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Review

Perfluoroaryl-substituted cyclopentadienyl complexes of transition metals

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This article is dedicated to the memory of my graduate advisor, Professor Paul G. Gassman, a pioneer in understanding electronic effects in organometallic chemistry, a gifted teacher, an inspiring mentor, and a statesman for science throughout America and around the globe.

Contents

Abbreviations: Cp, cyclopentadienyl; Cp^*, pentamethylcyclopentadienyl; $CpCF_3$, (trifluoromethyl)cyclopentadienyl; C_6F_5Cp, (pentafluorophenyl)cyclopentadienyl

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Abstract

A review with 172 references. Cyclopentadienyl (Cp) and its substituted congeners are among the most common ligands in organometallic chemistry. Ring substituents attached to Cp can influence the structure, physico-chemical properties, and reactivity of coordinated metal fragments. This article describes the synthesis of perfluoroaryl-substituted cyclopentadienes and indenes and their use as transition metal ligands. Emphasis is placed on trends in spectroscopic and electrochemical behavior, structure, and reactivity that arise from the highly electron-withdrawing character of the perfluoroaryl substituents.

Keywords: CF activation; Cyclopentadienyl; Electronic effects; Metallocene; Pentafluorophenyl

1. Introduction

1.1. Substituent effects

Cyclopentadienyl (Cp) complexes share a rich history that spans 50 years [1–4] and the entire periodic table [5–10]. The attachment of Cp ring substituents is an established and effective strategy for modulating the physical properties and chemical reactivity of Cp complexes. Practicing organometallic chemists find it useful to divide substituent effects into *steric effects*, which refer broadly to repulsive interactions among ligands resulting from van der Waals or Coulombic forces, and *electronic effects*, which describe the coupling of a metal ion through the molecular bonding framework to a remote substituent with an intrinsic polarizing quality. Outer sphere phenomena such as solvation and ion pairing often blur the distinction between these two categories, a distinction that seems arbitrary anyway when examined under the bright glare of modern electronic structure theory. But in the context of a review article it is appropriate to establish some historical context, and a fairly conventional view of steric and electronic substituent effects has been one of the most useful (if occasionally misleading) conceptual tools in the recent development of transition metal Cp chemistry.

1.2. Steric effects

One reason why simple "steric-versus-electronic-effects" thinking works so well for Cp complexes is that the basic sandwich structure of a complex (for example, the 10 carbons and 2 halogens bound to the metal ion in group 4 metallocene dihalides) remains surprisingly unperturbed when substituents are added unless they are very large or numerous [11]. And yet, Cp substituents are close to the metal, so small changes in the number of Cp substituents or even in their shape and positioning can impart dramatic changes in metal-centered chemical reactivity and especially in the approach of substrates in catalytic processes. The sensitivity of reactivity to subtle changes in the structure of Cp ligands has been exploited to great effect, particularly in stereoselective catalysis [12–22]. Tethering Cp ligands to one another or to other ligands further enhances steric approach control by restricting the otherwise free Cp–M bond rotation [23,24]. An exhaustive review of steric effects in Cp complexes is well beyond the scope of this article. Nevertheless it is worth making the simple point here that although we still frequently use the η^5-$C_5(CH_3)_5$ (Cp^*) ligand in place of Cp to impart kinetic stability or to decrease the oxidation potentials of coordinated metal ions [25,26], we have also come a long way in our ability to design molecules – notably catalysts – with a detailed knowledge of steric effects and to then make these molecules using rational synthesis.

1.3. Electronic substituent effects

Neither our fundamental understanding of *electronic* substituent effects in Cp complexes, nor especially our ability to apply that knowledge in catalyst design, has reached the same high level of sophistication. The point of this section is not to review electronic substituent effects (despite the heading), but to propose two reasons for this intellectual lag. The first reason is fundamental and was already mentioned: Cp substituents are close to the metal! In other words, steric effects generally dominate, and reactivity studies (especially in catalysis) must always establish proper controls to suppress steric factors [27–30]. The second reason broadly encompasses synthetic and chemical reactivity issues. Steric parameter space can be charted using alkyl substituents (which are highly inert) and the occasional silicon "bridge" atom. The required substituted cyclopentadienes inevitably yield to the refined techniques of modern organic synthesis, and subsequent coordination to the desired metal fragment is ordinarily just a matter of optimization.

But exploring electronic substituent effects over a wide range implies venturing well beyond methyl groups and the occasional silicon "bridge" atom.

1.3.1. Problems with electron-withdrawing substituents

If one examines a standard table of Hammett constants [31], one finds amino and hydroxy groups at the top (most negative σ_{para}) and cyano and nitro groups at the bottom (most positive σ_{para}). But suppose one wanted to explore electronic effects in a highly electrophilic catalytic system. Group 4 metallocene olefin polymerization catalysts spring immediately to mind. Even if one could prepare zirconocene dichlorides bearing an NH_2, OH, CN, or NO_2 group (not one has been), these groups would be summarily dismissed from the catalytic study because they all contain lone pairs of electrons that would poison the highly electrophilic active species. For electron-donating, Brønsted-acidic groups like amino and hydroxy [32], or with certain electrophilic groups like dihaloboryl (BX_2) [33], protecting groups can suppress some of the unwanted side reactions.

