chart 1



route are the cyclopentadienides **5**,^{12,13,30} **82**,³¹ **83**,¹³ **84**,^{13,32} and **85**³³ as well as the isomeric [2-(diphenylphosphanyl)ethyl]cyclopentadienes **4**^{29,30,34} and di-(*tert*-butyl) derivative **86**³² (one isomer) (Scheme 12).

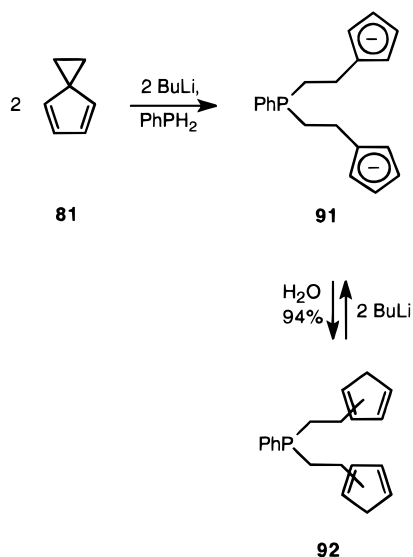
Scheme 12



Tetramethylspiro[2.4]hepta-4,6-diene **87** was transformed to ligand **88** accordingly in almost quantitative yield. When **88** was treated with chlorotrimethylsilane, **89** was obtained in 99% yield, and treatment with methanol gave **90** as a mixture of three isomers.^{35,36}

A particularly interesting example of the application of the ring opening of **81** in the formation of cyclopentadienyl ligands with a pendant phosphane ligand has recently been provided by Curnow, who treated 2 equiv of **81** with phenylphosphane in the presence of 2 equiv of butyllithium. A sequence of two ring opening reactions provided bis(cyclopentadienyl) dianion **91**, which was hydrolyzed to **92** (mixture of isomers) in 94% yield (Scheme 13). **92** can be depro-

Scheme 13



tonated by two equivalents of butyllithium to give dianion **91**.^{37,38}

Related to these ligand syntheses are preparations of similar indenyl systems starting from spiroindene **93**. Treatment with LiPPh_2 or with LiPCy_2 ($\text{Cy} = \text{cyclohexyl}$) gave ligands **94** (45%) and **95**, the latter one being stored as its CS_2 adduct **96** (64%), which is air stable (Scheme 14). Homologues **98** and **99** were obtained by nucleophilic substitution of 1-chloro-3-(diphenylphosphanyl)propane (**9**) or 1-chloro-4-(diphenylphosphanyl)butane with indene (**97**) after metalation in 21% and 28% yield.³⁹

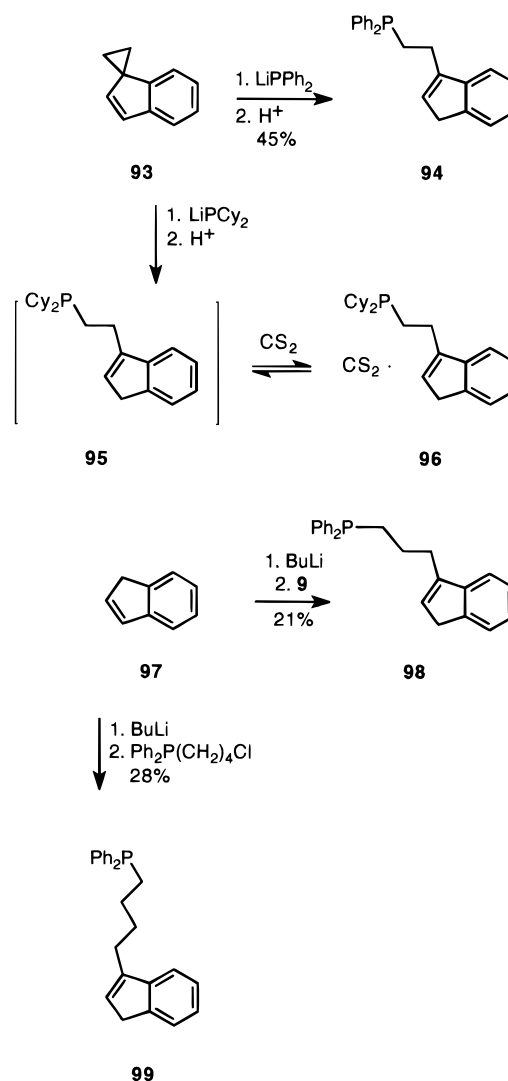
More complex derivatives **102** and **105** were prepared in high yields by reactions of heterocycles **100** and **103** with phenyllithium via lithium phosphides **101** and **104**, respectively, followed by **81** and hydrolysis^{11,40} (Scheme 15).

A route to ligand system **108**, in which the cyclopentadienyl system is constructed in the presence of the phosphane part of the ligand, was recently published by Trost.¹⁵ The synthesis starts from **106**, to which after lithiation 2-cyclopentenone is added to provide **107** in 52% yield, followed by water elimination (56%) to give **108** as a mixture of regioisomers (Scheme 16).

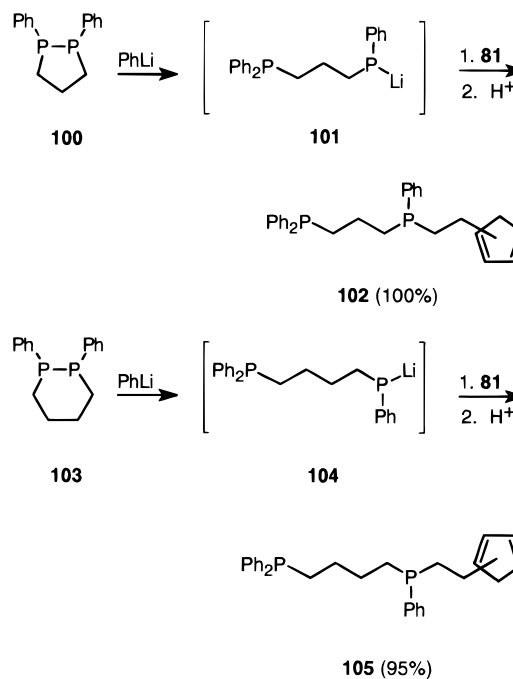
A similar but chiral ligand system **110** was developed by Hidai by treatment of the known ferrocene **109**⁴¹ with hydrogen peroxide followed by methylation with MeI and subsequent treatment of the ammonium salt with sodium cyclopentadienide and reduction of the phosphane oxide with LiAlH_4 ⁴² (Scheme 17).

After the syntheses of **102** and **105** by Olbrich and Kauffmann,^{11,40} a new class of chiral tripod ligands

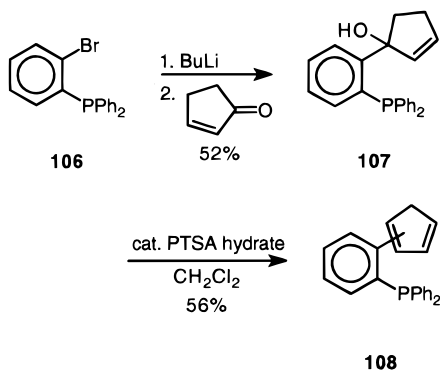
Scheme 14



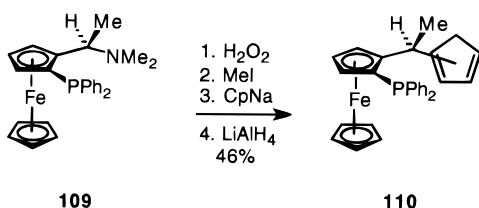
Scheme 15



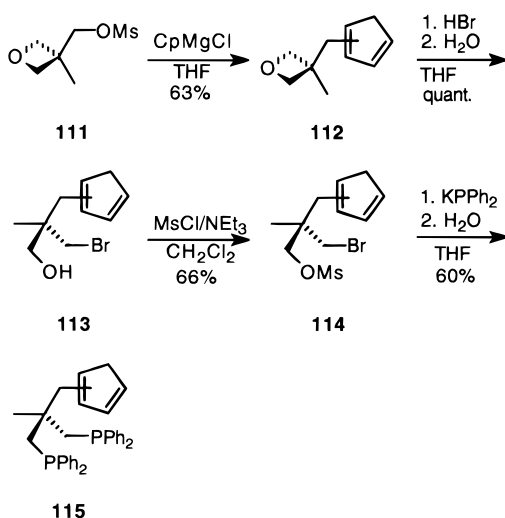
Scheme 16



Scheme 17



Scheme 18

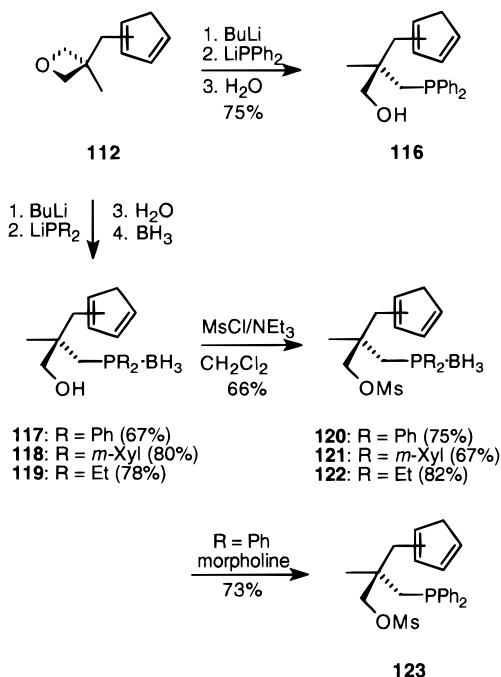


incorporating cyclopentadienyl and phosphane functionalities were introduced in 1997 by Huttner.⁴³ These ligands were prepared starting from oxetane **111**. Nucleophilic substitution with cyclopentadienyl-magnesium bromide gave **112** (63%), from which **113** was obtained quantitatively by acidic nucleophilic ring opening with HBr (Scheme 18). Subsequent mesylation afforded **114** in 66% yield. Treatment with KPPH₂ gave achiral tripod ligand **115** in 60% yield.⁴³

Alternatively, **112** was opened under basic reaction conditions by treatment with butyllithium followed by LiPR₂ (R = Ph) and aqueous workup to give **116** in 75% yield (Scheme 19). The phosphane functionality can be protected with borane to **117–119**, allowing mesylation of the hydroxy group to give **120–122**. Deprotection of **120** leads to **123**.⁴³

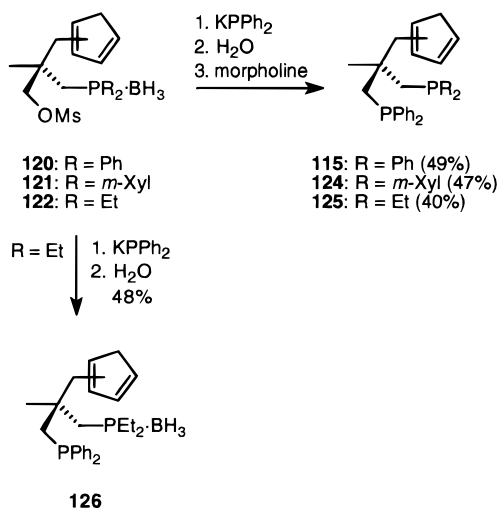
The mesyl group in **120–122** can be replaced by a diphenylphosphanyl group by treatment with KPPH₂ to give after deprotection with morpholine either **115** or cyclopentadienyl heterodiphosphane and therefore chiral tripod ligands **124** and **125** in racemic form

Scheme 19



(Scheme 20). When no morpholine was used, **126** was obtained.⁴³

Scheme 20



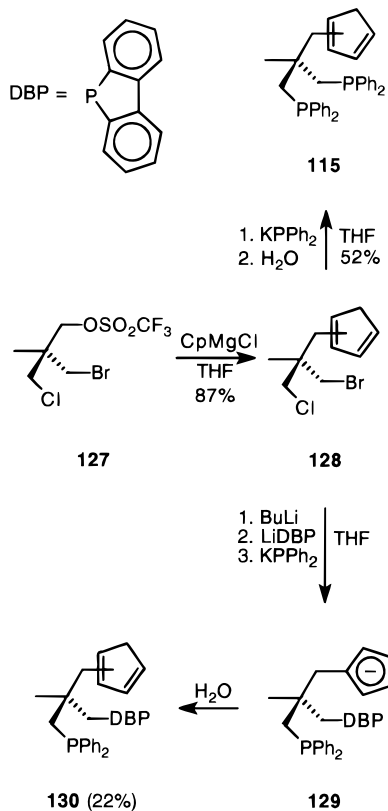
A similar route provided tripods **115** and **130** from **127** via **128** and **129**⁴³ (Scheme 21).

A particularly sterically demanding ligand system with an anthracene substitution was prepared by Trost. The synthesis started from the known Diels–Alder adduct **131** and proceeded via lactone **132** and phosphino acid **133** (not isolated) to **134**, which was transformed to either **135** or **136**¹⁵ (Scheme 22).

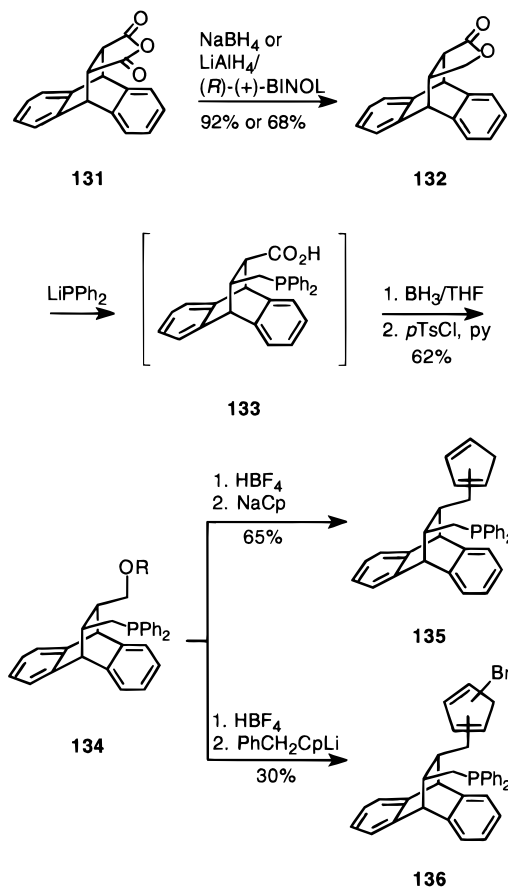
B. Main Group and Groups 3, 4, and 5 Metal Complexes

Very recently Karsch succeeded in the synthesis and structural characterization of the potassium complex **137** corresponding to lithium salt **5** (Chart 2). **137** was obtained by treatment of spiro[2.4]hepta-4,6-diene (**81**) with potassium diphenylphosphide in THF, and the structure shows that the pendant

Scheme 21

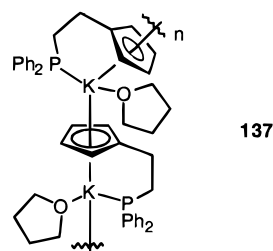


Scheme 22



phosphane arm, the cyclopentadienyl ligand, and one THF molecule are coordinated to the metal. The structure is polymeric by complexation of the next

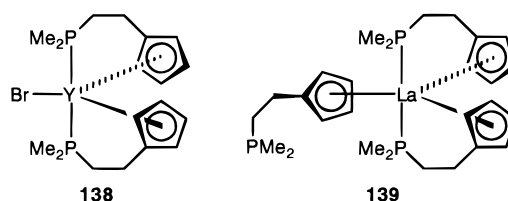
Chart 2



potassium atom to the other face of the cyclopentadienyl ligand.⁴⁴

It was also Karsch who reported the only yttrium and lanthanum complexes. Yttrium complex **138** was obtained by treatment of ligand **82** with yttrium triflate and lithium bromide in 75% yield (Chart 3).

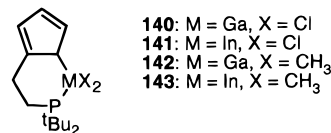
Chart 3



Lanthanum complex **139** was obtained in 92% yield by treatment of lanthanum triflate with ligand **82**. In addition to their spectroscopic data, both complexes were characterized by X-ray crystallography.³¹

Besides **137**, gallium and indium complexes **140**–**143** are the only known chelated examples with main group metals (Chart 4). [2-(Di-*tert*-butylphosphanyl)-

Chart 4



ethyl]cyclopentadienyllithium (**84**)^{13,32} was treated with gallium and indium trichloride to give chelated η^1 -cyclopentadienylgallium and -indium complexes **140** and **141** (70%) besides lithium chloride. **140** and **141** have been structurally characterized. Electro-neutral phosphanylethylcyclopentadienes **86** were reacted with trimethylgallium and trimethylindium with formation of methylated η^1 complexes **142** and **143**.³²

Complexes of titanium and zirconium were made by reaction of the anionic cyclopentadienyl ligands with TiCl₄, CpTiCl₃, and ZrCl₄. These reactions yielded titanocenes and zirconocenes **144**–**148** in good yields^{13,45} (Scheme 23, Chart 5). Attempts to achieve a chelation of the pendant phosphane ligand by reductive removal of chloro ligands was only partially successful. Reduction of titanium complexes **144** and **147** gave titanium(III) complexes whose ESR spectra indicate complexation of a phosphane ligand. However, it could not be decided whether monomeric chelates **149** and **150** or dimeric species such as **151** or **152** were formed (Chart 5). Bimetallic complexes of molybdenum and rhodium using **144**, **145**, or **146** as phosphane ligands have been reported.⁴⁵

Scheme 23

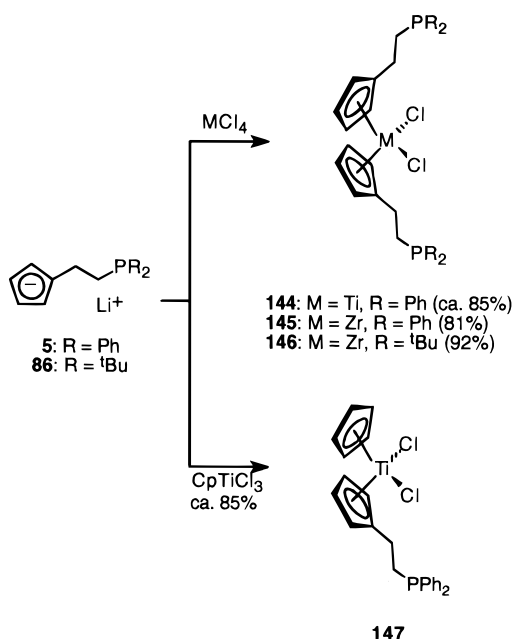
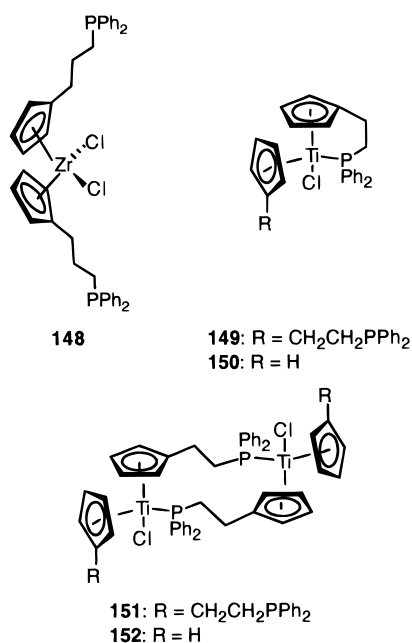
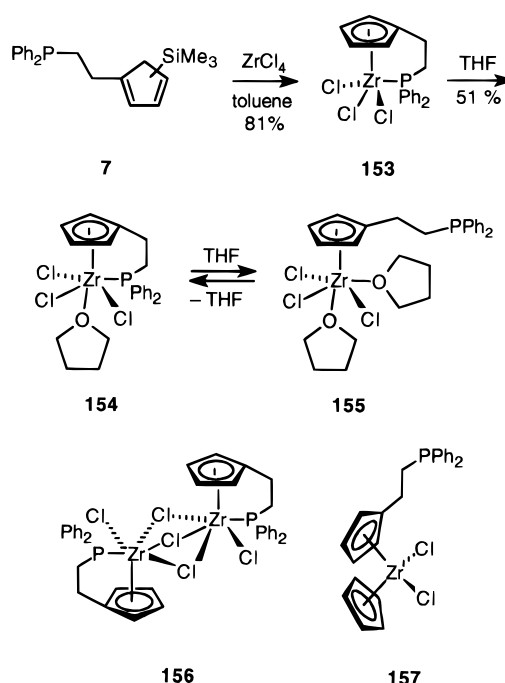


Chart 5



Krut'ko prepared half-sandwich complexes by treatment of ZrCl₄ with silyl-substituted ligands **7**. Zirconium chelate **153** was obtained in 81% yield as a crude product; following treatment of **153** with THF afforded **154** as a pure compound in 51% yield (Scheme 24). **154** shows dynamic behavior in THF as evidenced by a variable-temperature NMR investigation. Presumably, the pendant phosphane ligand is decoordinates with complexation of another THF molecule to give **155**. **154** was subjected to an X-ray structure analysis and exists in two modifications available by crystallization from dichloromethane or from THF. When no THF was added to **153**, after a longer period of time, dimer **156** was obtained from the mother liquors by crystallization and identified by an X-ray structure analysis. Reaction of **153** with sodium cyclopentadienide in THF gave **157** in 80% yield in addition to smaller amounts of **145** and Cp₂-

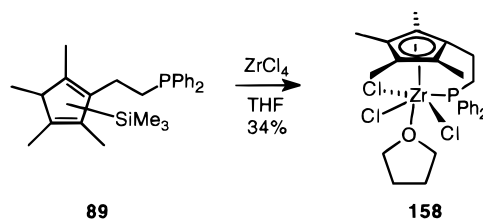
Scheme 24



ZrCl₂. **157** was obtained as the sole reaction product in 57.5% yield upon treatment of **154** with trimethylstannylcyclopentadienes.⁷

In a similar way **158** was obtained from **89** in 34% yield and was characterized by an X-ray structure analysis³⁶ (Scheme 25).