The intrinsic reactivity of electrophilic substituents implies new synthetic challenges. Many Cp complexes are prepared by ligand substitution of transition metal halides with cyclopentadienyl *anions*, which are most commonly delivered as salts of electropositive metals (Li, Na, Mg, etc.). The Cp anion and the substituent may simply be synthetically incompatible. This problem more than any other led us to pursue perfluoroaryl-substituted cyclopentadiene chemistry in our laboratories. As a student in the research group of Professor Paul G. Gassman (to whose memory this article is respectfully dedicated), I became keenly aware of the problems surrounding the use of the (trifluoromethyl)cyclopentadienyl ligand (CF_3Cp) [34]. The diene (CF_3CpH) is easily prepared from nickelocene and iodotrifluoromethane [35]. Homologues derived from perfluoroalkyl iodides have also been prepared [36]. Deprotonation with sodium hydride or butyllithium affords a system resembling an electron-rich arene bearing a labile benzylic halide: rapid fluoride elimination gives difluorofulvene which is immediately recognized even in small quantities by its characteristic stench. Only the thallium(I) salt of the CF_3Cp anion (but not of the homologous $CF_3(CF_2)_nCp$ anions [36]) was sufficiently stable to explore its use as a CF_3Cp anion synthetic equivalent [34]. Preparation of early transition metal CF_3Cp complexes largely failed. A few titanocene derivatives were obtained [34,37,38], but all attempts to coordinate CF_3Cp to the more fluorophilic Zr^{4+} or Hf^{4+} ions resulted only in decomposition to difluorofulvene. An interesting Cp derivative bearing four methyl groups and one CF_3 group [39–41], as well as several CF_3-substituted indenes [42,43], were prepared by Nazarov-type cyclodehydration chemistry. However in both cases the anion is further destabilized (more basic) and not even the thallium salts could be isolated [39,42]. The syntheses of tetrakis- and pentakis(trifluoromethyl)cyclopentadiene are stunning *tours de force*, but those interested in using these compounds will encounter "extremely difficult" reactions, intermediates that require "great care in handling," and products mixtures that require separation by preparative gas chromatography [44–46]. Cyclopentadienyl anions bearing four or five CF_3 groups are stable but weakly nucleophilic. They react only with "naked" metal-fragment precursors such as $[(\eta^5\text{-}Me_5C_5)Ru(NCCH_3)_3][OSO_2CF_3]$ or $[(COD)M(THF)_2][OSO_2CF_3]$ (M = Ru, Ir) to form mixed ruthenocenes or CpM(COD) derivatives, respectively [47]. Cp ligands with two or three CF_3 groups might strike the right balance of stability and nucleophilicity, but they have not been prepared. The alkylated analogue 1,2,4-trimethyl-3,5-bis(trifluoromethyl)cyclopentadiene was prepared [48], but the procedure was never published in the open literature.

Cp substituents must also be compatible with the reagents and conditions of metal complexation. In this regard, one distinct problem with many electron-withdrawing substituents is that they are also Lewis bases. A good examples is the cyano group, which is strongly electron-withdrawing on the carbon end, whereas nitriles are excellent ligands on the nitrogen end. Cyclopentadienes bearing 1–5 cyano groups are obtained by one-pot, stepwise cyanation of NaCp with cyanogen chloride [49,50]. Monocyanocyclopentadiene is subject to rapid dimerization and must be prepared freshly and handled carefully [51]. Alkali salts of the cyanocyclopentadienes are thermally stable and react with Mn, Re, and Fe halides to form complexes having the general formula $(\eta^5\text{-}C_5(CN)_nH_{5-n})M(CO)_3$ (n = 1–2, M = Mn, Re) and $(\eta^5\text{-}C_5(CN)_nH_{5-n})_2Fe$ (n = 1–2) [52,53]. However, with increasing cyanation the Cp moiety becomes less basic [49], and analogous attempts to prepare the higher homologues (n = 3–5) led instead to ill-characterized, insoluble, involatile network polymers in which metal ions were bound instead to the N-terminae of the nitrile groups [54,55].

Similarly, cyclopentadienes bearing 1–5 carbomethoxy groups are prepared either by alkaline decarboxylation of pentakis(carbomethoxy)cyclopentadiene or by reaction of NaCp with methyl chloroformate [56,57]. Alkali mono(carbomethoxy)cyclopentadienides react efficiently with a wide variety of both early and late transition metal halides to afford stable pentahapto complexes [58–62], although highly oxophilic ions like Zr^{IV}, Hf^{IV}, and Ta^{V} are conspicuously absent. The pentakis(carbomethoxy)cyclopentadienyl anion exhibits two different coordination modes [57]. With early or oxophilic metals, as well as many of the harder ions of the first transition series such as Cr^{3+}, Fe^{2+}, Co^{2+}, and even Cu^{2+}, coordination complexes involving the ester oxygens are obtained [57]. With soft metal fragments including $Mn(CO)_3$ [63], Sn^{2+} [64], and low-oxidation-state ions late in the second and third transition series (particularly Rh^{1+}) [57], pentahapto coordination of the Cp moiety is observed.