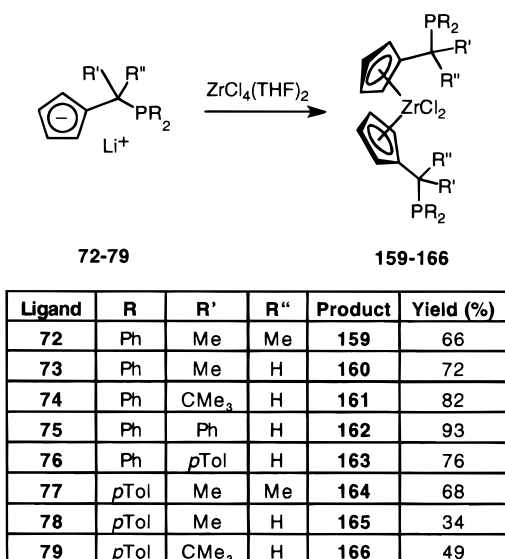
Scheme 25



Erker reported the internal stabilization of zirconocene cations by phosphane chelation. Ligands **72**–**79** were treated with ZrCl₄ to give **159**–**166**²⁷ (Scheme 26).

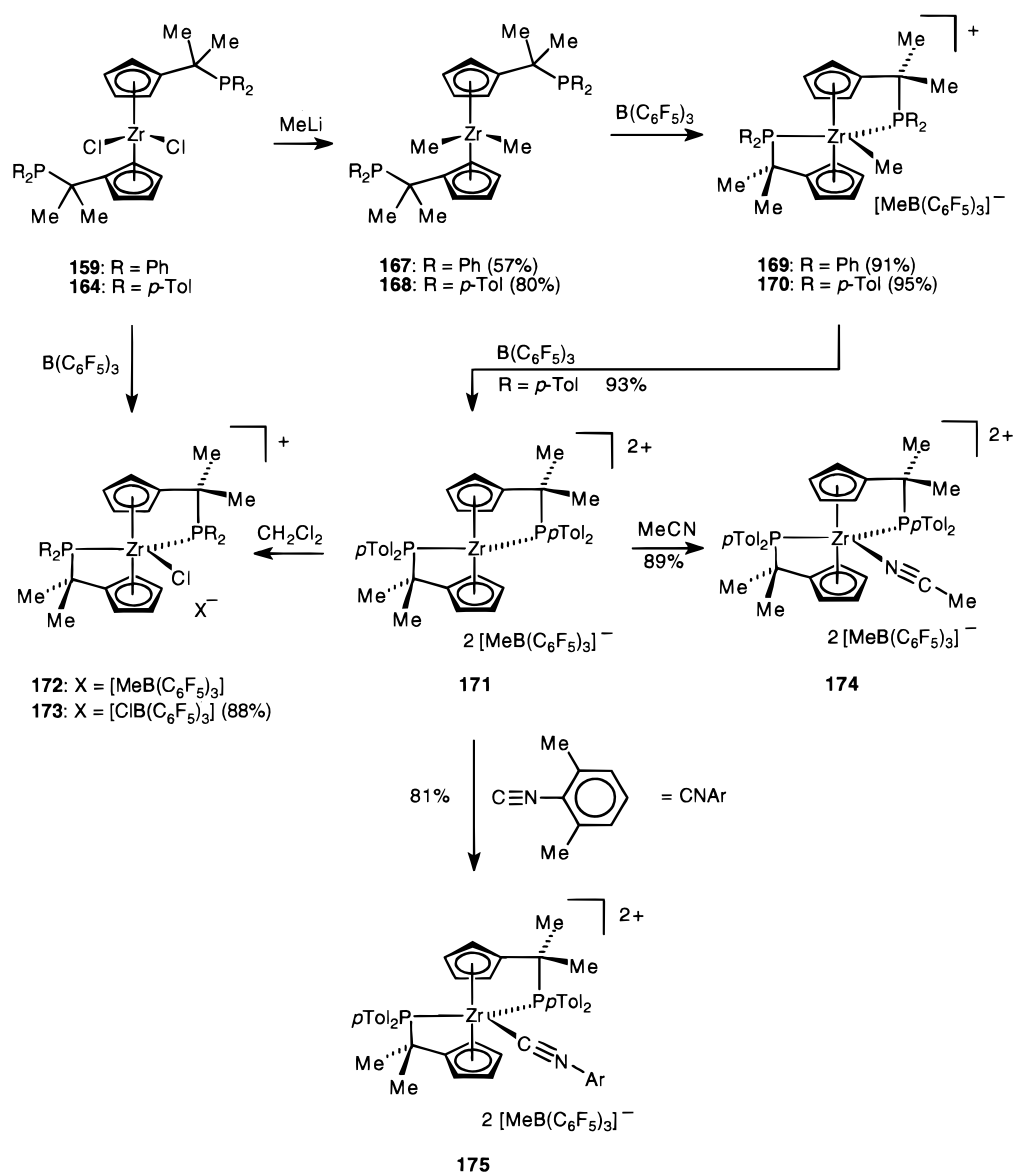
By treatment of **159** and **164** with methyl lithium, Erker obtained **167** and **168** in 57% and 80% yield, respectively; the latter was also characterized by X-ray-crystallography (Scheme 27). Treatment of **167** and **168** with 1 equiv of tris(pentafluorophenyl)borane caused a methyl transfer with formation of cationic zirconium complexes **169** (91%) and **170** (95%); **169** was also structurally characterized. Addition of a second equivalent of the borane gave dicationic **171** in 93% yield. Treatment of **171** with dichloromethane resulted in an immediate reaction to give **172**, which also was structurally characterized. The similar complex **173** was obtained by treatment of **164** with tris(pentafluorophenyl)borane (88%). Addition of acetonitrile to **171** gave **174** (89%), and with 2,6-dimethylphenylisocyanide, **175** was formed in 81% yield. Complexes **169**, **170**, and **172** show an interesting dynamic NMR behavior corresponding to

Scheme 26



a temporary decomplexation of the phosphane side-

Scheme 27

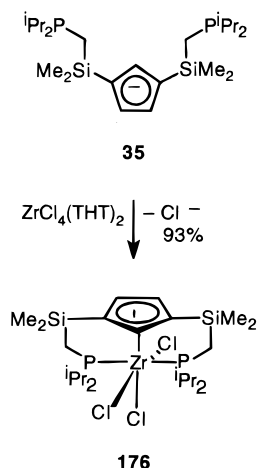


arms. Following recomplexation results in a formal equivalence of the methyl substituents on the NMR time scale.²⁶

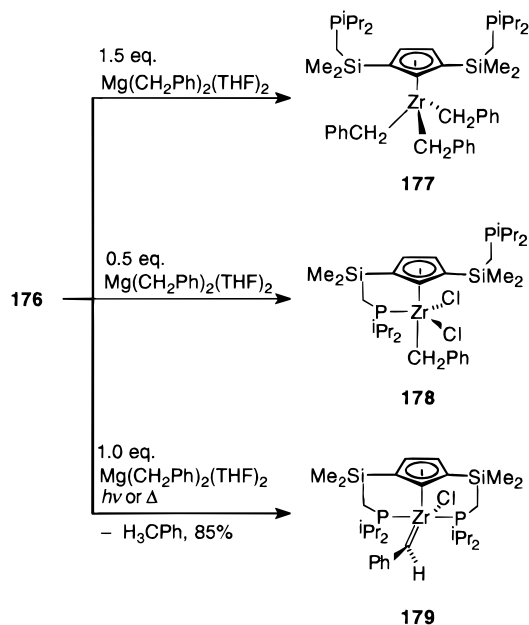
Zirconium complexes with ligand system **35** have been prepared by Fryzuk, and their chemistry has been investigated.^{18,46–48} Anion **35** was treated with $\text{ZrCl}_4(\text{THT})_2$ (THT = tetrahydrothiophene) in toluene to obtain zirconium complex **176** in 93% yield (Scheme 28). The authors emphasize the use of noncoordinating toluene as the solvent to be crucial. **176** has been structurally characterized. If one assumes the cyclopentadienyl ligand to occupy one site, the coordination can be described as quasi-octahedral with a P–Zr–P angle of 159.53(4)°.

The reactions of **176** with dibenzylmagnesium have been investigated in detail. Reaction of **176** with 1.5 equiv of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$ in toluene at -78°C results in **177** as the result of a substitution of all three chloro ligands by benzyl groups and a decomplexation of both phosphane arms (Scheme 29). In a similar way, **178** is formed upon treatment of **176** with 0.5 equiv of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$. **177** and **178** are described as extremely soluble in pentane and

Scheme 28



Scheme 29

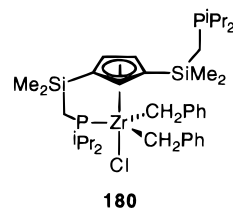


as yellow air- and moisture-sensitive, thermally stable oils.

178 shows interesting NMR properties: At higher temperatures the two phosphane arms undergo rapid exchange as indicated by ^{31}P NMR. NMR line shape analysis gave the following activation parameters from the calculated rate constants: $\Delta H^\ddagger = 36.8$ kJ/mol, $\Delta S^\ddagger = -54.8$ J/mol·K. From the negative entropy of activation the authors conclude that the transition state is a six-coordinated structure within an associative exchange mechanism. When **176** is treated with 1 equiv of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$, an equimolar mixture of **177** and **178** is formed. No disubstitution product is observed by ^1H or ^{31}P NMR. However, when this mixture is photolyzed or thermolyzed, benzylidene complex **179** is formed in 85% yield in addition to toluene.¹⁸ **179** is the first example of a stable alkylidene complex of zirconium formed via an α -hydrogen abstraction process. The X-ray crystal structure analysis shows the benzylidene ligand to be oriented perpendicular to the cyclopentadienyl system with the phenyl ring syn to the cyclopentadienyl system. Very recently a mechanistic study concerning the formation of **179** has been published.⁴⁷ The authors

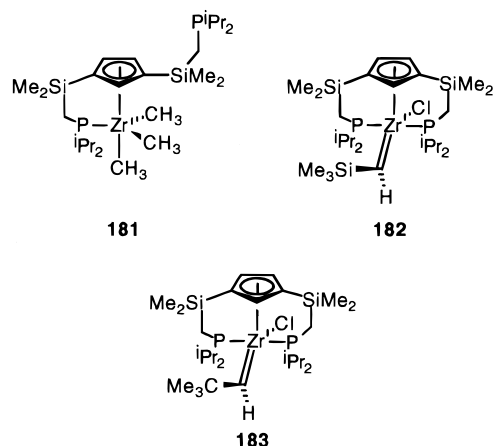
reported the NMR spectroscopic identification of **180** as an intermediate in the formation of **179** (Chart 6).

Chart 6



When **176** was treated with 3 equiv of methylmagnesium bromide at -78°C , a trisubstitution product was obtained in 70% yield. A ^{31}P NMR investigation showed a fluxional behavior similar to that of **176**: At low temperature ($<-40^\circ\text{C}$) two resonances were observed at $\delta = 9.8$ and $\delta = -9.7$; a reasonable formula for the product is **181** (Chart 7). At higher

Chart 7

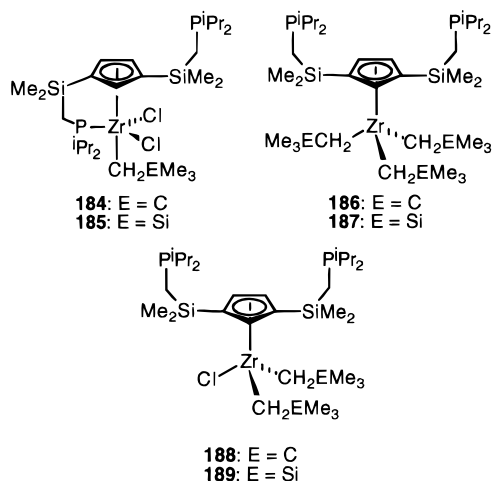


temperatures a fast exchange of the phosphorus atoms is observed, presumably as a result of a complexation/decomplexation process of the phosphane arms at the zirconium atom. Activation parameters were determined to be $\Delta H^\ddagger = -55.2$ kJ/mol and $\Delta S^\ddagger = 61.0$ J/mol·K. The fluctuality seems to be a result of a more complicated process, and associative as well as dissociative paths for this intramolecular process are discussed.⁴⁶

Recently silyl derivative **182** has been mentioned in a paper which describes the reactivity of **179** and **182** with ethene, acetone, CO, and *tert*-butylisocyanide.⁴⁸ In a following publication, **182** and **183** were described as obtained from **176** by treatment with 2 equiv of $\text{LiCH}_2\text{SiMe}_3$ or $\text{LiCH}_2\text{CMe}_3$ in 82% and 65% yield, respectively. **182** was characterized crystallographically. With different amounts of the lithium reagent, **184**–**189** were formed, and equilibria between them were investigated⁴⁷ (Chart 8).

179, when treated with ethene, reacts with formation of isomeric ethene complexes **190** and **191** in 92% yield, the latter having been characterized by an X-ray crystal structure analysis (Scheme 30). On the basis of kinetic measurements, the authors propose a reaction mechanism via a [2+2] cycloaddition to a metallacyclobutane from which the phenyl- or trimethylsilyl-substituted propene is eliminated followed by ethene complexation. Upon treatment with

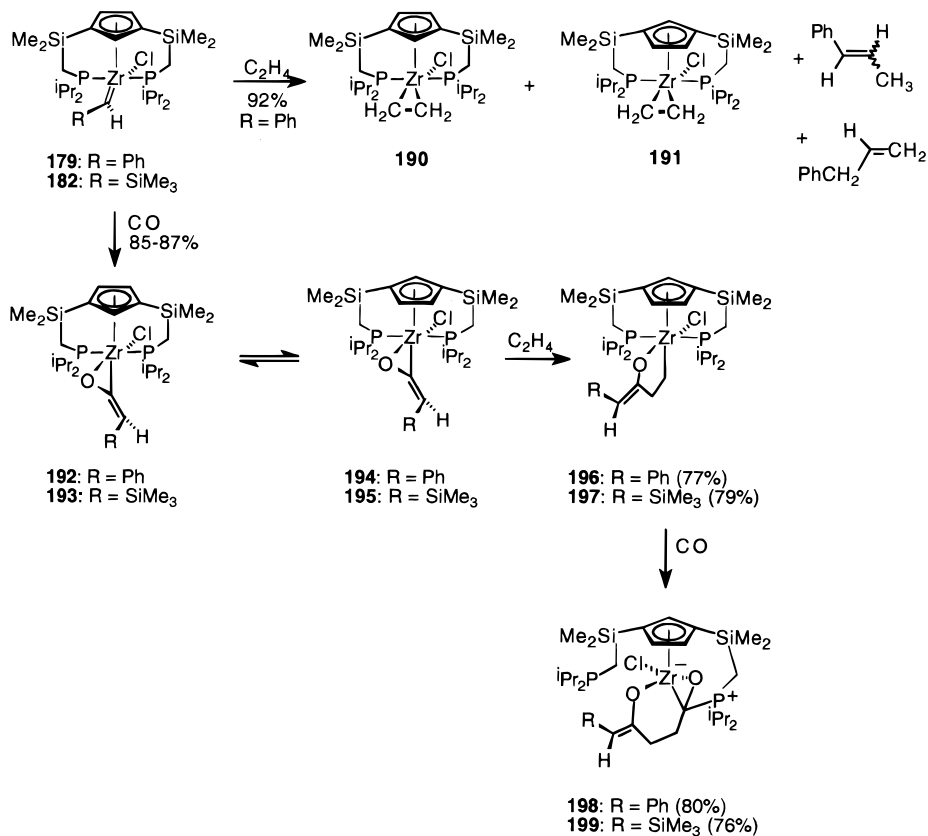
Chart 8



acetone, the olefin corresponding to the Wittig product was isolated; however, the suggested zirconium complex, which should have formed in the course of the reaction, could not be detected. Reaction of **179** or **182** with CO resulted in a coupling reaction yielding ketene complexes **192/193** (87%) and **194/195** (85%), equilibration of which was observed. Treatment of the ketene complexes with ethene caused a ring expansion due to an insertion with formation of oxazirconacyclopentane derivatives **196** (77%) and **197** (79%), whose carbonylation afforded **198** and **199**, respectively. **179** was transformed to ketenimine complex **200** in 77% yield⁴⁸ (Scheme 31).

Zirconium(IV) bischelate **176** was reduced with sodium amalgam to give zirconium(III) bischelate **201** in 85% yield (Scheme 32). **201** is paramagnetic;

Scheme 30



the ESR spectrum shows a triplet at $g = 1.96$, the coupling indicating coordination of both pendant phosphanes. Treatment of **201** with methylmagnesium chloride resulted in the replacement of only one chloro ligand by methyl to give **202** in 70% yield, even when 2 equiv of the methylating reagent was used. Carbonylation with CO caused a disproportionation, and an equilibrium mixture of **176** and **203** was obtained¹⁹ (Scheme 33).

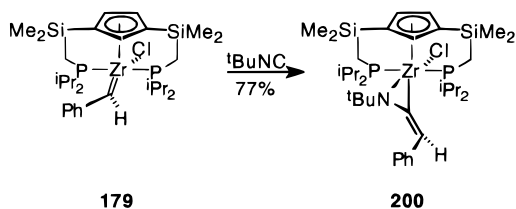
Treatment of ligand **91** with $\text{ZrCl}_4(\text{THF})_2$ gave complex **204** in 22% yield, which reacted to **205** in wet methanol (Scheme 34). Treatment of **204** with potassium thiocyanate gave **206** in 80% yield. All three complexes **204**, **205**, and **206** were characterized crystallographically.⁴⁹

The first group 5 cyclopentadienyl complexes with a pendant phosphane ligand were reported very recently by Fryzuk. Ligands **35** and **36** were treated with $\text{NbCl}_3(\text{DME})$ to give niobium bischelates **207** and **208** in 80% yield (Scheme 35). Carbonylation gave **209** and **210** in 80% yield; both were characterized by X-ray structure analyses. Oxidation with PbCl_2 resulted in formation of trichlorides **211** and **212**, which can also be obtained from the anionic ligands by treatment with $\text{Nb}(\text{O})\text{Cl}_3(\text{THF})_2$ (Scheme 36). **211** was structurally characterized.¹⁹

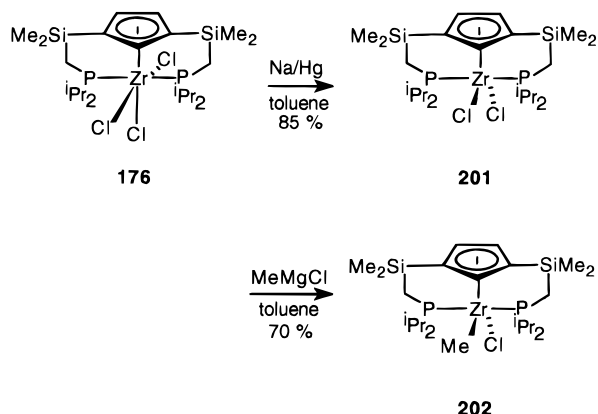
C. Groups 6 and 7 Metal Complexes

The reaction of $\text{Cr}(\text{THF})_3\text{Cl}_3$ with lithium salt **85** afforded chelate **213** in 82% yield (Chart 9). Subsequent treatment with methyllithium gave dimethyl derivative **214** in 40% yield. **213** has been characterized by a crystal structure analysis. **213** can be used

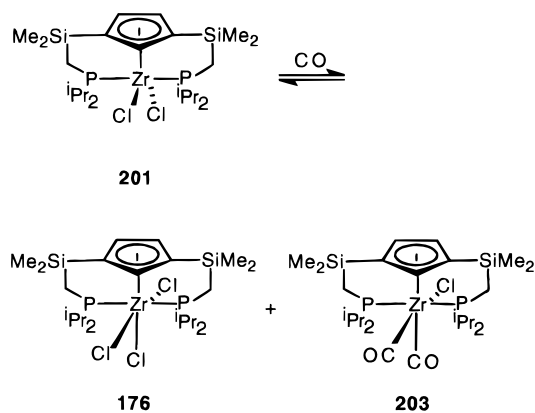
Scheme 31



Scheme 32



Scheme 33



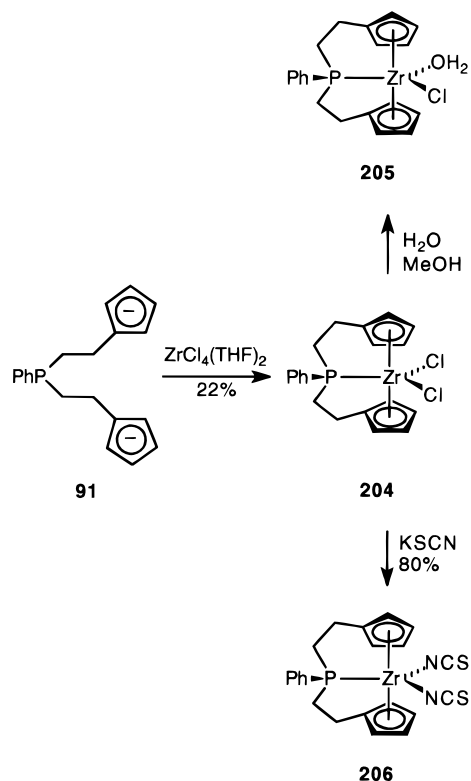
with methyl alumoxane ($\text{Al}:\text{Cr} = 100:1$) as a catalyst for the polymerization of ethene.³³

Huttner obtained molybdenum complex **215** upon treatment of ligand **115** with butyllithium, followed by $\text{BH}_3 \cdot \text{THF}$, tris(acetonitrile)tricarbonylmolybdenum, iodine, and 1,4-diazabicyclo[2.2.2]octane (DABCO), in 76% yield as a mixture of two isomers (Scheme 37). Irradiation of **215** with a mercury high-pressure lamp caused ligand exchange with chelation of the remaining phosphane sidearm to give **216** in 72% yield. Oxidation of **215** with O_2 under irradiation resulted in a decarbonylation to give cationic oxomolybdenum complex **217** in 65% yield.⁵⁰

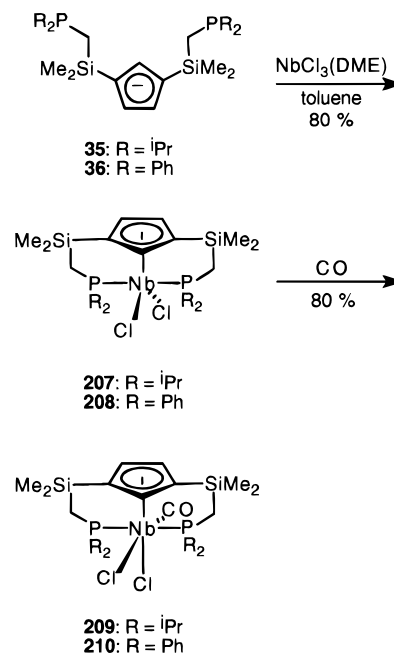
When ligands **35** and **36** were treated with $\text{MoCl}_3 \cdot (\text{THF})_3$ in toluene at 65°C , molybdenum(III) bischelatates **218** and **219** were obtained in 85% and 65% yield, respectively; **219** was structurally characterized¹⁹ (Scheme 38).

Pentamethylcyclopentadienyl tungsten complex **221** is generated with C,H activation of one of the trimethylphosphane methyl groups by reduction of **220** with sodium amalgam (Scheme 39). When this compound, which can be regarded as a tungstenphos-

Scheme 34



Scheme 35



phirane or a phosphalkene tungsten complex, is treated with lithium diphenylphosphide or with lithium dicyclohexylphosphide, the Cp^* methyl substituents are attacked, and chelated complexes **222** and **223** are formed in 58% and 69% yield, respectively. The structure of **223** has been determined by X-ray crystallography. It is described as a "distorted four-legged piano stool with an unusually acute $\text{P}-\text{W}-\text{P}$ angle ($97.42(4)^\circ$) between the PMe_3 ligands and a large $\text{H}-\text{W}-\text{P}'$ angle ($160(2)^\circ$)."⁵¹

For the synthesis of the first manganese complex with a phosphanylalkylcyclopentadienyl ligand, the

Scheme 36

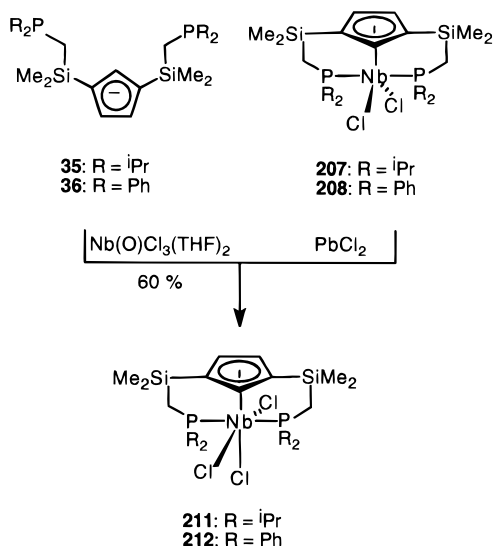
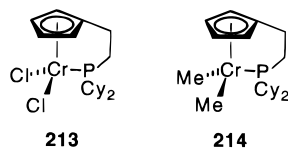
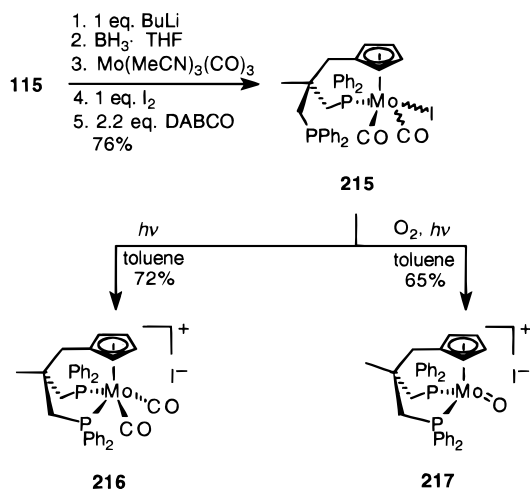


Chart 9



Scheme 37



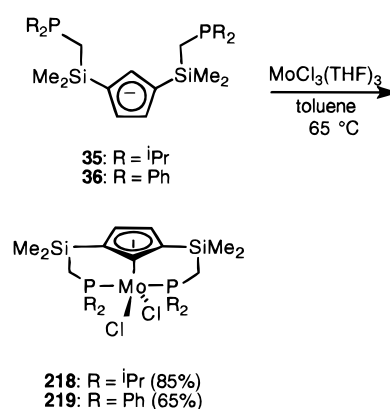
authors made use of the earlier mentioned stannylated ligand **6**. **6** was treated with BrMn(CO)₅ to give nonchelated complex **224** in 31% yield (Scheme 40). The authors mention that attempts to prepare **225** by treatment of BrMn(CO)₅ with the anionic ligand **5** led to a complicated mixture of products, and **5** is therefore unsuitable for the preparation of **224**. Chelated **225** was finally obtained in 60% yield by irradiation of **224**.^{4,6}

In a way similar to the formation of **225**, manganese complex **226** was prepared from ligand **115** in 25% yield (Scheme 41). **226** was crystallographically characterized.⁴³

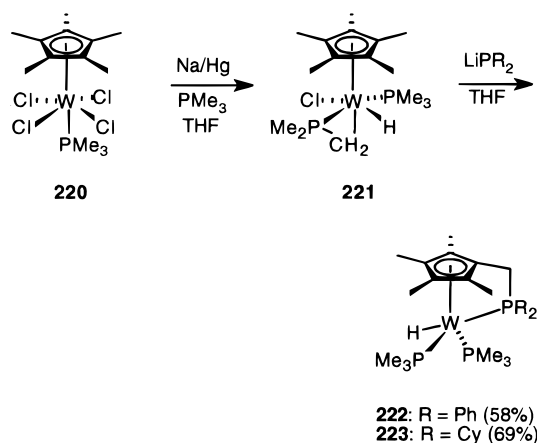
D. Group 8 Metal Complexes

A number of (phosphanlyalkyl)cyclopentadienyl complexes of iron and ruthenium were prepared by

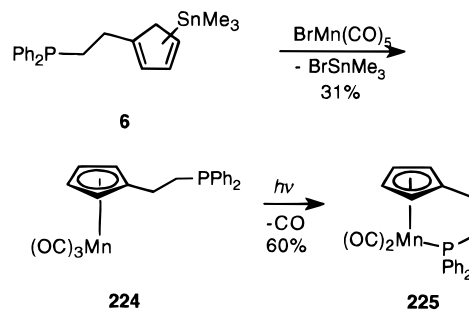
Scheme 38



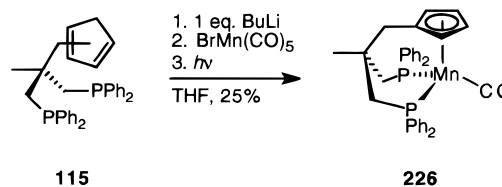
Scheme 39



Scheme 40

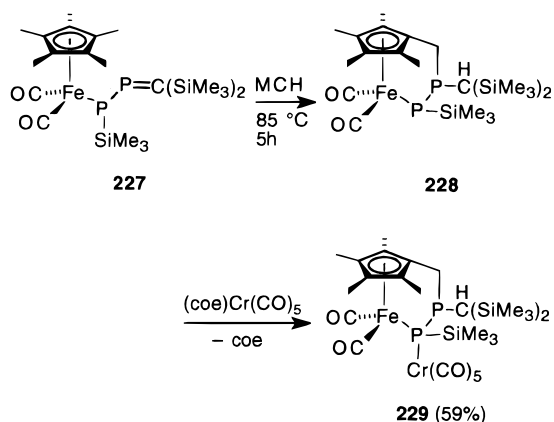


Scheme 41



a variety of methods. As in tungsten complexes **222** and **223**, a pentamethylcyclopentadienyl ligand can undergo an intramolecular C,H activation process resulting in a (phosphanlyalkyl)tetramethylcyclopentadienyl ligand. Remarkably, complexes containing a phosphalkene substructure show this behavior under rather mild reaction conditions. Heating of diphosphopropene complex **227**⁵² in methylcyclohexane (MCH) at 85 °C for 5 h led to a complete disappearance of the ³¹P NMR signals of **227**. Instead,

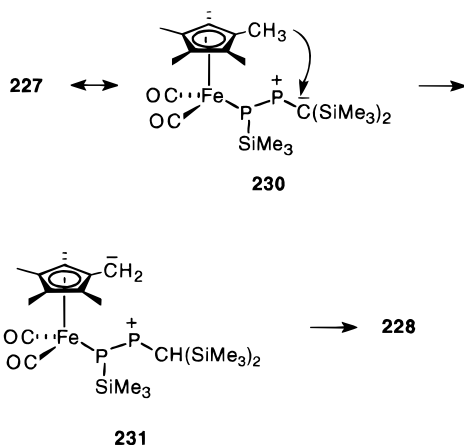
Scheme 42



two resonance signals appeared as doublets and were in accord with other analytical data assigned to chelated complex **228** (Scheme 42). **228** was isolated as a deep brown, viscous oil which could not be crystallized nor purified. Therefore, **228** was treated with [(*Z*)-cyclooctene]pentacarbonylchromium [(*coe*)-Cr(CO)₅], and the orange-yellow chromium complex **229** was formed in 59% yield from **227** in addition to cyclooctene (*coe*). **229** has been characterized by X-ray crystal structure analysis.⁵³

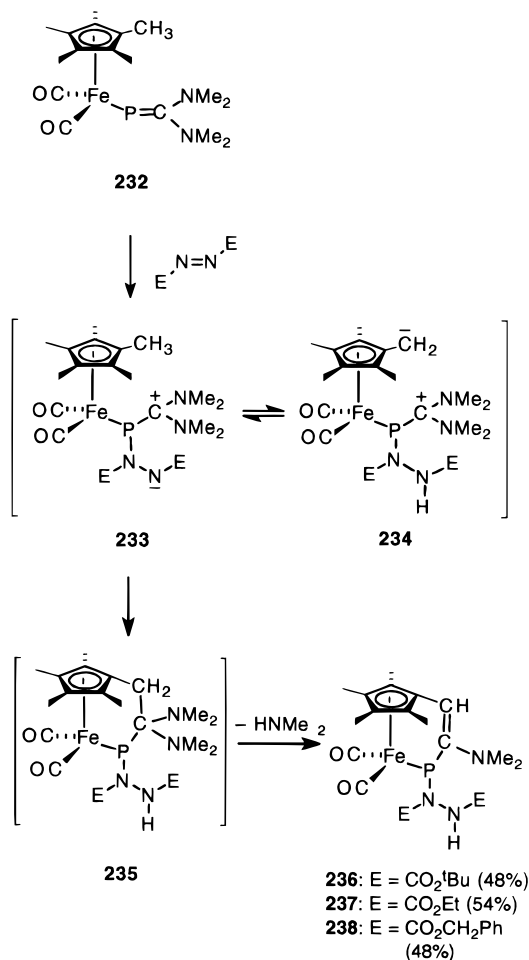
The formation of **228** can be regarded as an insertion of the P=C fragment into 1 of the 15 C–H bonds of the Cp* ligand. This would be novel in phosphalkene chemistry. However, the authors do not exclude an alternative possibility, in which the basic phosphalkene methylene carbon atom in resonance formula **230** deprotonates a methyl group of the Cp* ligand to give **231**, which then forms the new C–P bond to give **228**⁵³ (Scheme 43).

Scheme 43



In another reaction with intramolecular C,H activation of a Cp* methyl group, iron complex **232** was treated with azidodicarboxylates, resulting in the formation of unsaturated chelate complexes **236–238** in 48%, 54%, and 48% yield with loss of 1 equiv of dimethylamine (Scheme 44). The authors discuss **233–235** as intermediates in this remarkable process. The constitution of **236** was confirmed by an X-ray structure analysis. An interesting feature is the unsymmetrical coordination of the cyclopentadienyl system, with the carbon atom bearing the phosphane

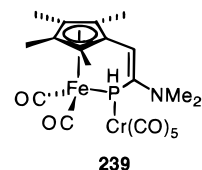
Scheme 44



arm and the two carbon atoms adjacent to this being located slightly closer to the iron atom than the two other Cp* carbon atoms.⁵⁴

With (cyclooctene)pentacarbonylchromium, **232** reacts in a similar way to give a 66% yield of **239**^{55,56} (Chart 10).

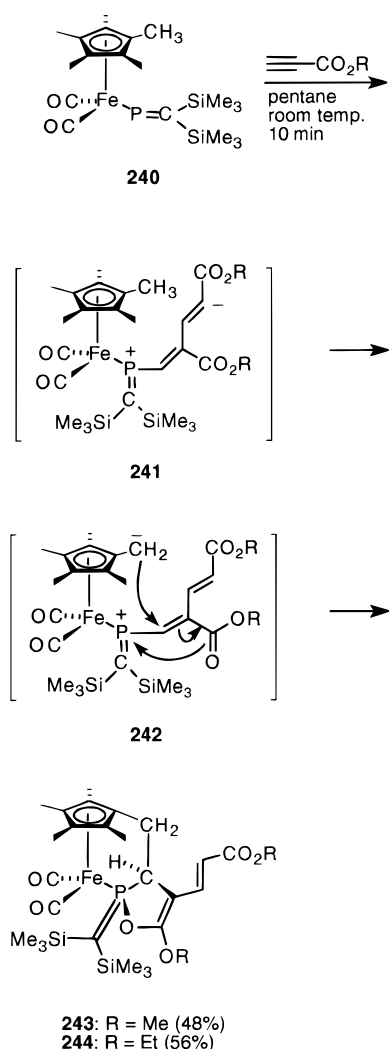
Chart 10



Another case where the formation of the phosphane arm is the result of a Cp* methyl C,H activation process is the reaction of bis(trimethylsilyl)derivative **240**, which is closely related to **232**, with 2 equiv of methyl or ethyl propynoate. The two propynoate units are coupled, and the unusually complex structures **243** and **244** are formed (Scheme 45). **243** has been the subject of an X-ray crystallographic investigation.⁵⁷ Although the authors do not specifically comment on the stereochemistry, the fact that both compounds show one singlet in the ³¹P NMR spectrum indicates that **243** and **244** are formed diastereoselectively, presumably via **241** and **242**.

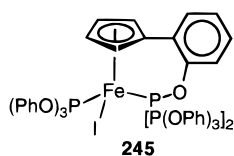
The synthesis of cyclopentadienylbis(triphenyl phosphite)iron iodide is another case with formation

Scheme 45



of a phosphanylalkylcyclopentadienyl complex by C,H activation. When the dimeric complex $\{\text{CpFe}[\text{P}(\text{OPh})_3]_2\}_2$ was treated with iodine, two isomeric products were obtained and crystallographically identified. One isomer was **245**, in which the ligand is formed as a result of the abstraction of an *ortho* hydrogen atom at one of the phenyl groups and one Cp hydrogen atom⁵⁸ (Chart 11).

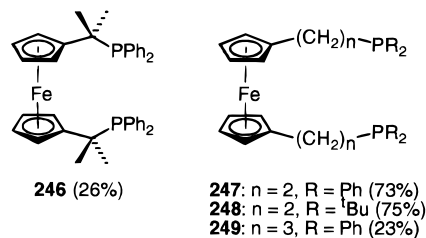
Chart 11



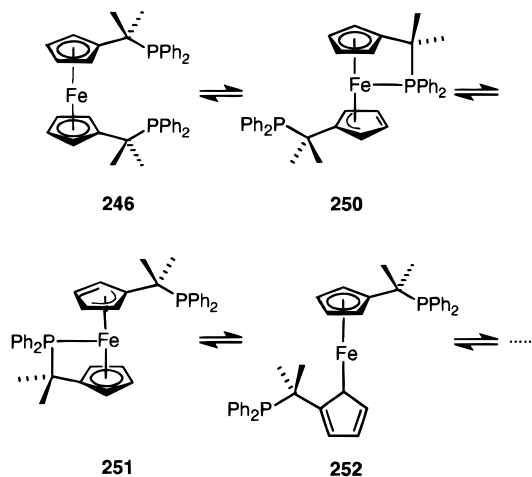
Phosphanylalkyl substituted ferrocenes **246–249** have been prepared by treatment of the anionic ligands with $\text{FeCl}_2 \cdot \text{THF}$ ¹³ (Chart 12).

Normally, these compounds would be regarded as beyond the scope of this review, because the phosphane arms cannot be expected to coordinate with formation of a chelate. In contrast to this, it is interesting to note that a Chinese group published some ³¹P NMR evidence for a fluxionality of **246** in which vacant coordination sites for chelation are

Chart 12

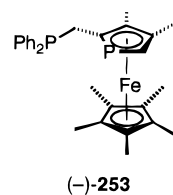


Scheme 46



created by a $\eta^5-\eta^3-\eta^1$ ring slippage reaction⁵⁹ of the cyclopentadienyl systems, thus giving rise to an equilibrium involving species **250–252** besides **246** (Scheme 46). In addition, an X-ray structural analysis of **246** is provided.²⁵ In this context it might be mentioned that a heterocyclic ferrocene, **253**, has been prepared in enantiomerically pure form and can be used as a catalyst in enantioselective hydrogenation reactions⁶⁰ (Chart 13).

Chart 13

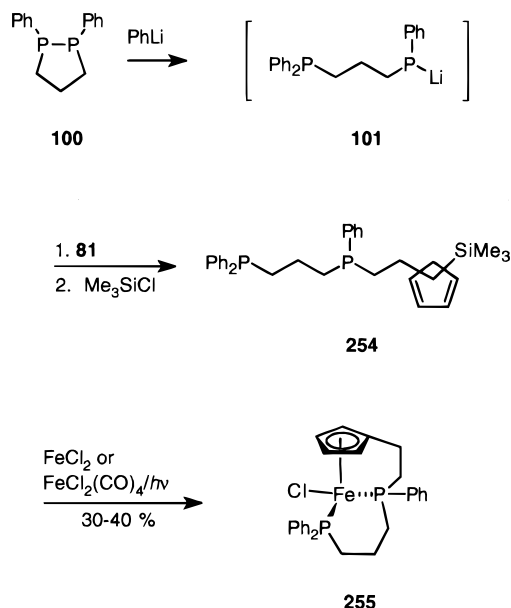


Another chelated system was obtained after an in situ modification of ligand **102** via **100** and **101** by introduction of a trimethylsilyl group at the cyclopentadienyl ring to give **254**, which was not isolated but treated with FeCl_2 to produce a 30% yield of multiply chelated complex **255** (Scheme 47). If the reaction was performed with $\text{FeCl}_2(\text{CO})_4$ under irradiation instead of FeCl_2 , the yield increased to 40%.¹¹

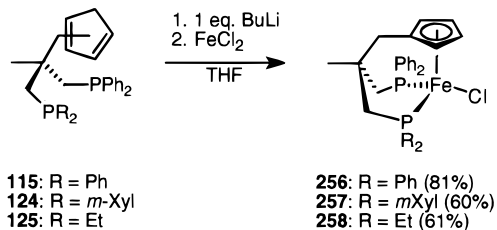
Huttner used his ligands **115**, **124**, and **125** to prepare iron(II) complexes **256–258** by treatment with butyllithium followed by FeCl_2 (Scheme 48). All three complexes were characterized by X-ray crystallography. Following reaction of **256** with phenyllithium or NaPF_6 and acetonitrile provided **259** and **260** in 69% and 75% yield, respectively.⁶¹

It was further shown that **256** can reversibly be oxidized to **261** by treatment with Ph_3CPF_6 for

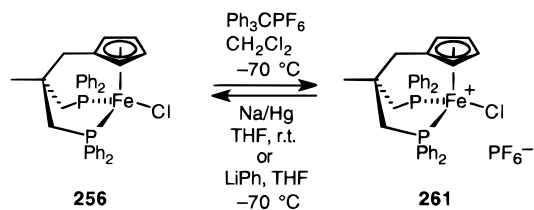
Scheme 47



Scheme 48



Scheme 49

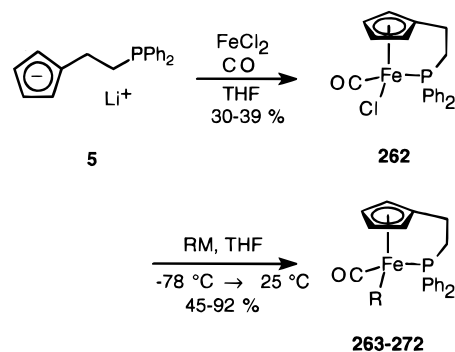


oxidation and Na/Hg for reduction (Scheme 49). The reduction could also be performed by treatment of **261** with phenyllithium in THF at $-70\text{ }^\circ\text{C}$.⁶¹

Another group of iron chelate complexes with the 2-(diphenylphosphanyl)ethylcyclopentadienyl ligand

has been published by Wang.³⁰ These authors used anionic ligand **5** and treated it with FeCl₂ and CO to obtain chelated complex **262** in 30–39% yield (Scheme 50). Attempts to prepare (2-diphenylphosphanyl)-

Scheme 50



RM	Product	Yield (%)
H ₃ C MgCl	263	92
BuLi	264	58
H ₂ C=CHCH ₂ MgCl	265	72
H ₅ C ₆ CH ₂ MgCl	266	55
H ₅ C ₆ Li	267	45
H ₂ C=CHMgBr	268	60
H ₅ C ₆ C≡CLi	269	87
cyclohexyl-C≡CLi	270	85
pentyl-C≡CLi	271	75
(H ₃ C) ₃ Si-C≡CLi	272	80

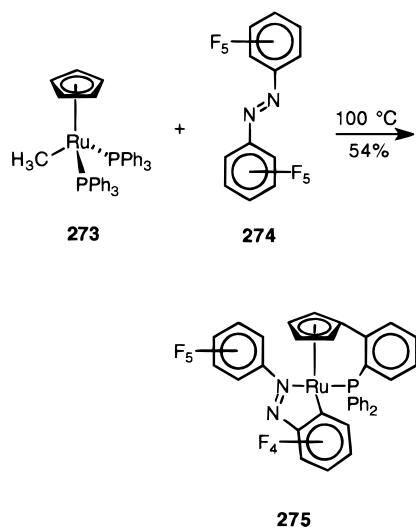
ethylcyclopentadienyl complexes by treatment of ligand **4** with Fe₂(CO)₉ led to a complexation of the phosphane part only; no chelate was formed. **262** was treated with a variety of organometallic reagents to replace the chloro ligand by an organic one. This provided high yields (up to 92%) of complexes **263–272**, three of which were characterized by crystal structure analyses. Reactions of complexes **263–272** have so far not been reported.