1.3.2. Alternative strategies for working with reactive substituents

Fortunately there is no apparent limit to the ingenuity and effort that organometallic chemists are willing to apply in circumventing the difficulties associated with reactive, electron-withdrawing substituents. Just a few examples are provided here. The thallium(I) ion generally stabilizes Cp anions, as was illustrated earlier in the discussion of CF_3-substituted cyclopentadienes. The same technique has also been used to prepare TlCp compounds bearing halo [65,66], acetyl [67], carbomethoxy

[59], and cyano [58] substituents. The toxicity of thallium is a major drawback. Trialkylsilyl and trialkylstannyl Cp derivatives are formally neutral compounds, but the C–Si and C–Sn bonds are labile. Metathesis reactions with metal halides release the corresponding R_3EX (R = alkyl; E = Si, Sn; X = halogen) as stable, often volatile byproducts. This strategy has enabled the synthesis of Cp complexes bearing highly electrophilic substituents such as the $SiMe_2Cl$ [68] without requiring protective groups.

Starting with ferrocene, ruthenocene, cymantrene, and a few other famously stable complexes, one can conduct electrophilic substitutions, metalations, side-chain rearrangements, and sigma-coupling reactions. These methods furnish acyl [69] nitro [70], halo [71–74], amino [75,76], cyano [77], fluorous "ponytail" [62,78–82], *p*-haloaryl [83], and boryl [68,84,85] derivatives.

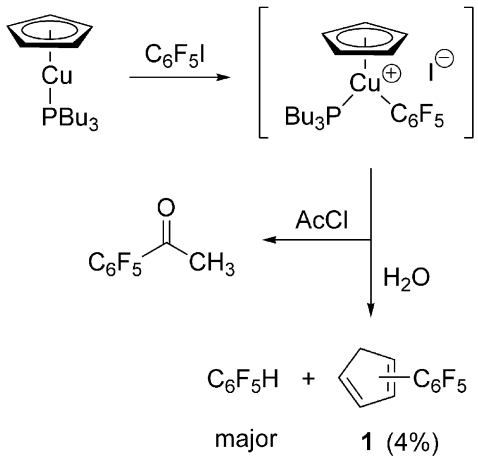
Finally, in two cases, η^6-arene complexes undergo thermolytic ring-contraction reactions to afford Cp complexes bearing electron-withdrawing groups. In the first example, thermolysis of a manganese η^6-azidobenzene complex gave the corresponding cyano-substituted Cp complex (presumably via an η^6-phenylnitrene intermediate) [86]. In the second example, thermolysis of (η^5-pentafluorocyclohexadienone)$RuCp^*$ gave (η^5-C_5F_5)$RuCp^*$, the first example of an organometallic complex containing the η^5-C_5F_5 ligand [87], via CO extrusion. The latter reaction is general for all the possible partially fluorinated $C_5F_nH_{5-n}$ ligands and noteworthy for its regiospecificity [88], but so far it has not been adapted to other systems.

1.4. Why perfluoroaryl substituents?

Notwithstanding the depth and breadth of substituted cyclopentadiene chemistry described in the preceding sections, when we began our work in 1995, we still found something lacking. We needed a method of attaching highly electron-withdrawing substituents to cyclopentadienes that met the following criteria. First, the synthesis should be simple, inexpensive, and scalable. Second, one should be able to attach as many of the electron-withdrawing substituents as needed without reworking the entire synthetic strategy, preferably even in the presence of other ring substituents such as methyl groups, and ideally with regiocontrol. Third, the substituted cyclopentadienes should be readily converted to the corresponding substituted Cp anions, which themselves should be isolable and thermally stable as salts of common, non-toxic metal ions like Na^+. Fourth and finally, the substituents themselves should be sufficiently inert to withstand complexation to both early and late transition metal ion, and they should also be compatible with subsequent chemistry including catalytic transformations. The body of this article intends to demonstrate that perfluoroaryl substituents meet all four of these criteria.

2. Ligand synthesis

Early examples of perfluoroaryl-substituted ferrocenes were prepared by reactions of ferrocenyllithium with perfluoroarenes. The specific organometallic compounds obtained by this route are reviewed in Section 3.4.1. However, a *general* route to perfluoroaryl-substituted Cp complexes depends on the availability of the *free ligands* in *preparative quantities*. This section describes the synthesis of cyclopentadienes and sodium cyclopentadienides bearing perfluoroaryl substituents.



Scheme 1.