There is an increasing number of papers describing the synthesis as well as some reactions of ruthenium complexes with chelating (phosphanylalkyl)cyclopentadienyl ligands. The historically first case was observations made in connection with metalation studies at perfluorinated azobenzenes. When ruthenium complex **273** was treated with decafluoroazobenzene (**274**) in light petroleum at 100 °C, as a result of a C,H activation at one of the triphenylphosphane ligands, chelated complex **275** was obtained in 54% yield and characterized spectroscopically as well as by an X-ray crystal structure analysis^{62–64} (Scheme 51).

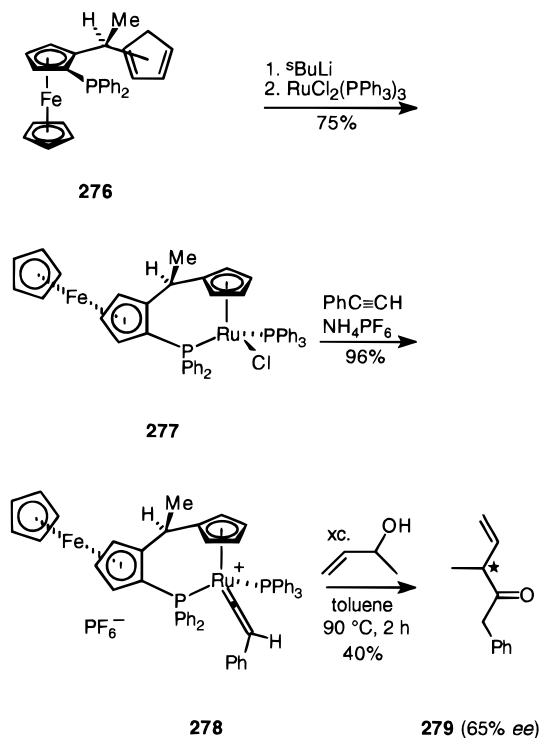
In a more planned manner, a number of ligands were treated with RuCl₂(PPh₃)₃ to give the corresponding chelated complexes. Thus, enantiopure chiral ferrocenes **276** gave bimetallic complex **277** in 75% yield (Scheme 52).

When **277** was treated with phenylethyne in the presence of ammonium hexafluorophosphate, the chloro ligand was replaced by a phenylvinylidene ligand in 96% yield to give **278**. **278** was treated with an excess of 1-buten-3-ol at 90 °C for 2 h in toluene to give a 40% yield of **279** with 65% ee. This

Scheme 51



Scheme 52

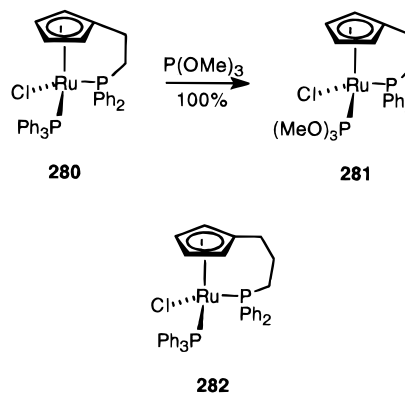


constitutes the first example of an asymmetric reaction with a chiral vinylidene complex as the source of chirality.⁴²

Ruthenium complexes **280** and **282** were prepared by reaction of the ligands with $\text{RuCl}_2(\text{PPh}_3)_3$. These compounds were initially described as somewhat less stable and were incompletely characterized.^{11,40} Later a modified preparation was published which resulted in a 41% yield of **280**, which was then completely characterized, including an X-ray structural analysis.³⁴ Treatment of **280** with trimethyl phosphite results in a quantitative ligand exchange to give **281** (Scheme 53).

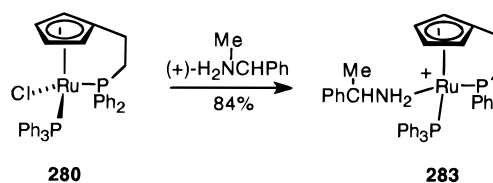
280 contains an asymmetric ruthenium atom, and a chiral resolution was tried by replacement of the chloro ligand by a chiral amine, (+)- $\text{H}_2\text{NCH}(\text{Me})\text{Ph}$. However, the substitution product **283**, which was

Scheme 53



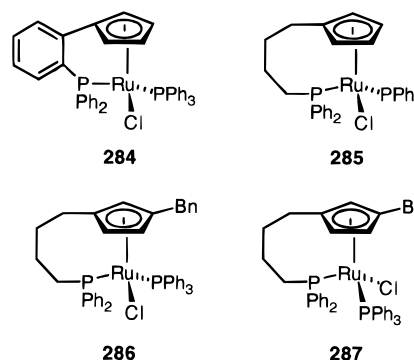
obtained as a mixture of diastereomers by treatment of **280** with (+)- $\text{H}_2\text{NCH}(\text{Me})\text{Ph}$ in the presence of AgBF_4 , proved to be too unstable for this purpose³⁴ (Scheme 54).

Scheme 54



In a similar way Trost obtained complexes **284**–**287** by treatment of the anionic ligands with $\text{RuCl}_2(\text{PPh}_3)_3$; **286** and **287** were formed as a 1:1 mixture of diastereomers¹⁵ (Chart 14).

Chart 14

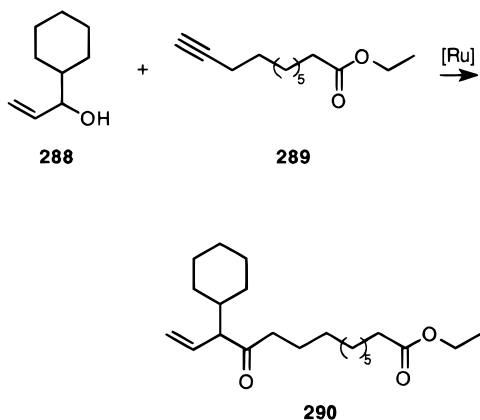


280, **282**, **284**, **285**, and **286/287** were used as catalysts in a reconstitutive addition of **288** and **289** to give **290** (Scheme 55). Although all catalysts reacted slower than the original one lacking a phosphane chelate tether, the best results were obtained with **285**.¹⁵

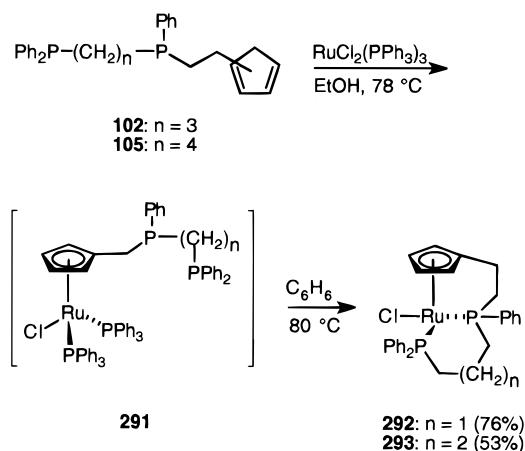
The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with ligands **102** and **105** afforded chelated ruthenium complexes **292** and **293** in 76% and 53% yield, respectively^{11,40} (Scheme 56). Intermediates **291** were not isolated.

Complexes **292** and **293** were used as highly active and selective homogeneous catalysts for the hydrogenation of cyclohexene to cyclohexane, of norbornene to norbornane, and of butanal to 1-butanol.^{11,40} Chirality can also be introduced by using a chiral (phosphanylalkyl)cyclopentadienyl ligand such as **38**, the lithium salt of which has been treated

Scheme 55

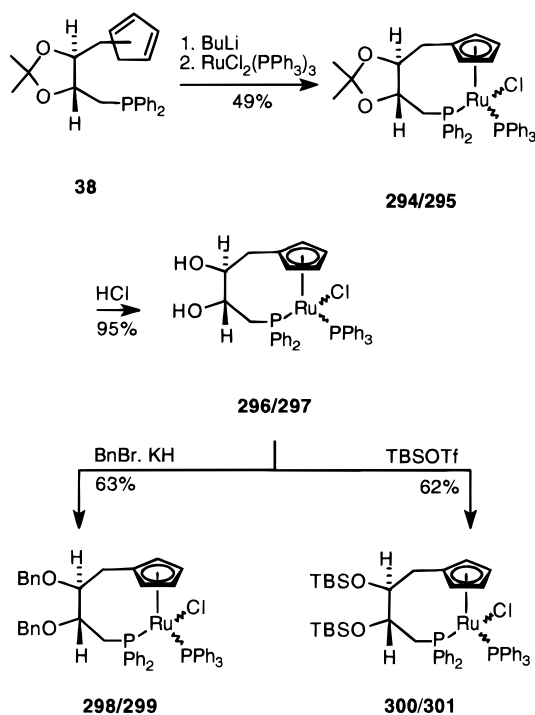


Scheme 56



with $RuCl_2(PPh_3)_3$ to give a 49% yield of **294** and **295** as a 59:41 or 41:59 mixture of diastereomers^{20,21} (Scheme 57). In a footnote a brief mention is made that **294/295** is an effective catalyst for “asymmetric

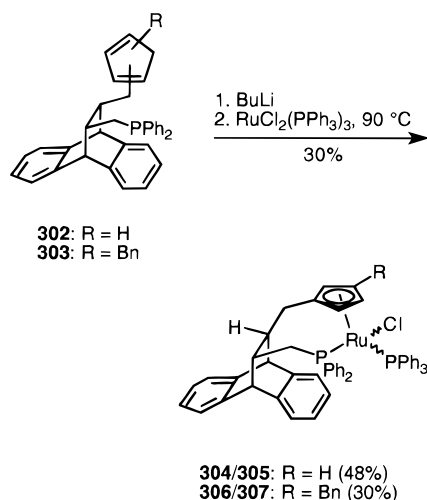
Scheme 57



condensation”; e.g., reaction of 1-dodecyne with 3-butene-2-ol in the presence of 10 mol % **294/295** and 20 mol % NH_4PF_6 gave optically active 3-methyl-1-pentadecen-4-one (no ee given).

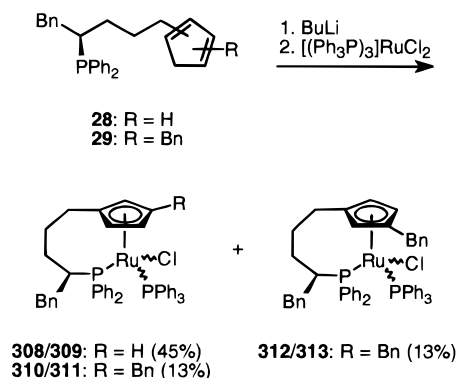
Treatment of **294/295** with HCl gave diols **296/297** in 95% yield. These diols were protected either by reaction with benzyl bromide to give benzyl ethers **298/299** (63%) or by reaction with *tert*-butyldimethylsilyl triflate to give silyl ethers **300/301** (62%). The latter silyl ethers were separable by semipreparative HPLC and were shown to equilibrate at 75 °C in toluene. In a similar way ligands **302** and **303** were used to prepare complexes **304/305** and **306/307**, as mixtures of diastereomers, respectively¹⁵ (Scheme 58).

Scheme 58



Finally, ligands **28** and **29** were coordinated to ruthenium by the same procedure to give complexes **308/309** and **310/311/312/313** as diastereomeric mixtures in 45% and 13% yield, respectively¹⁵ (Scheme 59).

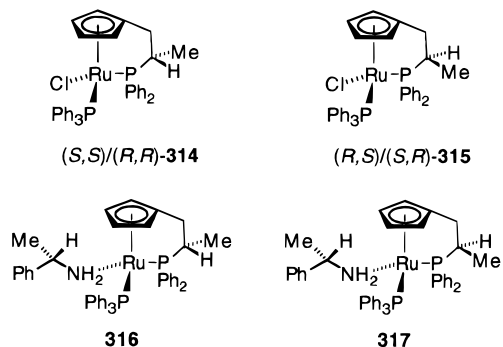
Scheme 59



The chiral ruthenium chelate complexes were tested as catalysts in the reconstitutive addition reaction of **288** and **289** to give **290**. In some cases the chemical yields were good; however, the ee remained rather low. It has been discussed whether this is the result of a poor enantioselectivity of the catalysis or a racemization process of the product.¹⁵

Van der Zeijden obtained chiral diastereomeric chelates **314** and **315** in nonracemic form (66% ee) by treatment of ligand (*S*)-**49** (66% ee) with $RuCl_2$ -

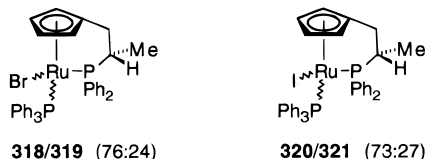
Chart 15



(PPh_3)₃ (Chart 15). **315** was crystallographically characterized. The ligand was generated in situ; the yield (8%) refers to intermediate **47**. The enantiomeric purity of **314** and **315** was determined by NMR after a ligand exchange with (*S*)- $\text{H}_2\text{NCH}(\text{Me})\text{Ph}$ in the presence of silver triflate, which gave **316** and **317**.

314/315 were treated with sodium bromide and with sodium iodide to give bromo and iodo complexes **318/319** and **320/321**, respectively, as mixtures of diastereomers (76:24, 73:27)²² (Chart 16).

Chart 16



314/315 were used in the presence of silver triflate as catalysts in Diels–Alder cycloadditions and in hydrocyanation reactions. However, no significant ee was observed.²²

E. Group 9 Metal Complexes

(Phosphanylalkyl)cyclopentadienyl complexes of cobalt, rhodium, and iridium are known. In some cases, not only the synthesis and structure of such complexes have been described, but a number of reactions have also been investigated.

Carbonylcobalt complexes **325–327**, **330**, and **331** were obtained by treatment of the anionic ligands **5**, **12**, **13**, **83**, or **84**, respectively, with $\text{ICo}(\text{CO})_4$ ⁶⁵ (Scheme 60). There is no doubt that the reaction proceeds via the unchelated intermediates **322–324**, **328**, and **329**; **322** has been observed by IR spectroscopy at $-25\text{ }^\circ\text{C}$ ($\tilde{\nu}_{\text{CO}} = 1949, 2013\text{ cm}^{-1}$) and chelates rapidly at room temperature with loss of CO.^{12,13}

In addition to an X-ray crystal structure analysis, **327** was subjected to a DSC analysis (DSC = differential scanning calorimetry). This showed that **327** melts at $119\text{ }^\circ\text{C}$ and decomposes at $175\text{ }^\circ\text{C}$. This means that the compound is quite stable thermally, and this is completely in accord with the result of treatments of **327** with other ligands: Heating of **327** with diphenylethyne in dibutyl ether at reflux resulted in 90% starting material recovery, and boiling it in 1,5-cyclooctadiene for 3 days gave cyclooctadiene complex **336** (vide infra) in only 15% yield. A ligand exchange reaction was possible, albeit in poor yield, under photochemical reaction conditions: Treatment

Scheme 60

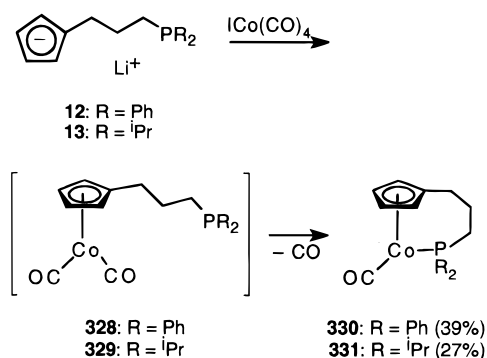
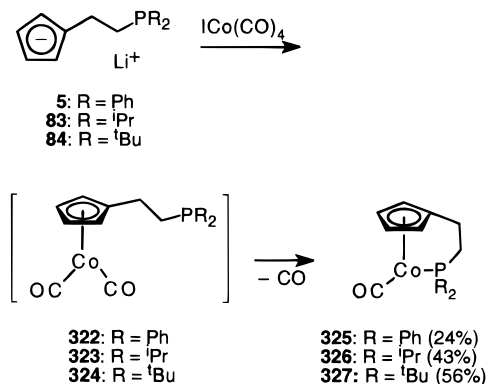
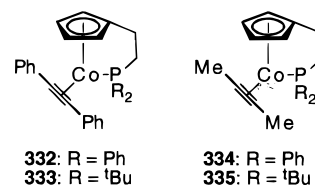


Chart 17

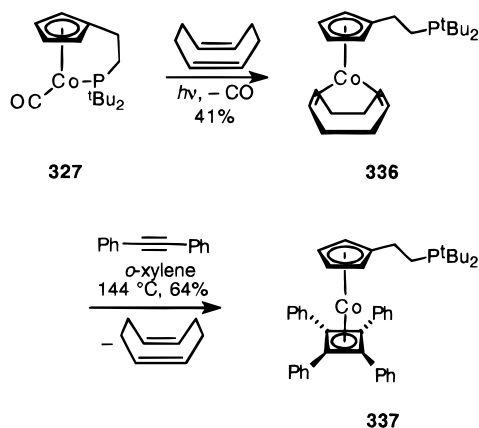


of **325** or **327** with diphenylethyne under irradiation with Duran-filtered light gave alkyne complexes **332** and **333** in 9% and 39% yield, respectively (Chart 17). Similar reactions with 2-butyne instead of diphenylethyne resulted in 30% conversion only to give **334** and **335**.

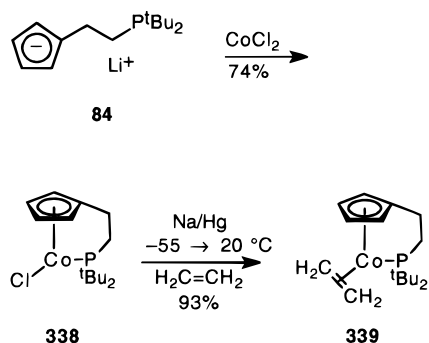
An important question in light of the ease of chelation in the synthesis of the carbonyl complexes is whether it is possible to decoordinate the phosphane arm, possibly to create a vacant coordination site for further chemistry. The question was addressed by treatment of **327** with 1,5-cyclooctadiene under photochemical reaction conditions, using the diene as the solvent, and resulted in a 41% yield of nonchelated cyclooctadiene complex **336** (Scheme 61). Treatment of this complex with diphenylethyne under reaction conditions normally allowing alkyne di- or trimerization reactions gave tetraphenylcyclooctadiene complex **337** in 64% yield, showing that chemistry at the cobalt atom is possible without inhibition by a chelating phosphane arm.^{12,13}

As **327** proved to be not a very reactive complex, the corresponding ethene complex **339** was prepared via paramagnetic chloride **338**. This is accessible in 74% yield in analogy to similar chemistry performed by Kölle^{66–68} by treatment of anion **84** with CoCl_2 (Scheme 62). ESR measurements confirm that **338** has a monomeric structure and is not a dimer as

Scheme 61



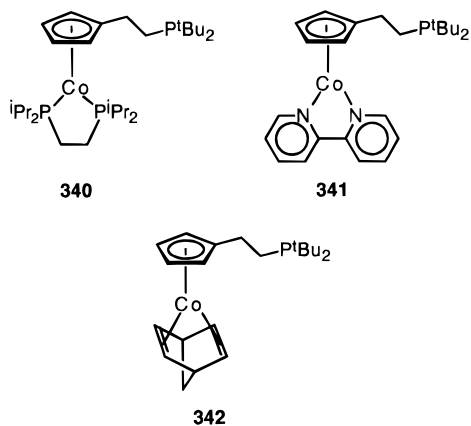
Scheme 62



assumed earlier.^{69,70} **338** was reduced with sodium amalgam at -55°C in the presence of ethene bubbling through the reaction flask to give **339** in 93% yield. **339** was fully characterized including an X-ray crystal structure analysis. One interesting feature of the molecule is the rotation of the ethene ligand around the alkene-cobalt coordination axis, giving rise to a coalescence in the NMR spectra. The energy of activation of this process is estimated to be $\Delta G^\ddagger \approx 62 \text{ kJ/mol}$ (326 K).⁷⁰

Ethene complex **339** is much more prone to ligand exchange reactions than carbonyl complex **327**. Treatment with the bidentate ligands 1,5-cyclooctadiene, bis(diisopropylphosphanyl)ethane, 2,2'-bipyridyl, and norbornadiene at 20°C results in the formation of unchelated complexes **336** and **340–342** in 82–93% yield; no irradiation is necessary⁷⁰ (Chart 18).

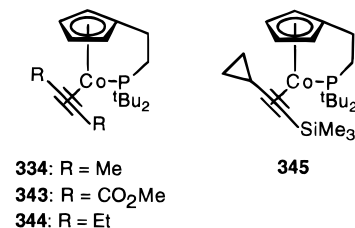
Chart 18



The ethene ligand in **339** is easily replaced by internal alkynes. Treatment of **339** with diphenyl-

ethyne at 20°C affords **333** in 83% yield as compared to 39% yield when starting from carbonyl complex **327**. Electron-poor alkynes can be coordinated as shown by the reaction of **339** with dimethyl butynedioate at 20°C to give **343** in 89% yield (Chart 19). For ligands not affected by sodium amalgam, an

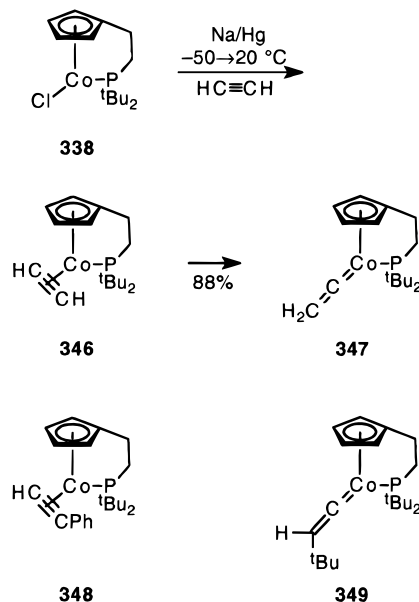
Chart 19



alternative route was established in which chloride **338** served as the starting material. The detour via ethene complex **339** was skipped; instead **338** was directly treated with the alkyne at low temperature in the presence of sodium amalgam. In this way, 2-butyne, 3-hexyne, and cyclopropyltrimethylsilyl-ethyne were used as ligands, and complexes **334**, **344**, and **345** were obtained in 74%, 87%, and 95% yield.⁷⁰

Ethyne and terminal alkynes show a different behavior. When ethene complex **339** was treated with ethyne at 20°C , vinylidene complex **347** was obtained in 20% yield. This yield was improved to 88% by using the alternative procedure starting from **338**, thus making **347** available in multigram quantities^{69,70} (Scheme 63). The characteristic spectroscopic

Scheme 63

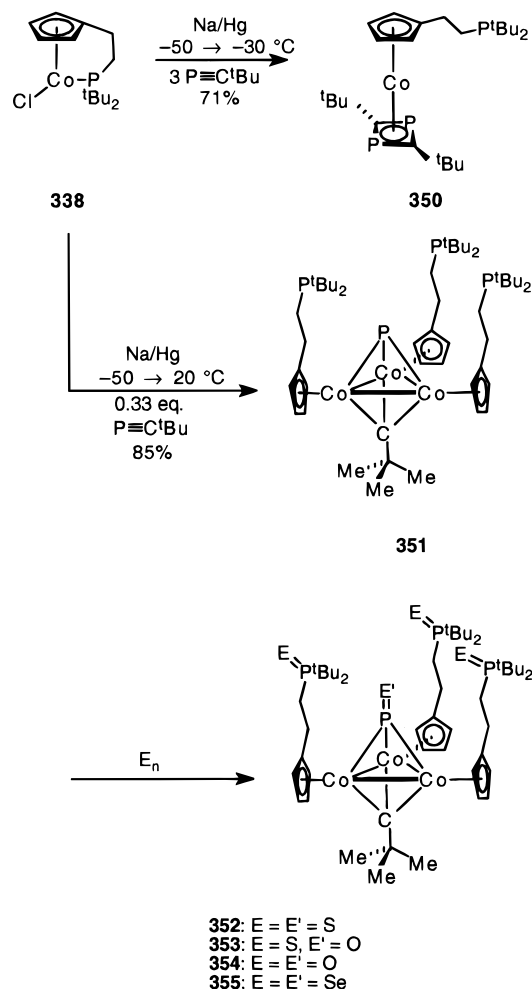


feature of **347** is the chemical shift of the vinylidene carbon atom, whose resonance is observed at $\delta = 303.7$. Although many vinylidene complexes are known,^{71–74} **347** is only the second example with cobalt as the metal and the first with a cyclopentadienylcobalt fragment.^{75–77} **347** is the result of a rearrangement of ethyne complex **346**, which can be isolated as a crystalline material at low temperature, and which rapidly isomerizes to **347** in solution. **346** was therefore characterized by ¹H NMR and MS only. The formation of **347** raised the question for the

reactions with terminal alkynes. Here, the situation is less clear: When **339** was treated with phenylacetylene at 0 °C, alkyne complex **348** was formed in almost quantitative yield. **348** is the first cyclopentadienylcobalt complex of a terminal alkyne. When **338** was treated with 3,3-dimethyl-1-butyne in the presence of sodium amalgam, *tert*-butylvinylidene complex **349** was isolated in 40% yield ($\delta_{\text{vinylidene-C}} = 302.7$).⁷⁰

As phosphoalkynes are known to react similarly to alkynes,^{78–82} **338** and **339** were treated with the most easily available representative of this class of compounds, *tert*-butylphosphaethyne, under the reaction conditions applied for alkynes. Treatment of **338** in the presence of sodium amalgam at low temperature (–50 → –30 °C) with a 3-fold molar excess of *tert*-butylphosphaethyne gives unchelated diphosphete complex **350**, which is in complete accord with the reaction of other cyclopentadienylcobalt complexes with *tert*-butylphosphaethyne^{83,84} (Scheme 64).

Scheme 64

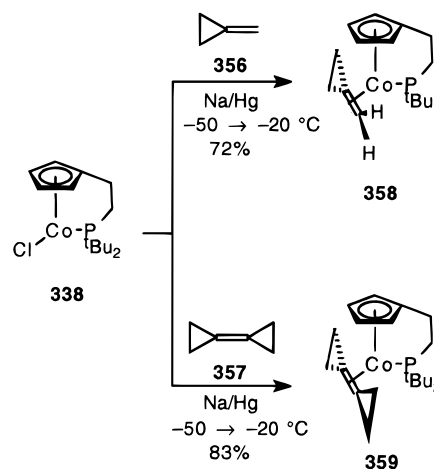


However, when *tert*-butylphosphaethyne is treated with a 3-fold molar excess of **338** in the presence of sodium amalgam at –50 → +20 °C, the μ_3 -carbyne- μ_3 -phosphidotricobalt cluster **351** is formed as the sole product in 85% yield.⁸⁵ It should be mentioned that analogous reactions of alkynes with cyclopentadienylcobalt complexes are known to take place at temperatures as high as 195 °C.^{86–88} **351** was oxidized to **352**, **353**, and **354**, which contain phosphorus

monoxide and phosphorus monosulfide as μ_3 ligands. **353** was characterized by a crystal structure analysis.⁸⁵ Recently phosphorus selenide cluster **355** was reported. The complex was characterized crystallographically and displays C_3 symmetry in the solid state.⁸⁹

Strained unsaturated molecules such as methylcyclopropane (**356**), bicycpropylidene (**357**), and cyclopropene derivatives have been used as ligands. Remarkably, **356** and even **357** could be coordinated to give **358** and **359** in 72% and 83% yield, respectively, without opening of the strained cyclopropane rings (Scheme 65). The X-ray crystal structure analy-

Scheme 65



sis of **359** shows that the strained double bond shows a remarkable out of plane bending of 40°. **359** is the first structurally characterized metal complex of bicycpropylidene (**357**).⁹⁰

Treatment of chloro complex **338** with 3,3-dimethylcyclopropene in the presence of Na/Hg at low temperature gave cyclopropene complex **360** in 71% yield (Scheme 66). Heating of **360** in THF at 65 °C for 2 h gave an almost quantitative yield of the rearranged isoprene complex **361**. The rearrangement presumably occurs via an insertion into one of the strained C–C single bonds of the cyclopropene ligand, resulting in a cobaltacyclobutene intermediate. Hydride migration (C,H activation) from one of the two methyl groups to cobalt followed by a reductive elimination then leads to **361**. In contrast, treatment of 3,3-dimethoxycyclopropene with **338** under comparable conditions resulted in cyclopropene complex **362** exclusively in 93% yield. The corresponding reaction with 3,3-diphenylcyclopropene resulted in a ring opening with formation of the diphenylvinylcarbene complex **363** in 91% yield. The reaction of **363** with *tert*-butylphosphaethyne at 20 °C gave a 3:1 mixture of 3-vinyl-(1)-phosphirene complex **364** and 1-phosphabutadiene complex **365**; the latter was characterized by X-ray crystallography.⁹¹

There are a number of cyclopentadienylrhodium(I) and -rhodium(III) complexes with a pendant phosphane ligand known. Poilblanc prepared chelate **366** in 70% yield by treatment of $[\text{RhCl}(\text{CO})_2]_2$ with anionic ligand **5** (Chart 20). In addition to **366** it was

Scheme 66

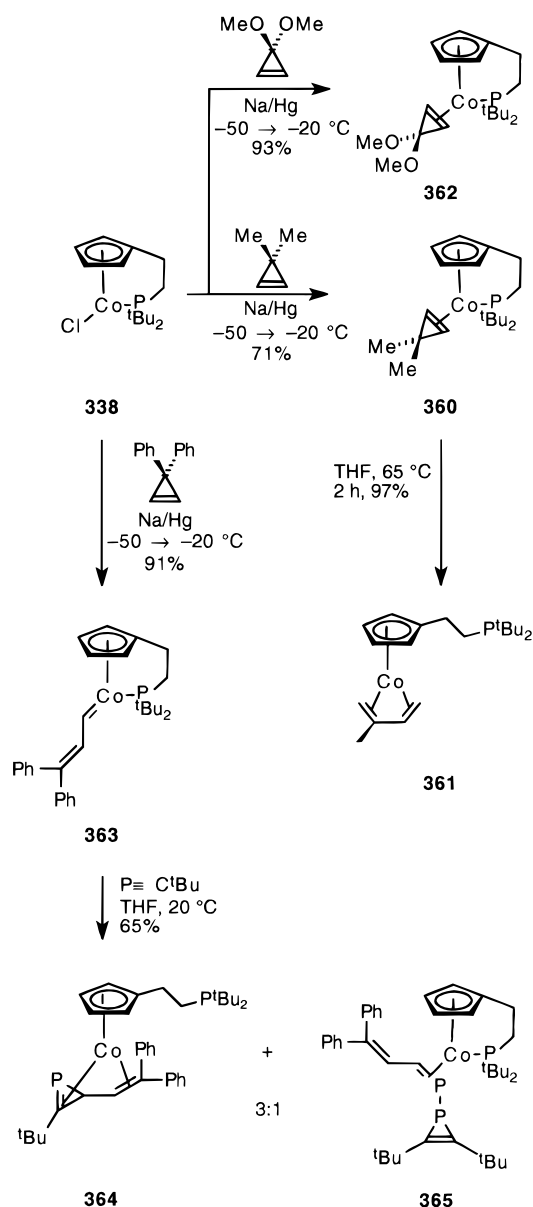
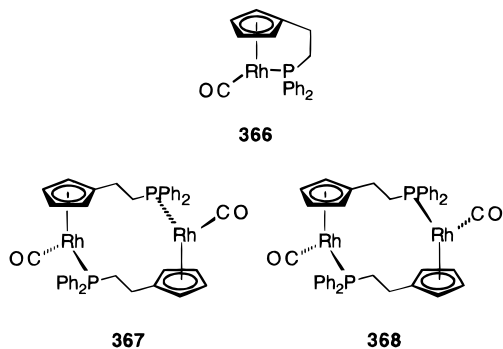


Chart 20

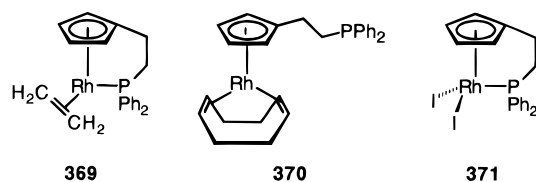


possible to observe the diastereomerically labile dimers **367** and **368** spectroscopically in solution. These complexes were shown to convert to **366** upon heating, and it was concluded that they are intermediates in the reaction to **366**.⁹²

Ethene complex **369** was obtained by treatment of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ with ligand **5**, and in a similar way

370 was prepared from $[\text{RhCl}(1,5\text{-cyclooctadiene})]_2$ (Chart 21). **366** was oxidized by addition of iodine to

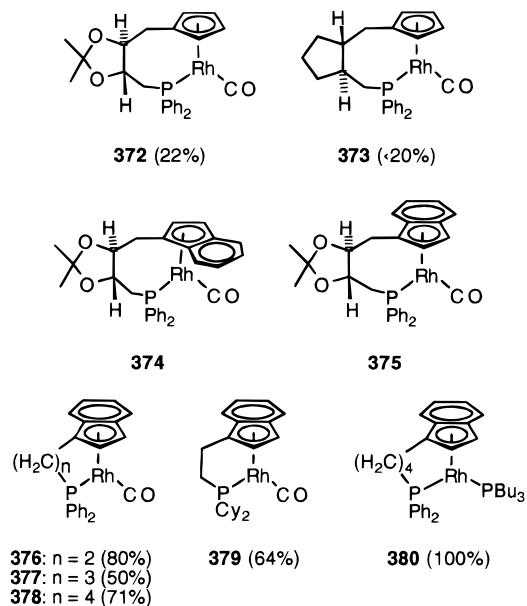
Chart 21



form rhodium(III) complex **371** (no yields reported). **369** and **371** were characterized by X-ray structure analyses.⁹²

Chiral rhodium complexes were obtained by Tani, who treated ligands **38**, **39**, and **43** with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to obtain enantiomerically pure complexes **372–375** (20–70%), **374/375** forming a 69:31 mixture of two unseparated diastereomers^{20,21} (Chart 22). In a simi-

Chart 22

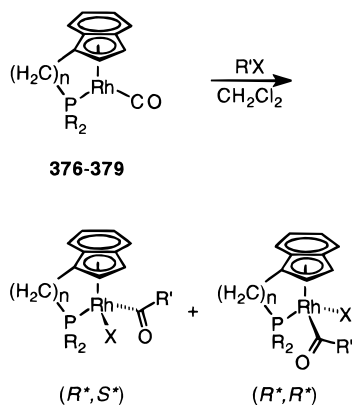


lar fashion, ligands **94**, **96**, **98**, and **99** were used to prepare complexes **376–379** in 50–80% yield. Treatment of **376** with tributylphosphane in boiling toluene gave **380** quantitatively. The reaction in benzene at room temperature also gave **380**; however, some NMR evidence is provided that the reaction proceeds via a decomplexation of the pendant ligand and complexation of tributylphosphane, followed by decarbonylation and recomplexation of the phosphane arm.³⁹

Chiral complexes **376–379** were treated with some alkyl halides to check the diastereoselectivity of the formation of the metal-centered chirality created by an oxidative addition (Scheme 67). The reaction leading to **381–388** is highly diastereoselective in some cases; complex **384** was characterized by X-ray crystallography. Diastereoselectivities were determined by ^1H and ^{31}P NMR.³⁹

Nelson reported the reaction of $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})\}_2]$ with vinylidiphosphane in the presence of azobis(isobutyronitrile) (AIBN) or potassium *tert*-butoxide to give a 1:2 mixture of chelates as

Scheme 67

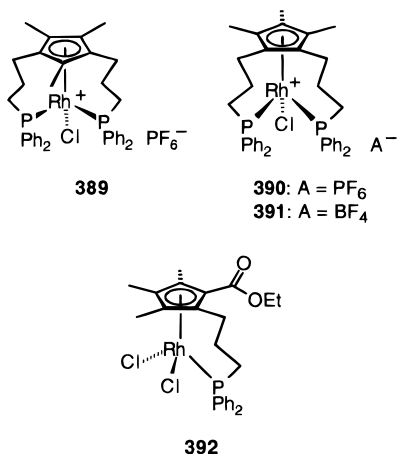


381-388

Starting mat.	R'X	Product	Yield (%)	R*, S* : R*, R*
376	MeI	381	90	33:67
376	EtI	382	98	4:96
376	EtBr	383	40	1:99
377	MeI	384	97	89:11
378	MeI	385	92	85:15
378	EtI	386	97	98:2
379	MeI	387	97	34:66
379	EtI	388	53	6:94

chlorides, isolated as their hexafluorophosphate salts **389** and **390** in 29% and 59% yield, respectively (Chart 23). **390** was transformed to the tetrafluoro-

Chart 23



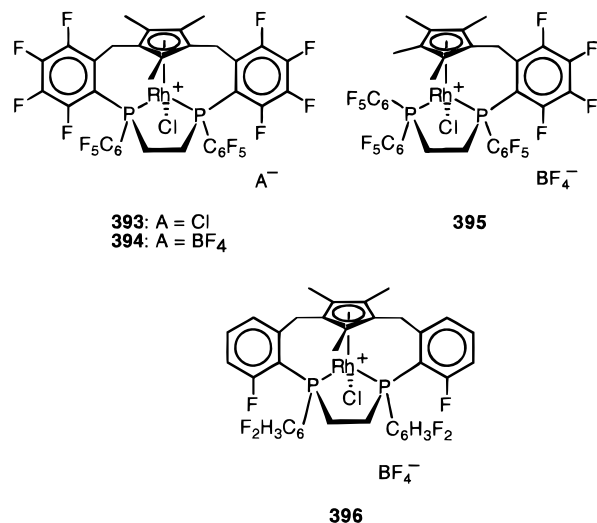
borate **391**, and **389** and **391** were characterized crystallographically.^{93,94}

In a mechanistic paper, the authors provide evidence that in the first step the vinylphosphane is coordinated to the metal and that the hydroalkylation step then takes place in an intramolecular manner. While the reaction of $[\{(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{RhCl}(\mu\text{-Cl})\}_2]$ with diphenylvinylphosphane in chloroform gave a ligand complexation product only, chelate **392** was obtained in 29% yield, when the reaction was carried out in ethanol. **392** was characterized by X-ray crystallography.⁹⁴

In a similar reaction Saunders found that $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})\}_2]$ reacts with bis(dipentafluorophenylphosphino)ethane (dfppe) with formation of **393**

as the result of an *ortho* C,F bond activation process in high yield (ca. 90%) (Chart 24). The corresponding

Chart 24

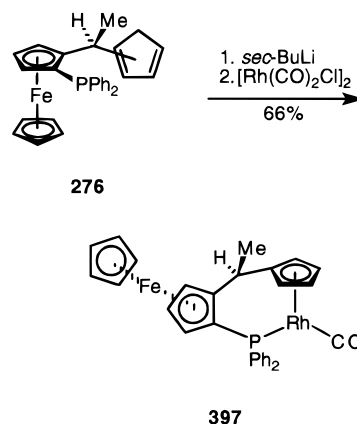


tetrafluoroborate **394** was obtained by anion metathesis and was characterized crystallographically. Variable-temperature NMR revealed a hindered rotation around the P–C₆F₅ bonds.^{95,96} Presumably for steric reasons only the *meso* diastereoisomer was obtained. The authors report the isolation of intermediate **395**, which, however, could not be obtained pure.⁹⁵

More recently, Saunders reported that treatment of $[\{(\eta^5\text{C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})\}_2]$ with 1,2-bis[di(2,6-difluorophenyl)phosphanyl]ethane resulted in the formation of an orange precipitate (81% yield), which was treated with ammonium tetrafluoroborate to give rhodium complex **396**, the result of C,H and C,F activation processes.⁹⁷

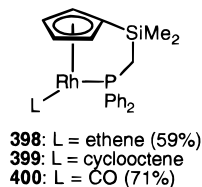
The chiral bimetallic chelate **397** was obtained by Hidai in 66% yield by treatment of ligand **276** with $[\text{Rh}(\text{CO})_2\text{Cl}(\mu\text{-Cl})_2]$ upon metalation and was characterized by X-ray crystallography⁴² (Scheme 68).

Scheme 68



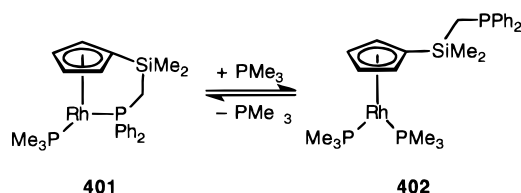
Jones used ligand **33** to prepare a number of silicon-containing rhodium complexes. Treatment of $[\text{RhL}_2\text{Cl}]_2$ with **33** gave chelates **398–400** in good yield; **399** was not obtained in pure form (Chart 25). All three complexes were characterized by X-ray crystallography.¹⁷

Chart 25



400 reacts with trimethylphosphane in a ligand exchange reaction to give **401** quantitatively. In the presence of 5 equiv of trimethylphosphane, an equilibrium between chelate **401** and nonchelated complex **402** is established (**401**:**402** = 9:1) (Scheme 69).