2.1. Cyclopentadienes bearing pentafluorophenyl substituents

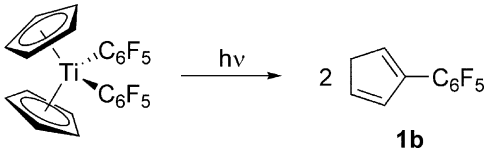
2.1.1. Early syntheses

The organocopper compound $CpCu(PBu_3)$ reacts with aryl iodides (Scheme 1) [89]. With iodopentafluorobenzene as the substrate, the major product is pentafluorobenzene, but small amounts of other products including 4% of (pentafluorophenyl)cyclopentadiene (C_6F_5CpH, **1**) are also obtained. Oxidative addition of the aryl iodide could be an initial mechanistic step; when the reaction was quenched with acetyl chloride instead of water, pentafluoroacetophenone was obtained instead of pentafluorobenzene, albeit with no change in the yield of **1** [89].

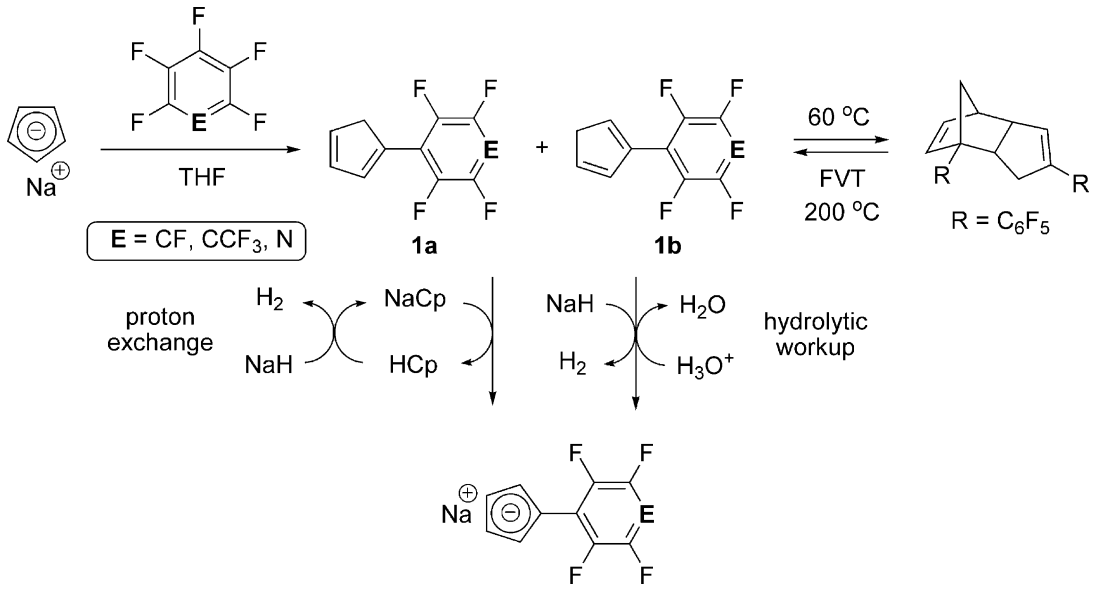
The titanocene derivative $Cp_2Ti(C_6F_5)_2$ undergoes photolytic decomposition to afford **1** (Scheme 2) [90,91]. The primary photoevent, presumed to be a ring-slip of one C_6F_5Cp ligand, exhibits unit quantum yield.

2.1.2. Synthesis by nucleophilic aromatic substitution

The direct reaction of NaCp with excess hexafluorobenzene (C_6F_6) under mild conditions affords diene **1aCF/1bCF** (Scheme 3, E = CF) [92]. The reaction is conducted in the presence of excess NaH, which traps the product in the anionic form so that starting material is not lost to proton exchange



Scheme 2.



Scheme 3.

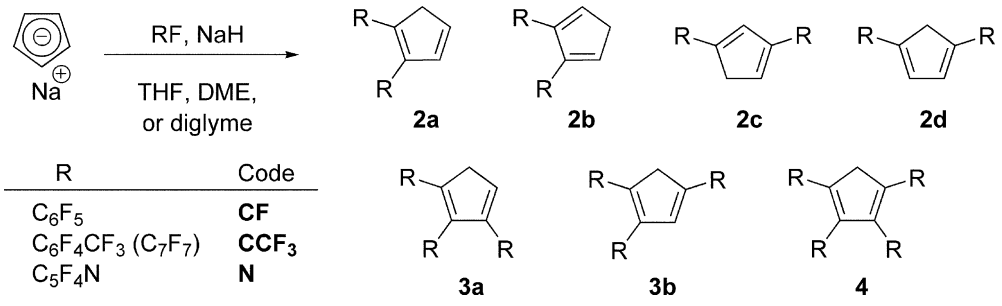
with the product. Diarylation is prevented by conducting the reaction below room temperature. In the original procedure [92], purification was accomplished by dimerization, recrystallization, and flash-vacuum-thermolytic cracking. Subsequent optimization of the workup and purification by flash chromatography enabled the product to be isolated directly (as a mixture of tautomers) in yields ranging from 65 to 80%; a detailed procedure has been accepted for publication in *Inorganic Syntheses* [93].