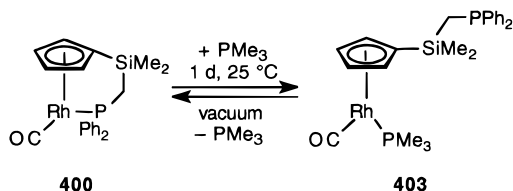
Scheme 69



The authors attribute the facile reversal of the reaction to the chelating ability of the ligand.¹⁷

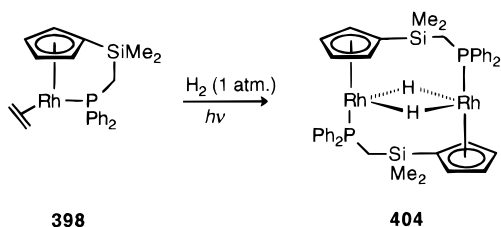
Under 1 atm of CO, **398** can be converted to **400** within 2 days at 80 °C. As with **401**, in the presence of 2 equiv of PMe_3 , the phosphane arm can reversibly be replaced by a PMe_3 ligand with formation of **403** (Scheme 70).

Scheme 70



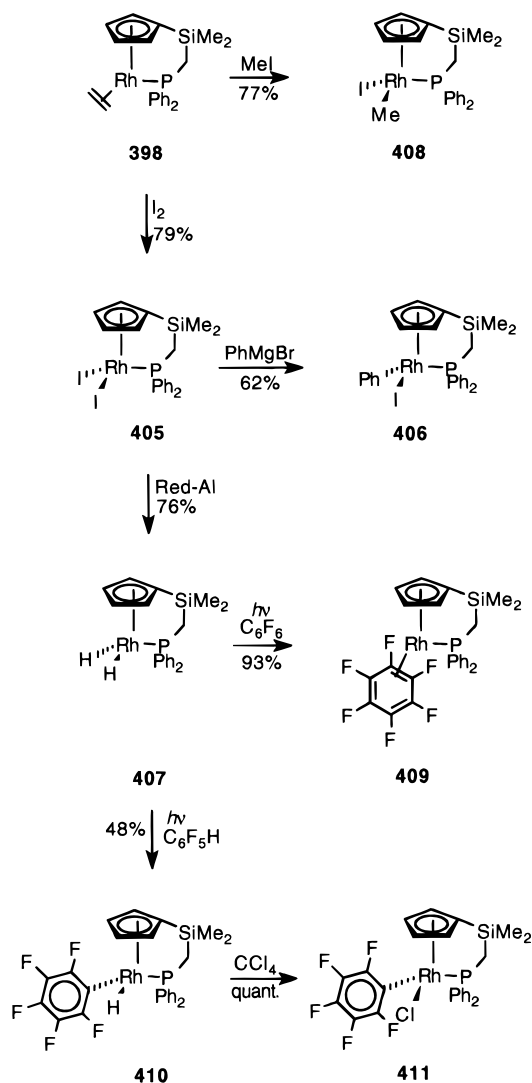
Interestingly, ethene complex **398** does not react with hydrogen upon heating. However, under irradiation with a 200 W Xe–Hg lamp, a slow reaction was observed, which led to dimeric hydride complex **404**, an X-ray structure analysis of which was reported¹⁷ (Scheme 71).

Scheme 71



Ethene rhodium(I) complex **398** can be oxidized by treatment with iodine to give **405** in 79% yield (X-ray structure) (Scheme 72). Reaction of **405** with phenylmagnesium bromide gave chiral iodophenylrhodium(III) chelate **406** in 62% yield (X-ray structure). Reduction of **405** with Red-Al ($\text{Na}[\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{H}_2]$) resulted in the formation of dihydride **406** (76%). Finally, oxidative addition of iodomethane

Scheme 72



to ethene complex **398** gave iodomethyl complex **408** (77%, X-ray structure).¹⁷

Dissolution of dihydride **407** in neat hexafluorobenzene under irradiation for 7 h did not result in a C,F activation but afforded η^2 -hexafluorobenzene complex **409** in 93% yield. In contrast, dissolution of **407** in pentafluorobenzene under otherwise identical reaction conditions resulted in a C,H activation to give complex **410**, which afforded chloro derivative **411** upon treatment with tetrachloromethane. **409** and **410** were crystallographically characterized.¹⁷

There are a few papers reporting the syntheses of cyclopentadienyliridium complexes with a pendant phosphane ligand. Treatment of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with ligand **5** gave complex **412** (Chart 26). Ethene, cyclooctene, and 1,5-cyclooctadiene complexes **413** (60%), **414**, and **415** (no yield given) were also reported and were characterized by NMR. Reaction of **413** with iodine gave Ir(III) complex **416**.⁹²

In a manner corresponding to the synthesis of rhodium complex **393** the iridium chelate **417** was obtained in 86% yield (Chart 27). Variable-temperature NMR revealed a hindered rotation around the P– C_6F_5 bonds.⁹⁵

Recently Bergman published the preparation of **418** (X-ray) by treatment of **80** with $[(\text{coe})_2\text{IrCl}]_2$ (coe

Chart 26

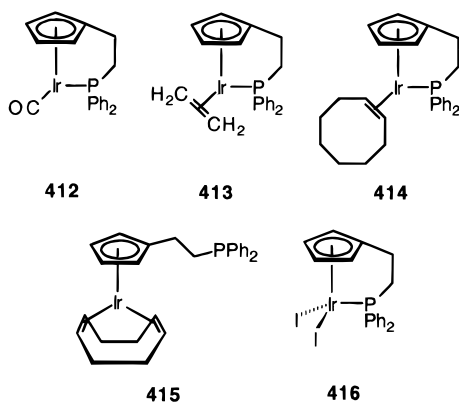
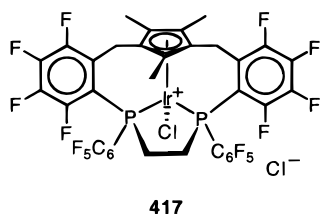
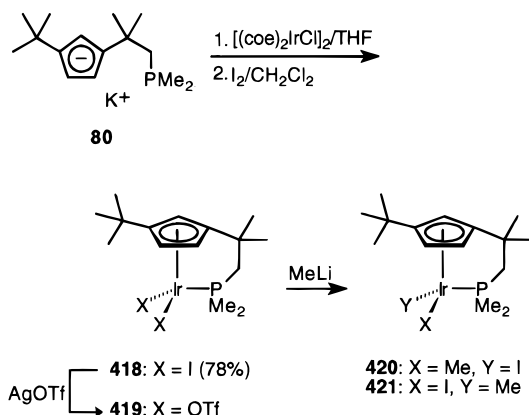


Chart 27



= cyclooctene) followed by iodine in THF in 78% yield (Scheme 73). Subsequent reaction with silver triflate

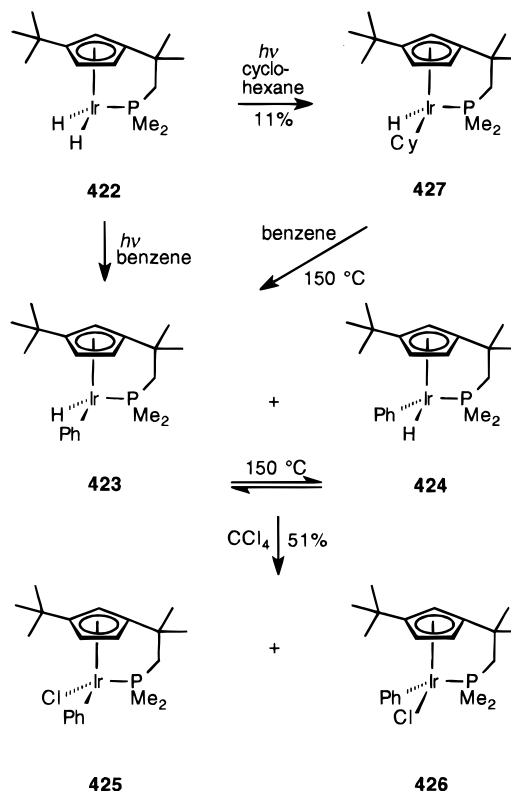
Scheme 73



provided **419**. **418** gave diastereomeric iodo methyl complexes **420** and **421** upon treatment with excess methyl lithium (1:1, no yield given). **421** was characterized by X-ray structure analysis to be the (*RR*), (*SS*) diastereomer.²⁸

Treatment of diiodide **418** with excess zinc and acetic acid in methanol gave dihydride **422** in 90–95% yield (X-ray structure analysis). A dilute benzene solution of **422** was irradiated (500 W, Pyrex) to facilitate a C,H activation process, resulting in the formation of diastereomers **423** and **424** (1:1, conversion after 5 h 66%, yield after workup 35%) (Scheme 74). At elevated temperature an interconversion of **423** and **424** was detected by ³¹P NMR. Reaction with CCl₄ gave air-stable chloro complexes **425** and **426** in 51% combined yield. The diastereomers could be separated chromatographically. Photolytic C,H activation with **422** was also achieved with cyclohexane to give **427** diastereoselectively, which gave **423** upon heating in benzene.²⁸

Scheme 74



No group 10–12 cyclopentadienyl complexes with pendant phosphane ligands have been reported thus far.

III. (Arsanylalkyl)cyclopentadienyl Complexes

Similar to the chemistry described in the preceding section, some (arsanylalkyl)cyclopentadienyl complexes were reported. Arsane ligands for transition metals in contrast to phosphanes have the advantage that they are not sensitive to oxidation by oxygen.⁹⁸

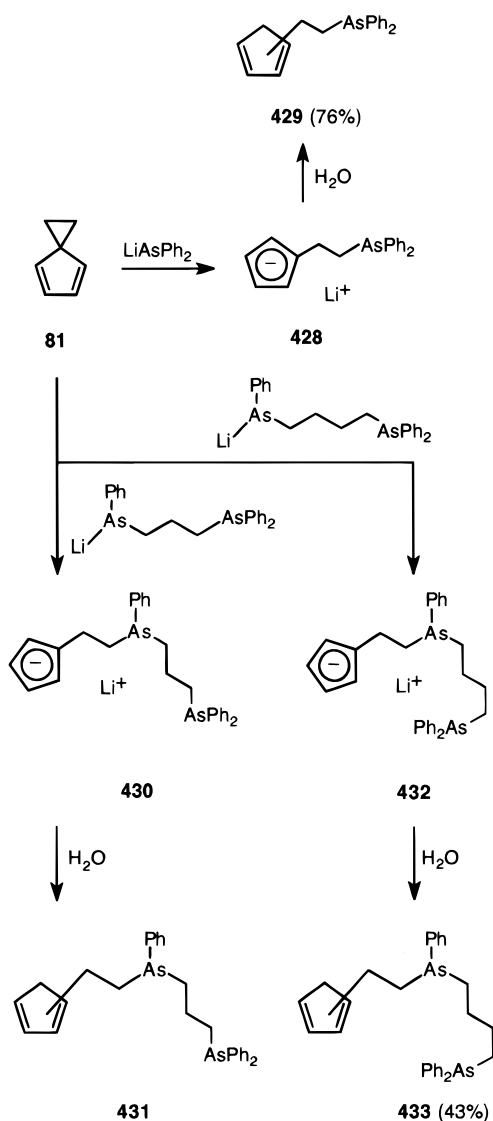
(Arsanylethyl)cyclopentadienyl ligands are easily prepared by addition of the appropriate lithium arsenide to spiro[2.4]hepta-4,6-diene (**81**). By this route **428**–**433** were obtained in moderate yields, respectively^{29,99} (Scheme 75). In a similar way, spiro[4.4]nona-2,4-diene (**434**) was treated with lithium diphenylarsenide to give (diphenylarsanylbutyl)cyclopentadienes **435** in 46% yield^{29,99} (Scheme 76).

Alternatively, **429** and **435** can be prepared by reaction of the corresponding ω -chloroalkyldiphenylarsanes **436** and **437**^{100,101} with sodium cyclopentadienide in 70% and 75% yield, respectively⁹⁹ (Scheme 77).

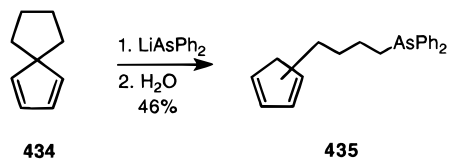
It is interesting to note how the concept of preparing the ligands by ring opening reactions of spiro compounds has been extended to the preparation of tridentate examples: The indenyl anion **438** formed by the nucleophilic ring opening reaction of spirocyclopropane-1,1'-indene (**93**) can be transformed into a new spiro[2.4]hepta-4,6-diene derivative, **439**, whose cyclopropane ring can again be opened by lithium diphenylarsenide with formation of **440** in 61% yield after hydrolysis¹⁰² (Scheme 78).

Another interesting tridentate ligand is formed by treatment of dilithium phenylarsenide¹⁰³ with 2 equiv

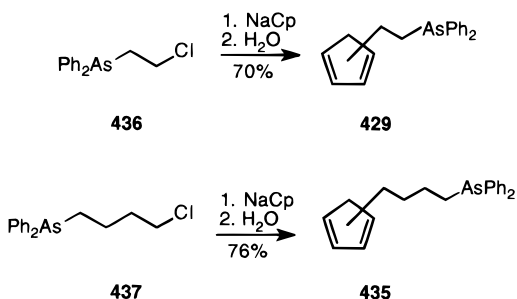
Scheme 75



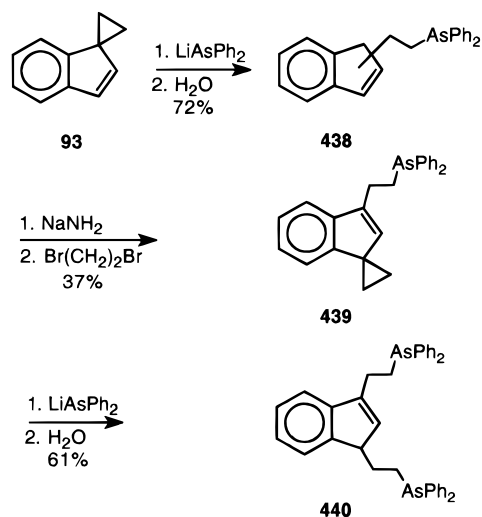
Scheme 76



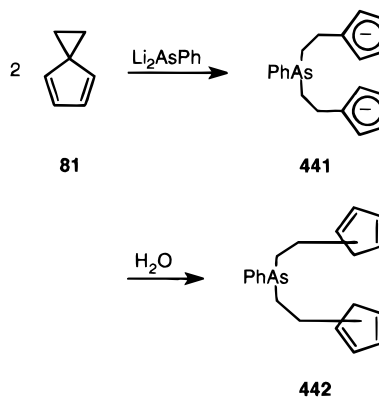
Scheme 77



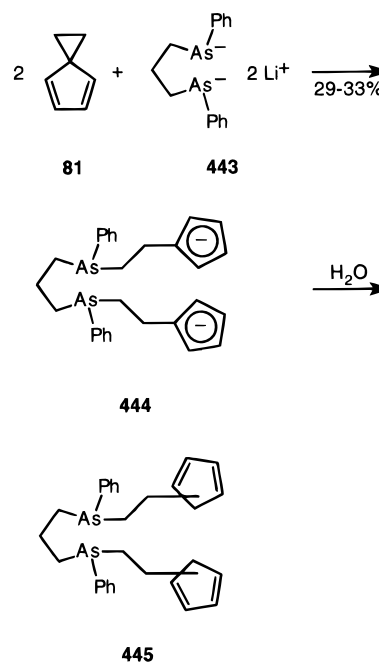
Scheme 78



Scheme 79



Scheme 80



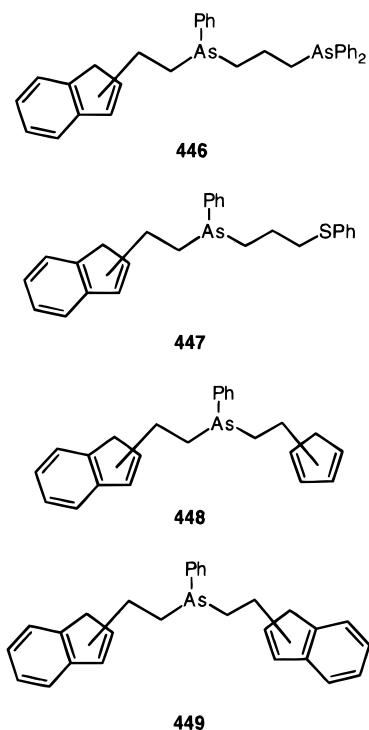
of spiro[2.4]hepta-4,6-diene (**81**). Via **441** one obtains after hydrolysis **442** in 76% yield⁹⁹ (Scheme 79).

Finally, tetradendate ligand **444** was made in 29–33% yield by addition of dianion **443** to 2 equiv of

spiro[2.4]hepta-4,6-diene (**81**) to give **444**, which was hydrolyzed to yield **445**⁹⁹ (Scheme 80).

Ligands prepared by similar reactions are **446**–**449**,¹⁰⁴ which were obtained via the corresponding anions by hydrolysis (Chart 28).

Chart 28



Some of the (arsanylalkyl)cyclopentadienyl ligands were reacted with metal halides to give the corresponding complexes.

Some titanium complexes were prepared and their catalytic properties investigated. Anion **428** can easily be converted to the silylated derivative **450**, which upon treatment with TiCl_4 forms complex **451** in 60% yield⁹⁸ (Scheme 81). However, it has not been proven beyond any doubt that the sidearm really is coordinated. The method of preparation resembles that applied to prepare manganese complex **224**; in that case Me_3SnBr was eliminated instead of Me_3SiCl . Remarkably, **451** was also obtained by treatment of **452** with TiCl_4 .⁹⁸

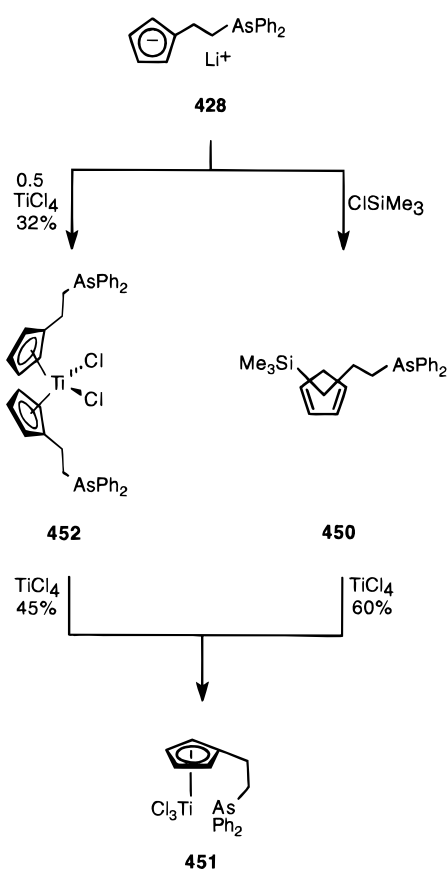
In a similar way, ligand **430** reacts with chlorotrimethylsilane followed by titanium tetrachloride to give a complex described by formula **453**, with, again, some uncertainty regarding whether the ligand is or is not chelated⁹⁸ (Scheme 82).

Finally titanocene **454** was prepared by reaction of ligand **441** with TiCl_4 in 72% yield⁹⁸ (Scheme 83).

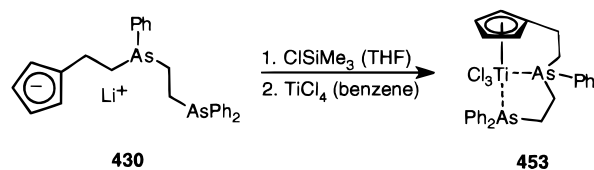
Some experiments regarding the reactivity of complexes **451**, **453**, and **454** were performed with respect to their catalytic properties. It was found that **451** catalyzes the dimerization of isoprene. When 0.001 equiv of **451** was used, the chemical yield was 90% with a ratio of cyclic (**456** + **457**) to acyclic (**458**) dimers of 0.94:1 and 450 turnovers per titanium atom (Scheme 84). When 0.002 equiv of **451** was used, the chemical yield was 84% with a ratio of 0.83:1 and 840 turnovers per titanium atom.⁹⁸

As another catalysis, the authors investigated the reaction of complexes **451**, **453**, and **454** with butadiene. Although **454** was not catalytically active, **451** and **453** were. To achieve the reaction, the complexes were treated with butadiene in the presence of 10 equiv of diethylaluminum chloride. Whereas **451** resulted in a *trans,trans,trans*- to *trans,trans,cis*-cyclododecatriene ratio of 0.5:1, this ratio was 3.9:1

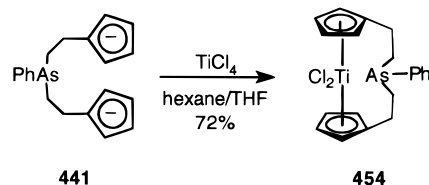
Scheme 81



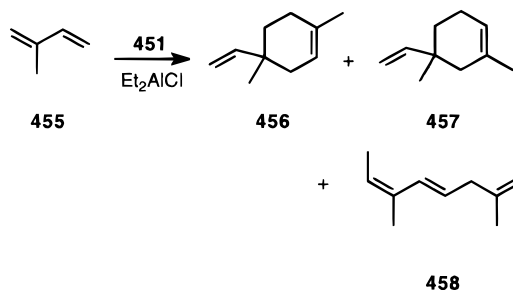
Scheme 82



Scheme 83



Scheme 84

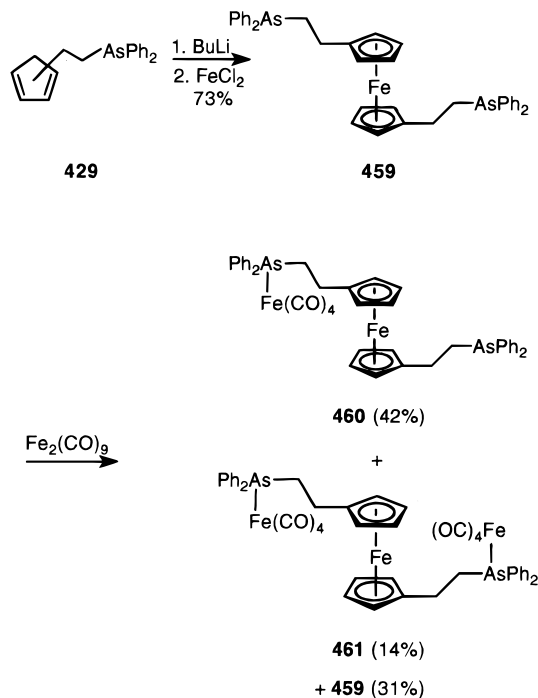


with **453** as the catalyst. **451** performed 80 turnovers per Ti atom, whereas this number was only 8 for **453**.⁹⁸

In addition to the titanium complexes, some interesting iron complexes were made. Anion **428**, which

was obtained from **429** by deprotonation with butyllithium, was treated with FeCl_2 to give ferrocene **459** in 73% yield (Scheme 85). Subsequent reaction with

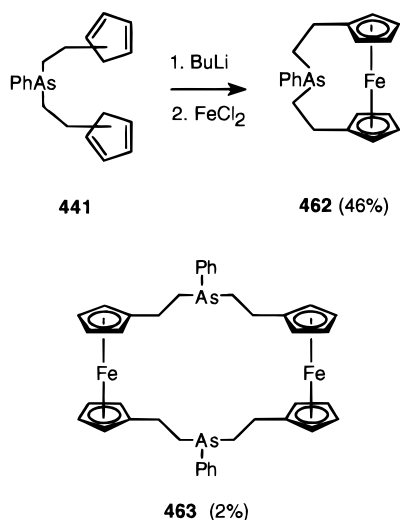
Scheme 85



$\text{Fe}_2(\text{CO})_9$ gave **460** (42%) and **461** (14%) along with 31% of the starting material **459**.

In a similar way, the reaction of dianion **441** with FeCl_2 gave ferrocenes **462** (46%) and a small amount of **463** (2%) (Scheme 86). The authors report unusual

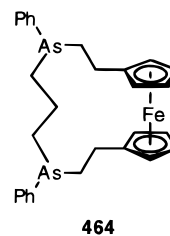
Scheme 86



NMR and UV properties concerning the cyclopentadienyl rings and discuss as a reason a possible bending of the cyclopentadienyl rings against each other as a consequence of a slight coordination of the bridging arsenic atom. However, the UV data gave no evidence for such a coordination. Similar chemistry leads to ferrocene **464** (22%)⁹⁹ (Chart 29).

In summary, there are quite a number of interesting cyclopentadienyl complexes with pendant arsenic ligands. However, all this has been found by a single

Chart 29



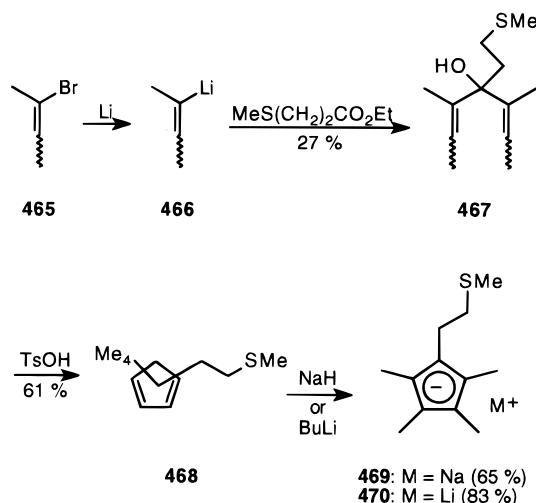
group, and therefore it is believed that much chemistry in this promising field still remains to be disclosed.

IV. (Thianlyalkyl)cyclopentadienyl Complexes

There are few papers dealing with cyclopentadienyl complexes with pendant sulfur ligands.

Krut'ko prepared [2-(thiomethyl)ethyl]tetramethylcyclopentadienes **468** by treatment of 2-lithio-2-butenes **466**, obtained by lithiation of **465**, with ethyl 3-(thiomethyl)propanoate via dienol **467**, which underwent ring closure in the presence of *p*-toluene-sulfonic acid in moderate yield (Scheme 87). Treat-

Scheme 87



ment of **468** with sodium hydride or with butyllithium gave cyclopentadienides **469** and **470** in 65% and 83% yield, respectively.¹⁰⁵

The reaction of lithium cyclopentadienide **470** with ZrCl_4 gave chelate **471** in 64% yield (Scheme 88). **471**, which shows dynamic behavior in solution, was subjected to an X-ray structure analysis which showed the complex to be dimeric in the crystal. **471** was treated with sodium cyclopentadienide **469** to give unchelated **472** in 67% yield. **473** was prepared accordingly in 74% yield^{105,106} (Chart 30).

When sodium cyclopentadienide **469** was treated with trichloro(pentamethylcyclopentadienyl)zirconium(IV) (**474**), unchelated **475** was obtained in 71% yield (Scheme 89). This compound was characterized by an X-ray structure analysis.¹⁰⁵

When **475** was treated with magnesium amalgam, cleavage of the S–Me bond was observed with formation of chelate **476** in 82% yield (Scheme 90). In a similar way, sulfur chelate **477** was obtained from **473** in addition to a small amount of the corresponding O–Me bond cleavage product. Bischelate **478** was

Scheme 88

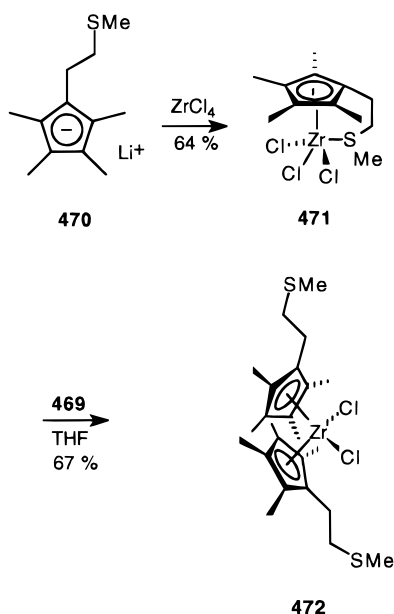
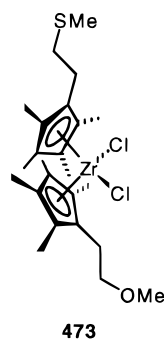
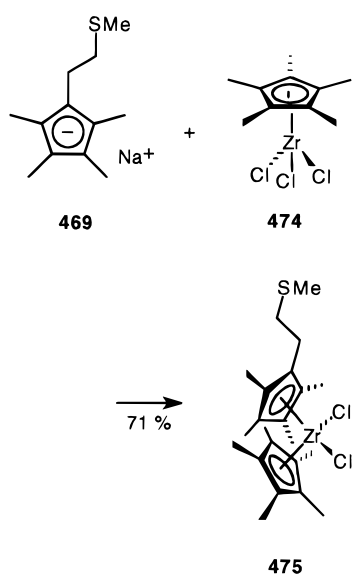


Chart 30



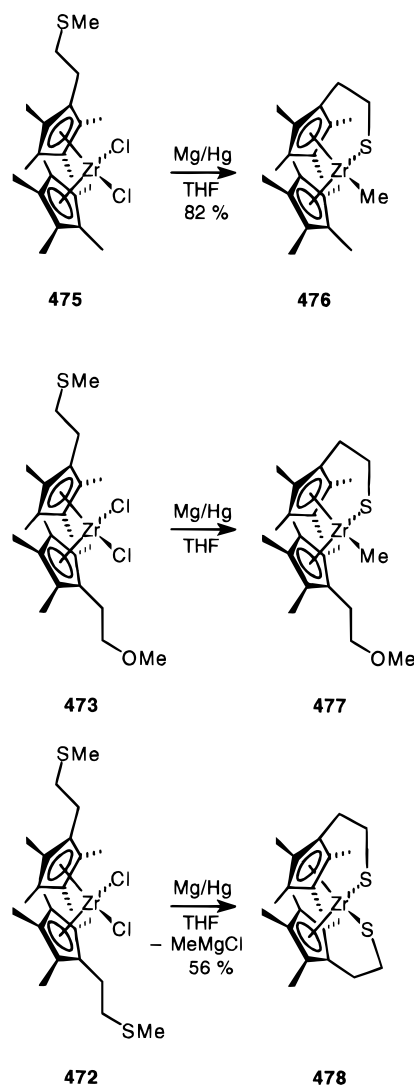
Scheme 89



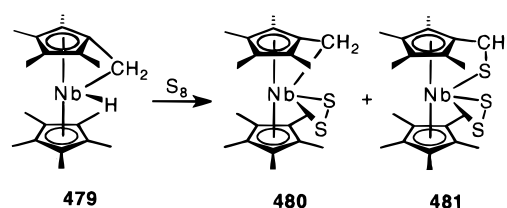
prepared from **472** with magnesium amalgam in 56% yield. This is the only complex in this series, which is air stable. **478** was structurally characterized.¹⁰⁷

Niobium fulvene hydride complex **479** reacted with elemental sulfur with formation of disulfur complex **480** and chelate **481**¹⁰⁸ (Scheme 91).

Scheme 90



Scheme 91



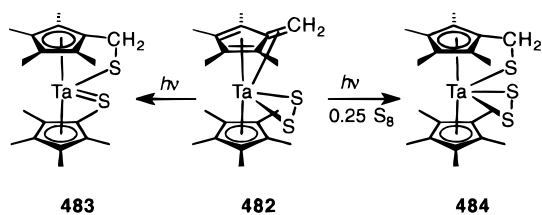
In a similar manner, fulvene sulfur complex **482** of tantalum was photochemically transformed to **483** or **484** in 20% and 62% yield, respectively¹⁰⁹ (Scheme 92).

Very recently a paper by Burkey and Heilweil reported photoacoustic measurements providing data concerning the energetics and dynamics of the ring closure of **485** and **486** to **487** and **488**, respectively¹¹⁰ (Scheme 93).

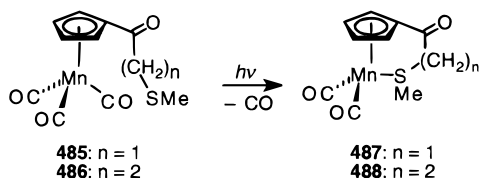
Dinuclear iron complex **489** was treated with excess carbon disulfide to give complexes **490** and **491** in 66% and 71% yield, respectively (Scheme 94). **490** was characterized by X-ray crystallography. The mechanistic proposal of the authors includes a disproportionation step.¹¹¹

In the context of η^1, S coordination of thiophene, which normally coordinates in a η^5 mode, the

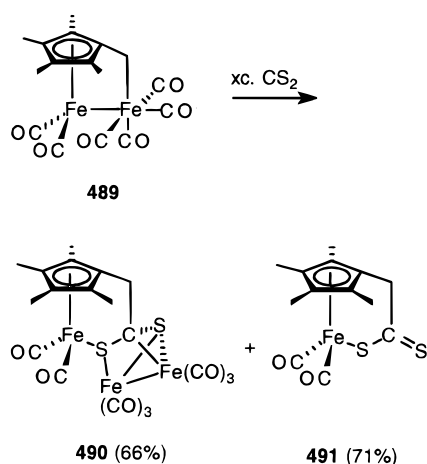
Scheme 92



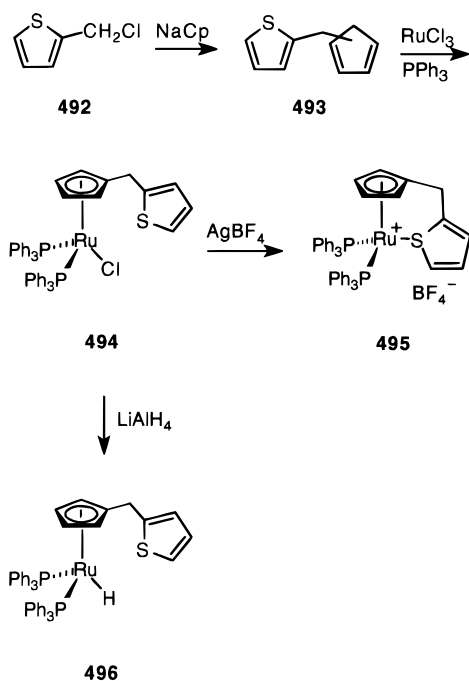
Scheme 93



Scheme 94



Scheme 95

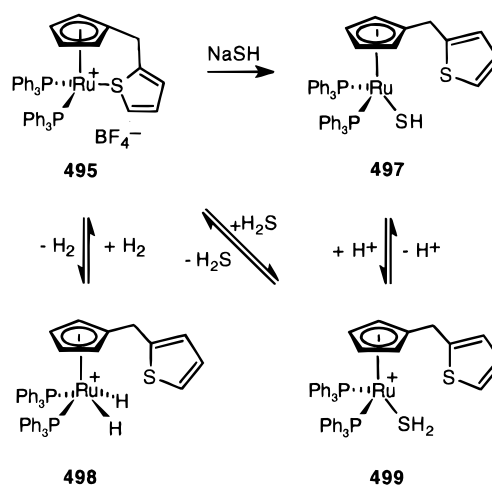


thiophene ring in **492** was connected via a methylene bridge to a cyclopentadienyl ligand to form **493** (Scheme 95). Coordination of **493** to ruthenium resulted in the formation of unchelated derivative **494**. The chloro ligand of **494** was dissociated by the

action of silver tetrafluoroborate. As the BF_4^- anion does not coordinate, the vacant coordination site thus created is occupied by the thiophene ligand, and the desired, chelate-stabilized η^1,S -thiophene complex **495** is formed. **495** was characterized by an X-ray structural analysis, which shows the sulfur atom to be pyramidalized.¹¹²

The chloro ligand in **494** was replaced by the triflate anion (67%), by thiolate (60%), and by hydride by reactions of **494** with AgOTf , followed by NaSH to give **497** or by reduction of **494** with LiAlH_4 to **496** (60%), respectively.¹¹³ The chemistry of chelate **495** was briefly examined, and equilibria between **495** and **497–499** were established, which were investigated by ^1H NMR, and it was found that hydrogen sulfide binds to the ruthenium center slightly better than dihydrogen, which in turn is able to displace S-bound thiophene in the chelate¹¹³ (Scheme 96).

Scheme 96



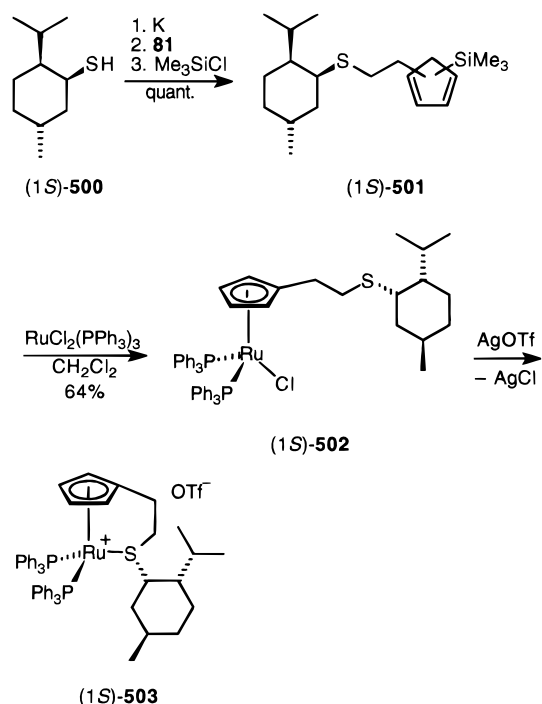
Recently van der Zeijden reported the synthesis of a chiral ligand and the formation of ruthenium complexes with it. When (1*S*)-neomenthanethiol (**500**) was treated with potassium followed by spiro[2.4]-hepta-4,6-diene (**81**) and chlorotrimethylsilane ligand, **501** was obtained in quantitative yield (Scheme 97). Reaction of **501** with $\text{RuCl}_2(\text{PPh}_3)_3$ afforded nonchelated complex **502** in 64% yield. Treatment with silver triflate gave chelate **503**, which decomposed within a few hours.²²

In summary, there are a few papers on cyclopentadienyl complexes with pendant sulfur ligands. The field has just begun to be developed, and certainly in the future there will be many new results.

V. Conclusion

This review reflects the increase in the number of cyclopentadienylmetal complexes bearing pendant phosphorus, arsenic, and sulfur ligands in the past few years. However, this increase is not a homogeneous one: as can be easily seen from Tables 3–5, it is mainly due to a growing variety of the cyclopentadienyl ligands bearing pendant phosphorus ligands and is concentrated at only a handful of metals. Clearly, cyclopentadienylmetal complexes bearing pendant phosphorus, arsenic, and sulfur ligands offer more possibilities for variation than simple cyclopentadienyl ligands. This has been exploited under a

Scheme 97



variety of aspects, for example, to introduce ligand chirality or higher or lower strain in the chelated complexes. As far as the metal part is concerned, most complexes were prepared with zirconium, iron, ruthenium, cobalt, or rhodium in addition to some iridium complexes. Given the comparatively large number of metals capable of forming cyclopentadienyl complexes, it becomes evident that syntheses of many new complexes of these will most likely be published in the future.

Beyond the syntheses of complexes relevant here, one can also observe an increase in attempts to use

them in chemical reactions, which are not always analogues of known cyclopentadienyl complex chemistry. For example, these include reactions with sensitive ligands, C,H and C,F activation processes, cleavage of a P,C triple bond, or, with increasing importance, catalytic processes. It can be expected that the application aspect of complexes discussed here will become more important in the future as compared to the bare synthesis of more or less interesting complexes.

The field of cyclopentadienylmetal complexes bearing pendant arsenic or sulfur ligands has remained rather limited up to date. However, their difference from the corresponding phosphane and oxygen representatives³ could, possibly in combination with other pendant ligands, become a basis for interesting developments in the future.

VI. Acknowledgment

Part of this review was written at Kyushu University, Japan, when I was a foreign visiting professor at the Institute of Advanced Materials Study in the summer of 1999. I thank Profs. Dr. S. Mataka and Dr. T. Thiemann for their hospitality and fruitful discussions. I appreciate helpful comments from Prof. Dr. H. H. Karsch, Garching, and Priv.-Doz. Dr. U. Siemeling, Bielefeld. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

VII. Note Added in Proof

Since the completion of this review, some more publications of relevance to the topic have come to our attention. These include ligands^{117–121} as well as complexes of titanium,^{118,119,122} zirconium,^{118,119,122} chromium,¹²¹ tungsten,¹²³ molybdenum,¹¹⁸ iron,¹²⁴ ruthenium,¹²⁵ and rhodium.^{119,126–128}

Table 1. ³¹P NMR Chemical Shifts of (*o*-Phosphanylalkyl)cyclopentadienes

compd	$\delta(^{31}\text{P})^a$	solvent	ref	compd	$\delta(^{31}\text{P})^a$	solvent	ref
2	126.8	CDCl ₃	4	86	29.2 (s)	C ₆ D ₆	32
	129.6			89	-13.8 (br)	C ₆ D ₆	36
4	-14.66	CDCl ₃	30	90	-13.0 (br)		
	-14.82				-14.4 (s)	C ₆ D ₆	36
7	-14.2	C ₆ D ₆	7		-13.9 (s)		
8	-16.4	C ₆ D ₆	8		-12.6 (s)		
	-16.9			92	-22.25	CDCl ₃	37,38
15	-17.8	C ₆ D ₆	14		-22.40		
	-17.9				-22.55		
	-18.0			99	-15.3		39
20	-15.6	CDCl ₃	15	115	-27.3	CDCl ₃	43
	-15.6			116	-27.4	CDCl ₃	43
28	-5.40	CDCl ₃	15	117	7.8 (bs)	CDCl ₃	43
	-5.58			118	6.2 (bs)	CDCl ₃	43
29	-26.3	CDCl ₃	43	119	11.6 (bs)	CDCl ₃	43
	11.5 (bs)			120	7.8 (bs)	CDCl ₃	43
38	-23.1 (s)	CDCl ₃	20	121	6.1 (bs)	CDCl ₃	43
	-22.7 (s)			122	11.9 (bs)	CDCl ₃	43
39	-23.0	CDCl ₃	20,21	123	-28.6	CDCl ₃	43
54	-10.6	C ₆ D ₆	23	124	-27.4	CDCl ₃	43
55	-9.3				-27.9		
56	-8.4			125	-26.6	CDCl ₃	43
	-8.0				-35.2		
	-6.0			130	-27.4	CDCl ₃	43
59	-40.0	CDCl ₃	24		-24.4		
	-26.2			135	-18.78	CDCl ₃	15
	-25.9				-18.83		
	-24.1						
	-22.3						

^a s = singlet, brs = broad singlet, br = broad.