Cyclopentadienes bearing more than one C_6F_5 group are obtained in one-pot polyarylation reactions (Scheme 4). Excess NaH converts each product diene to its conjugate base, which is then available for the subsequent arylation. The reaction is most easily followed either by TLC or by working up small aliquots and examining the product by ^{1}H NMR spectroscopy; the methylene region (δ 3.2–4.5 ppm) is particularly diagnostic. The diarylated and triarylated cyclopentadienes are typically obtained as a mixture (**2aCF**, **2bCF**, **2cCF**, **2dCF**, **3aCF**, and **3bCF**) that must be separated by silica gel chromatography (tautomeric pairs **2a/2b** and **2c/2d** do not separate) [92,94]. Analogous mixtures are obtained when cyclopentadienyl anions are alkylated using 2-(perfluoroalkyl)ethyl triflates [81]. The vicinal diarylated isomer (**2aCF/2bCF**) is obtained only in small amounts and not reproducibly, however no effort has been made to optimize its preparation. The yields of the other products vary but are typically in the 15–40% range. Although regiocontrol (*vicinal* versus *distal*) is poor, no byproducts bearing *geminal* C_6F_5 groups are ever observed in these reactions. The tetraarylated cyclopentadiene **4CF** is obtained selectively under forcing conditions in 50–60% yield [95]. Treatment of any of these cyclopentadienes with excess sodium hydride in THF gives the corresponding substituted cyclopentadienylsodium compounds in high yield (the sodium salt of **2aCF/2bCF** was not reported) [92,94].

To date, no pentakis(perfluoroaryl)cyclopentadiene has been prepared by the nucleophilic aromatic substitution technique. Instead, reduction of the corresponding tertiary carbinol gives the desired diene **5** in 58% overall yield (Scheme 5) [96].

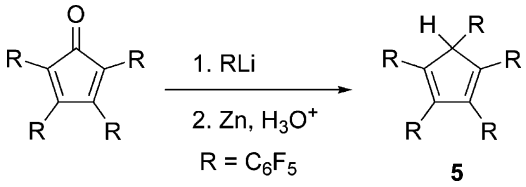
2.1.3. Cyclopentadienes bearing pentafluorophenyl and tert-butyl substituents

Cyclopentadienes bearing one *tert*-butyl and either one or two C_6F_5 substituents (**6** and **7**) were prepared by nucleophilic substitution (Scheme 6) [97]. The *tert*-butyl group directs the arylation exclusively to the *distal* carbons of the Cp ring. The number of C_6F_5 substituents is selected by adjusting the reaction temperature and the ratios of starting materials. The monoarylated diene **6** is obtained as an inseparable mixture of tautomers. Treatment of each cyclopentadiene with NaH afforded the corresponding substituted Cp anions as sodium salts in high yields.



R	Code
C_6F_5	**CF**
$C_6F_4CF_3$ (C_7F_7)	**CCF$_3$**
C_5F_4N	**N**

Scheme 4.

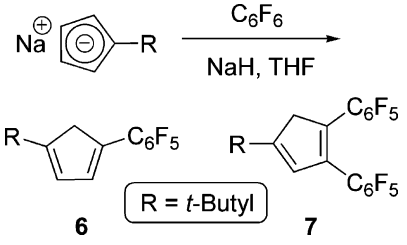


Scheme 5.

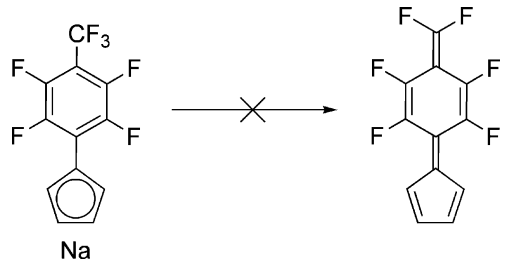
[Author's note: The published synthesis of **7** calls for K(^{t}BuCp) and KH, whereas we have found subsequently that sodium salts, as shown in Scheme 6, react more cleanly; see Section 2.5.]

2.2. Cyclopentadienes bearing perfluoro-4-tolyl substituents

Cyclopentadienes bearing one to four perfluoro-4-tolyl (C_7F_7) substituents are obtained by nucleophilic aromatic substitution reactions that are analogous to their C_6F_5-substituted counterparts (see Section 2.1) [98]. The monoarylated diene **1aCCF$_3$/1bCCF$_3$** is prepared using less than 1 equiv. of $C_6F_5CF_3$ to avoid diarylation (Scheme 3); upon cold hydrolytic workup the unreacted cyclopentadiene is removed with the solvent by evaporation. Using $C_6F_5CF_3$ the regiochemistry of arylation with respect to the perfluoroaryl moiety is exclusively *para* to the CF_3 group. Choice of reaction conditions (temperature, number of equivalents of $C_6F_5CF_3$, reaction time) selects moderately well for either the diarylated or triarylated dienes (**2CCF$_3$** or **3CCF$_3$**, Scheme 4) [98], and product separation based on the number of aryl substituents by flash chromatography is efficient. Regioselectivity with respect to the cyclopentadiene moiety is poor, and unfortunately neither the skeletal isomers nor the tautomers of the diarylated cyclopentadiene (**2aCCF$_3$**, **2bCCF$_3$**, **2cCCF$_3$**, and **2dCCF$_3$**) were separable by silica gel chromatography. On the contrary, the two skeletal isomers of the triarylated cyclopentadiene (**3aCCF$_3$** and **3bCCF$_3$**) separate easily. The tetraarylated cyclopentadiene **4CCF$_3$** is obtained selectively under forcing conditions. The corresponding pentakis(perfluoro-4-tolyl)cyclopentadiene is not known. Treatment of the monoarylated diene **1aCCF$_3$/1bCCF$_3$** with NaH in THF afforded the corresponding NaCp derivative. One could envision a fluoride elimination process analogous to that observed for $CpCF_3$ anions (Scheme 7), but no such reaction has been observed even at 100 °C.



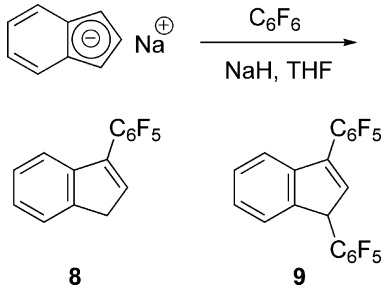
Scheme 6.



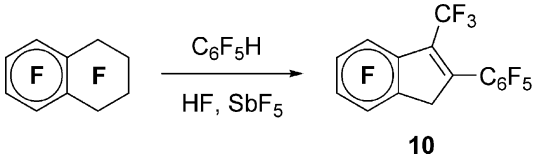
Scheme 7.

2.3. Cyclopentadienes bearing perfluoro-4-pyridyl substituents

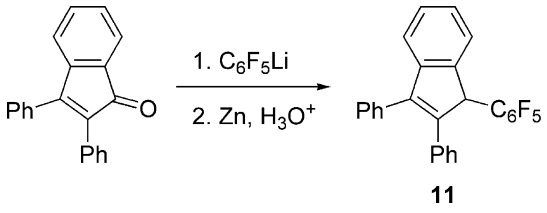
Cyclopentadienes bearing one or two perfluoro-4-pyridyl (C_5F_4N) substituents are obtained by nucleophilic aromatic substitution reactions that are closely analogous to those described above for C_7F_7 substituents (see Section 2.2) [99]. The monoarylated diene is obtained selectively as a mixture of tautomers (**1aN/2aN**) under mild conditions, using less than 1 equiv. of pentafluoropyridine (C_5F_5N) to prevent diarylation. Diarylated products are obtained selectively, and the skeletal isomers (**2aN/2bN** and **2cN/2dN**) are separable by flash chromatography, albeit not with particularly good resolution. Treatment of any of these cyclopentadienes with excess NaH in THF affords the corresponding substituted NaCp derivatives in high



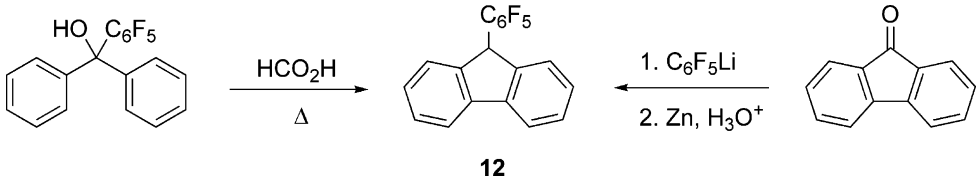
Scheme 8.



Scheme 9.



Scheme 10.



12

Scheme 11.

yields. [Author's note: The triarylated and tetraarylated homologues have been prepared in our laboratories, but these results have not been optimized and should be considered preliminary [100].]

2.4. Pentafluorophenyl-substituted indenes and fluorenes

The reaction of sodium or potassium indenide with C_6F_6 affords indenes with either one or two C_6F_5 groups (Scheme 8) [101]. Selection for mono- versus di-arylation is achieved by varying the temperature and the ratios of starting materials. No regioisomers of either **8** or **9** are observed. The electron-withdrawing effect of a C_6F_5 group at the 1-position of the indenyl anion prevents 1,1′-*gem*-diarylation.

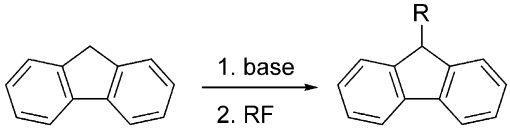
An indene bearing both a CF_3 group and a C_6F_5 group (**10**) was observed as a minor byproduct (13%) in an electrophilic rearrangement/defluorination of perfluoro-1-phenyltetralin (Scheme 9) and isolated in 90% purity by preparative GLC [102].