Table 2. ^{31}P NMR Chemical Shifts of (ω -Phosphanylalkyl)cyclopentadienides

compd	$\delta(^{31}\text{P})^a$	solvent	ref	compd	$\delta(^{31}\text{P})^a$	solvent	ref
5	-15.7	[D ₈]THF	13	75	11.5 (brs)	C ₆ D ₆	27
12	-15.1	[D ₈]THF	13	76	19.9	C ₆ D ₆ /[D ₈]THF	27
13	3.8	[D ₈]THF	13	80	-59.3	C ₆ D ₆	28
36	-22.12	C ₆ D ₆	19	82	-56.34 (s)	[D ₈]dioxane	31
69	21.2	[D ₈]THF	13	83	2.5	[D ₈]THF	13
71	2.5	[D ₈]THF	13	84	28.1	[D ₈]THF	13
72	21.5	C ₆ D ₆	27	88	-14.6 (br)	[D ₈]THF	36
73	0.2	C ₆ D ₆ /[D ₈]THF	27	137	-13.27	[D ₈]dioxane	44
74	12.7	C ₆ D ₆	27				

^a s = singlet, brs = broad singlet.**Table 3.** ^{31}P NMR Chemical Shifts of Chelated (ω -phosphanylalkyl)cyclopentadienyl Complexes; η^5 unless Otherwise Indicated

compd	metal	$\delta(^{31}\text{P})$	remarks ^b	solvent	ref
140	Ga (η^1)	8.3	s	C ₆ D ₆	32
141	In (η^1)	24.0	s	C ₆ D ₆	32
142	Ga (η^1)	5.5	s	C ₆ D ₆	32
143	In (η^1)	10.5	s	C ₆ D ₆	32
154	Zr	6.1		CD ₂ Cl ₂	7
158	Zr	5.8	s	CD ₂ Cl ₂	36
169	Zr	-22.3		CD ₂ Cl ₂	26
170	Zr	-22.0		CD ₂ Cl ₂	26
171	Zr	-48.3		C ₆ D ₅ Br	26
172	Zr	-33.0		CD ₂ Cl ₂	26
173	Zr	-33.0		CD ₂ Cl ₂	26
174	Zr	-44.7		CD ₂ Cl ₂	26
175	Zr	51.7		CD ₂ Cl ₂	26
176	Zr	10.69	s	C ₆ D ₆ or [D ₈]toluene	46
178	Zr	5.8	70 °C; fluctuality, -10 °C, $\delta = 14.2, -6.9$	C ₆ D ₆ or [D ₈]toluene	46
179	Zr	18.81		C ₆ D ₆	18
180	Zr	0.1	s	C ₆ D ₆	47
181	Zr	2.3	ambient temp; fluctuality, -78 °C, $\delta = 9.8, -9.7$		46
182	Zr	16.2	s	C ₆ D ₆	47
183	Zr	14.0	s	C ₆ D ₆	47
184	Zr	0.7	brs	C ₆ D ₆	47
185	Zr	1.5	brs	C ₆ D ₆	47
190/191	Zr	19.5	s	C ₆ D ₆	48
192/193	Zr	9.5	s	C ₆ D ₆	48
194/195	Zr	11.9	s	C ₆ D ₆	48
196	Zr	11.8	s	C ₆ D ₆	48
197	Zr	8.2	s	C ₆ D ₆	48
198	Zr	-5.1	s	C ₆ D ₆	48
		46.8	s		
199	Zr	-5.9	s	C ₆ D ₆	48
		46.2	s		
200	Zr	11.8	s	C ₆ D ₆	48
202	Zr	31.6	s	C ₆ D ₆	19
204	Zr	17.50	s	CDCl ₃	49
206	Zr	32.1	s	[D ₆]acetone	49
207	Nb	24.62	brs	C ₆ D ₆	19
208	Nb	22.50	brs	C ₆ D ₆	19
209	Nb	25.66	brs	C ₆ D ₆	19
210	Nb	18.19	brs	C ₆ D ₆	19
215	Mo	47.6	s	CDCl ₃	50
		-26.3	s		
216	Mo	45.2	s	CD ₂ Cl ₂	50
217	Mo	51.6	s	CD ₂ Cl ₂	50
222	W	-34.4	d, PMe ₃ , $J_{\text{P,P}} = 37$ Hz, $J_{\text{P,W}} = 333$ Hz	[D ₈]THF	51
		-84.3	t, PPh ₂ , $J_{\text{P,W}} = 229$ Hz		
223	W	-34.9	d, PMe ₃ , $J_{\text{P,P}} = 34.5$ Hz, $J_{\text{P,W}} = 333$ Hz	[D ₈]THF	51
		-89.8	t, PPh ₂ , $J_{\text{P,W}} = 174$ Hz		
225	Mn	96.19		CDCl ₃	6
226	Mn	86.3		CDCl ₃	43
229	Fe	-62.6	dm, $^1J_{\text{P,P}} = 234$ Hz, PFe dd, $^1J_{\text{P,P}} = 234$ Hz,		53
		49.0	$^2J_{\text{P,H}} = 25$ Hz, PCHSi		
236	Fe	169.1		C ₆ D ₆	54
237	Fe	171.8		C ₆ D ₆	54
238	Fe	174.0		C ₆ D ₆	54
239	Fe	4.6	s	C ₆ D ₆	55
243	Fe	184.5	s	C ₆ D ₆	57
244	Fe	181.9	s	C ₆ D ₆	57
256	Fe	46.1	brs	CD ₂ Cl ₂	61
257	Fe	47.9	brs, 223 K	CD ₂ Cl ₂	61
258	Fe	49.4	d, PPh ₂ , $^2J_{\text{P,P}} = 95$ Hz	CD ₂ Cl ₂	61
		56.1	d, PEt ₂ , $^2J_{\text{P,P}} = 95$ Hz		
259	Fe	60.4	s	CD ₂ Cl ₂	61
260	Fe	52.5	s, CH ₂ P	CD ₂ Cl ₂	61
		-144.3	sept, PF ₆		

Table 3. (Continued)

compd	metal	$\delta(^{31}\text{P})$	remarks ^b	solvent	ref
262	Fe	71.2		CDCl_3	30
263	Fe	96.4		CDCl_3	30
264	Fe	94.6		CDCl_3	30
265	Fe	93.6		CDCl_3	30
266	Fe	94.1		CDCl_3	30
267	Fe	89.2		CDCl_3	30
268	Fe	90.0		CDCl_3	30
269	Fe	84.4		CDCl_3	30
270	Fe	83.0		CDCl_3	30
271	Fe	83.5		CDCl_3	30
272	Fe	82.3		CDCl_3	30
277	Ru	28.5	d, $J = 41$ Hz		42
		45.5	d, $J = 41$ Hz		
278	Ru	31.8	d, $J = 27$ Hz		42
		44.9	d, $J = 27$ Hz		
280	Ru	43.2	$J_{\text{P,P}} = 38$ Hz	C_6D_6	34
		52.0			
281	Ru	60.4	(aromatic) $J_{\text{P,P}} = 68$ MHz	CDCl_3	34
		156.2	(phosphite)		
282	Ru	45.7	d, $J_{\text{P,P}} = 41.0$ Hz	CDCl_3	15
		27.9	d, $J_{\text{P,P}} = 41.0$ Hz		
283	Ru	51.7/53.2	$J_{\text{P,P}} = 66$ Hz,	CDCl_3	34
		59.6/62.2	mixture of diastereomers		
284	Ru	-13.4	d, $J_{\text{P,P}} = 39.5$ Hz	CDCl_3	15
		-16.1	d, $J_{\text{P,P}} = 39.5$ Hz		
285	Ru	39.9	d, $J_{\text{P,P}} = 43.2$ Hz	CDCl_3	15
		34.5	d, $J_{\text{P,P}} = 43.2$ Hz		
286	Ru	40.6	d, $J_{\text{P,P}} = 41.5$ Hz	CDCl_3	15
		33.9	d, $J_{\text{P,P}} = 41.9$ Hz		
287	Ru	38.68	d, $J_{\text{P,P}} = 40.7$ Hz	CDCl_3	15
		32.3	d, $J_{\text{P,P}} = 41.2$ Hz		
294/295	Ru	36.7	$J_{\text{P,P}} = 42.2$ Hz	CDCl_3	15
		36.6	$J_{\text{P,P}} = 43.4$ Hz		
		32.0	$J_{\text{P,P}} = 42.2$ Hz		
		28.7	$J_{\text{P,P}} = 43.4$ Hz		
296/297	Ru	39.0	d, $J_{\text{P,P}} = 39.5$ Hz	C_6D_6	15
		37.9	d, $J_{\text{P,P}} = 41.6$ Hz		
		34.0	brd, $J_{\text{P,P}} = \text{ca. } 41$ Hz		
298/299	Ru	30.4-29.7	very brd		
		41.8	AB line system,	C_6D_6	15
		41.6	$J_{\text{P,P}} = 41.7$ Hz		
		41.5	$J_{\text{P,P}} = 39.5$ Hz		
		41.2	$J_{\text{P,P}} = 39.5$ Hz		
		40.9			
		35.6			
300/301	Ru	38.1	$J_{\text{P,P}} = 37.9$ Hz	C_6D_6	15
		38.0	$J_{\text{P,P}} = 41.6$ Hz		
		36.0	$J_{\text{P,P}} = 41.6$ Hz		
		35.6	$J_{\text{P,P}} = 37.9$ Hz		
304/305	Ru	43.19	$J_{\text{P,P}} = 42.6$ Hz	CDCl_3	15
		42.58	$J_{\text{P,P}} = 42.3$ Hz		
		39.04	$J_{\text{P,P}} = 42.3$ Hz		
		32.83	$J_{\text{P,P}} = 42.6$ Hz		
306/307	Ru	44.77	d, $J_{\text{P,P}} = 39.8$ Hz	CDCl_3	15
		34.09	d, $J_{\text{P,P}} = 40.0$ Hz		
308/309	Ru	43.14	d, $J_{\text{P,P}} = 41.5$ Hz	CDCl_3	15
		34.87	d, $J_{\text{P,P}} = 41.5$ Hz		
310/311/312/313	Ru	57.3	d, $J_{\text{P,P}} = 37.3$ Hz	CDCl_3	15
		43.7	d, $J_{\text{P,P}} = 39.2$ Hz		
		43.7	d, $J_{\text{P,P}} = 39.3$ Hz		
		38.2	d, $J_{\text{P,P}} = 40.2$ Hz		
		38.2	d, $J_{\text{P,P}} = 39.8$ Hz		
		31.6	d, $J_{\text{P,P}} = 39.0$ Hz		
		31.6	d, $J_{\text{P,P}} = 39.3$ Hz		
314	Ru	67.1	C^iPPh_2		22
		42.3	PPh_3		
315	Ru	66.3	C^iPPh_2		22
		46.2	PPh_3		
318/319 (76:24)	Ru	65.7/66.5	C^iPPh_2		22
		41.1/45.0	PPh_3		
320/321 (74:26)	Ru	63.3/67.2	C^iPPh_2		22
		40.3/44.5	PPh_3		
325	Co	85.2		C_6D_6	12,13
326	Co	108.1		C_6D_6	12,13
327	Co	128.9		C_6D_6	12,13
330	Co	62.0		C_6D_6	12,13
331	Co	78.6		C_6D_6	12,13
332	Co	69.5		$[\text{D}_8]\text{toluene}$	13
333	Co	94.9		$[\text{D}_8]\text{toluene}$	13
334	Co	79.5		$[\text{D}_8]\text{toluene}$	13
335	Co	97.3		$[\text{D}_8]\text{toluene}$	13
339	Co	92.6		$[\text{D}_8]\text{toluene}$	70

Table 3. (Continued)

compd	metal	$\delta(^{31}\text{P})$	remarks ^b	solvent	ref
343	Co	95.9		C ₆ D ₆	70
344	Co	96.4		C ₆ D ₆	70
345	Co	96.8		C ₆ D ₆	70
347	Co	111.7		[D ₈]THF	70
348	Co	97.3		[D ₈]THF	70
349	Co	110.3	very br	[D ₈]THF	70
360	Co	88.1		C ₆ D ₆	91
362	Co	92.5		C ₆ D ₆	114
363	Co	89.9		C ₆ D ₆	91
365	Co	-177.3	phosphirene P	C ₆ D ₆	115
		-11.1	C=P-P		
		93.5	Co-P		
366	Rh	73.65	d, ¹ J _{P,Rh} = 204.4 Hz	C ₆ D ₆	92
367	Rh	43.68	d, ¹ J _{P,Rh} = 195.2 Hz	C ₆ D ₆	92
368	Rh	44.11	d, ¹ J _{P,Rh} = 194.6 Hz	C ₆ D ₆	92
369	Rh	69.39	d, ¹ J _{P,Rh} = 213.6 Hz	C ₆ D ₆	92
371	Rh	54.58	d, ¹ J _{P,Rh} = 146.7 Hz	C ₆ D ₆	92
372	Rh	38.0	¹ J _{P,Rh} = 196.8 Hz	C ₆ D ₆	20,21
373	Rh	43.7	¹ J _{P,Rh} = 194.8 Hz	C ₆ D ₆	20,21
374/375	Rh	30.3	¹ J _{P,Rh} = 198.7 Hz	C ₆ D ₆	20,21
		32.0	¹ J _{P,Rh} = 196.8 Hz		
376	Rh	71.1	d, ¹ J _{P,Rh} = 211 Hz		39
377	Rh	42.0	d, ¹ J _{P,Rh} = 195 Hz		39
378	Rh	39.0	d, ¹ J _{P,Rh} = 203 Hz		39
379	Rh	89.5	d, ¹ J _{P,Rh} = 197 Hz		39
380	Rh	23.3	dd, ¹ J _{P,Rh} = 209, 44 Hz		39
		38.6	dd, ¹ J _{P,Rh} = 227, 44 Hz		
389	Rh	22.0	d, ¹ J _{Rh,P} = 134.9 Hz		94
		-143.6	sept, ¹ J _{Rh,P} = 712.8 Hz		
390	Rh	18.2	d, ¹ J _{Rh,P} = 134.0 Hz		94
		-143.5	sept, ¹ J _{Rh,P} = 712.6 Hz		
391	Rh	18.3	d, ¹ J _{Rh,P} = 133.8 Hz		94
392	Rh	30.3	d, ¹ J _{Rh,P} = 135.9 Hz		94
393	Rh	71.28	dm, ¹ J _{Rh,P} = 144.2 Hz	CDCl ₃	96
395	Rh	83.68	dm, ¹ J _{Rh,P} = 141.3 Hz, P(C ₆ F ₅)(C ₆ F ₄)	[D ₆]acetone	95
		49.14	dm, ¹ J _{Rh,P} = 152.1 Hz, P(C ₆ F ₅) ₂		
396	Rh	60.0	d, ¹ J _{Rh,P} = 139 Hz	CDCl ₃	97
397	Rh	45.7	d, ¹ J _{Rh,P} = 197 Hz		42
398	Rh	49.08	d, ¹ J _{Rh,P} = 206 Hz	C ₆ D ₆	17
399	Rh	51.28	d, ¹ J _{Rh,P} = 210 Hz	[D ₈]THF	17
400	Rh	45.31	d, ¹ J _{Rh,P} = 199 Hz	[D ₈]THF	17
401	Rh	50.1	dd, ¹ J _{Rh,P} = 225 Hz, ¹ J _{P,P} = 57 Hz	C ₆ D ₆	17
		-2.84	dd, ¹ J _{Rh,P} = 211 Hz		
404	Rh	44.9	d, ¹ J _{Rh,P} = 187 Hz	[D ₈]THF	17
405	Rh	23.1	d, ¹ J _{Rh,P} = 137 Hz	CDCl ₃	17
406	Rh	34.14	d, ¹ J _{Rh,P} = 154 Hz	CDCl ₃	17
407	Rh	55.3	d, ¹ J _{Rh,P} = 172 Hz	[D ₈]THF	17
408	Rh	40.51	d, ¹ J _{Rh,P} = 160 Hz	[D ₈]THF	17
409	Rh	45.4	d, ¹ J _{Rh,P} = 200 Hz, ¹ J _{F,P} = 54.4 Hz	[D ₈]THF	17
410	Rh	54.3	d, ¹ J _{Rh,P} = 154 Hz	[D ₈]THF	17
411	Rh	34.3	d, ¹ J _{Rh,P} = 154 Hz, ¹ J _{F,P} = 9.7 Hz	[D ₈]THF	17
412	Ir	34.64	s	C ₆ D ₆	92
413	Ir	26.97	s	C ₆ D ₆	92
414	Ir	26.96	s	C ₆ D ₆	92
416	Ir	15.52	s	C ₆ D ₆	92
419	Ir	23.1		CD ₂ Cl ₂	28
420	Ir	-15.7		C ₆ D ₆	28
421	Ir	-16.5		C ₆ D ₆	28
422	Ir	-15.8		C ₆ D ₆	28
423	Ir	-13.5		C ₆ D ₆	28
424	Ir	-12.9		C ₆ D ₆	28
425	Ir	-4.7		C ₆ D ₆	28
426	Ir	-19.0		C ₆ D ₆	28

^a η^5 unless otherwise indicated. ^bs = singlet, br s = broad singlet, d = doublet, t = triplet, dm = doublet of multiplets, dd = doublet of doublets, sept = septet, br d = broad doublet, br = broad.

Table 4. ³¹P NMR Chemical Shifts of Some Unchelated (ω -Phosphanylalkyl)cyclopentadienyl Complexes

compd	metal	$\delta(^{31}\text{P})$	remarks ^a	solvent	ref
144	Ti	-16.22	s	CDCl ₃	45
145	Zr	-16.04	s	CDCl ₃	45
146	Zr	29.5		[D ₈]THF	13
148	Zr	-16.0		[D ₈]THF	13
157	Zr	-14.3		[D ₈]THF	7
159	Zr	33.2		CDCl ₃	27
160	Zr	9.8	mixture of diastereomers	C ₆ D ₆ , [D ₈]THF	27
		9.7			

Table 4 (Continued)

compd	metal	$\delta(^{31}\text{P})$	remarks ^a	solvent	ref
161	Zr	12.0		CD ₂ Cl ₂	27
		11.8			
162	Zr	7.0		CDCl ₃	27
		5.5			
163	Zr	6.0		C ₆ D ₆	27
		4.5			
164	Zr	31.8		CD ₂ Cl ₂	27
165	Zr	8.1		C ₆ D ₆ /[D ₈]THF	27
		8.0			
167	Zr	32.5		C ₆ D ₆	
168	Zr	31.2		C ₆ D ₆	26
177	Zr	-5.20	s	C ₆ D ₆ or [D ₈]toluene	46
178	Zr	5.8	70 °C; fluctuality, -10 °C, $\delta = 14.2, -6.9$	C ₆ D ₆ or [D ₈]toluene	46
181	Zr	2.3	ambient temp; fluctuality, -78 °C, $\delta = 9.8, -9.7$		46
186	Zr	-5.5	s	C ₆ D ₆	47
187	Zr	-5.9	s	C ₆ D ₆	47
188	Zr	-5.9	s	C ₆ D ₆	47
189	Zr	-4.59	s	C ₆ D ₆	47
215	Mo	47.6	s	CDCl ₃	50
		-26.3	s		
246	Fe	26.8		[D ₈]toluene	13
247	Fe	14.8		[D ₈]toluene	13
248	Fe	30.4		[D ₈]toluene	13
249	Fe	-16.0		[D ₈]toluene	13
336	Co	30.7		[D ₈]THF	13
337	Co	29.8		[D ₈]THF	13
340	Co	30.1	s, 1P, P1	[D ₈]THF	70
		114.1	s, 2P, P2		
341	Co	30.2		[D ₈]THF	70
342	Co	29.08		[D ₈]THF	70
350	Co	37.8	P ₂ CCCH ₃	C ₆ D ₆	85
		28.9	PCCH ₃		
351	Co	27.0	s	C ₆ D ₆	85
		189.9	brs		
352	Co	78.5	C(<i>t</i> Bu ₃) ₂ P=S	CDCl ₃	85
		578	Co ₃ P=S		
355	Co	78.3	s, Se=P <i>t</i> Bu ₂ , ¹ J _{P,Se} = 715 Hz	C ₆ D ₆	89
361	Co	29.3		C ₆ D ₆	91
364	Co	-66.5	PCCH ₃	C ₆ D ₆	91
		29.2	phosphirene P		
370	Rh	-16.66	s	C ₆ D ₆	92
402	Rh	-2.3	d, ¹ J _{Rh,P} = 214 Hz, 2P	C ₆ D ₆	17
		-20.6	s, 1P		
403	Rh	1.18	d, ¹ J _{Rh,P} = 187 Hz, 1P	C ₆ D ₆	17
		-21.0	s, 1P		
415	Ir	-16.14	s	C ₆ D ₆	92

^a s = singlet, brs = broad singlet, d = doublet.**Table 5. Listing of (phosphanylalkyl)Cyclopentadienyl Complexes Characterized by X-ray Crystallography**

compd	metal	ref	compd	metal	ref	compd	metal	ref	compd	metal	ref
137	K	44	257	Fe	61	205	Zr	49	371	Rh	92
138	Y	31	258	Fe	61	206	Zr	49	384	Rh	116
139	La	31	263	Fe	30	209	Nb	19	389	Rh	93, 94
140	Ga (η^1)	32	269	Fe	30	210	Nb	19	391	Rh	93, 94
141	In (η^1)	32	272	Fe	30	211	Nb	19	392	Rh	94
154	Zr	7	275	Ru	62, 63	213	Cr	33	394	Rh	96
156	Zr	7	277	Ru	42	215	Mo	50	395	Rh	42
158	Zr	36	278	Ru	42	216	Mo	50	398	Rh	17
160	Zr	27	281	Ru	34	217	Mo	50	399	Rh	17
167	Zr	26	315	Ru	22	218	Mo	19	400	Rh	17
170	Zr	26	327	Co	13	223	W	51	404	Rh	17
172	Zr	26	333	Co	70	226	Mn	43	405	Rh	17
176	Zr	46	339	Co	69	228	Fe	53	406	Rh	17
179	Zr	18	343	Co	70	236	Fe	54	408	Rh	17
182	Zr	47	353	Co	85	239	Fe	55	409	Rh	17
191	Zr	48	355	Co	89	243	Fe	57	411	Rh	17
192	Zr	48	359	Co	90	245	Fe	58	418	Ir	28
197	Zr	48	365	Co	91	246	Fe	25	421	Ir	28
204	Zr	49	369	Rh	92	256	Fe	61	422	Ir	28

VIII. References

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