An indene derivative bearing two phenyl groups and one C_6F_5 group (**11**) was prepared by addition of C_6F_5Li to diphenylindone followed by dissolving-zinc reduction in 54% overall yield (Scheme 10) [96].

9-(Pentafluorophenyl)fluorene (**12**) has been prepared by three methods. Reduction of diphenyl(pentafluorophenyl)carbinol (Scheme 11) with 90% formic acid gave **12** as the major product (48%) [103] along with the expected triarylmethane (36%). A second, more deliberate synthesis of **12** was based on addition of C_6F_5Li to fluorenone (carbinol isolated in 45% yield) followed by reduction (70%) [104].

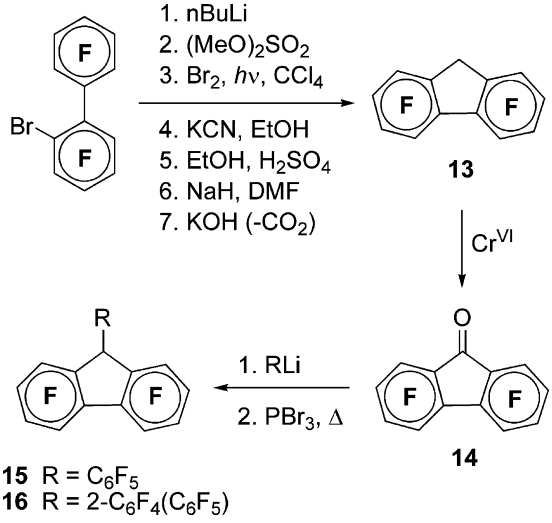
In a third, more recent approach, the technique of nucleophilic aromatic substitution has been applied to the synthesis of 9-perfluoroarylfluorenes (Scheme 12) [105].

Other highly fluorinated fluorenes have been prepared. Octafluorofluorene (**13**) is prepared in seven steps from 2-bromononafluorobiphenyl (Scheme 13) [106]. Oxidation to the corresponding fluorenone (**14**) is efficient (70%) [106], and subsequent organolithium addition provides an entry point to the 9-aryl derivatives (**15**, **16**) [107].



R = C_6F_5, $C_6F_4CF_3$, C_5F_4N

Scheme 12.



15 R = C_6F_5
16 R = 2-$C_6F_4(C_6F_5)$

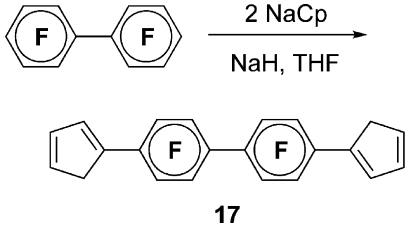
Scheme 13.

2.5. Cyclopentadienes bridged by the perfluoro-4,4′-biphenylene moiety

The reaction of decafluorobiphenyl with an excess of NaCp affords the bis(cyclopentadiene) derivative **17** [108] as a mixture of tautomers (Scheme 14). Although **17** slowly oligomerizes (Diels–Alder addition), reaction of freshly prepared material with NaH effects conversion to the corresponding bis(NaCp) derivative, which can be stored indefinitely in the dark and under nitrogen.

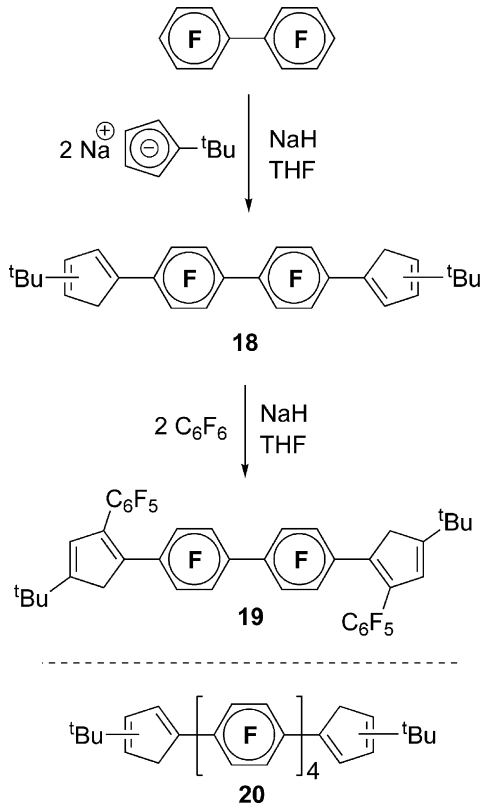
Arylation of Na(^{t}BuC$_5$H$_4$) furnishes the corresponding butylated derivative **18** (Scheme 15); no regioisomers are obtained in which arylation occurs *vicinal* to the *tert*-butyl group [109]. Further arylation of **18** afforded the bis(diene) **19**. When K(^{t}BuC$_5$H$_4$) was used instead, 4% of a coupled byproduct (**20**) was isolated along with **18** as the major product. Compounds **18**, **19**, and **20** are colorless crystalline solids and are structurally characterized.

Combining the regioselectivity of indene arylation and of substitution at decafluorobiphenyl furnished step-growth

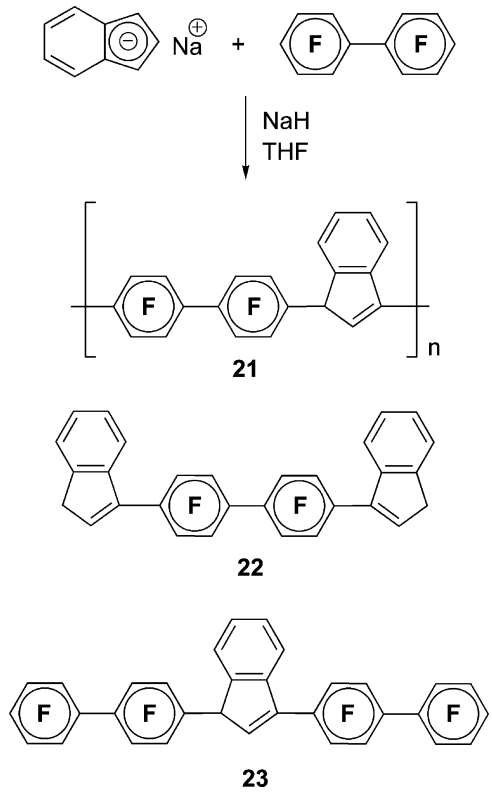


17

Scheme 14.



Scheme 15.



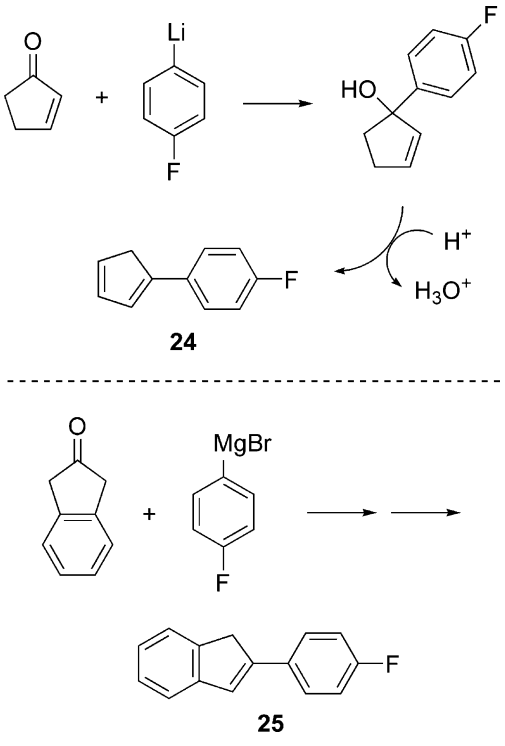
Scheme 16.

oligomers (**21** in Scheme 16, $n \sim 20$) [110]. Models for end group analysis (**22**, **23**) were prepared using extreme ratios of the two bifunctional starting materials.

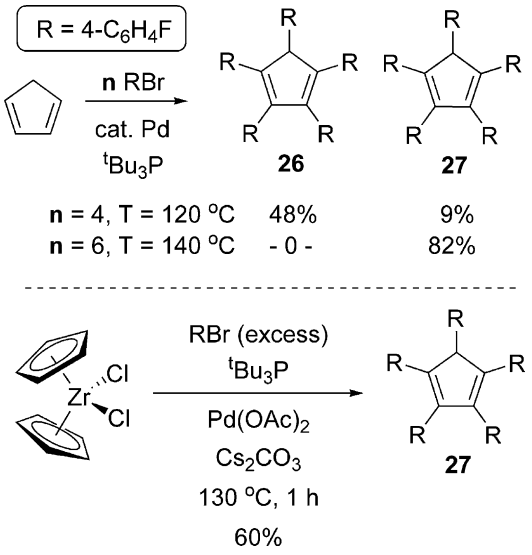
2.6. *Cyclopentadienes bearing partially fluorinated aryl substituents*

The topic defined by the heading of this section is beyond the scope of this review. This section illustrates the major synthetic strategies so that they can be compared with those used for perfluoroaryl substituents. One such strategy is addition of aryllithium or arylmagnesium bromides to cyclopentenones (Scheme 17) [111]. A key difficulty in this chemistry is conducting the dehydration step in a manner that will not lead to polymerization of the product arylcyclopentadiene (e.g., **24**). Arylindenes prepared in this manner (e.g., **25**) are not nearly as prone to polymerization [112]. This method can be used to prepare *per*fluoraryl-substituted cyclopentadienes and indenes, but the instability and low nucleophilicity of arylmetal reagents such as C_6F_5Li and C_6F_5MgBr often result in low yields. The tetracyclone addition chemistry shown in Scheme 5 is a notable exception, where there is no competing proton-exchange side reaction.

Cyclopentadiene undergoes palladium-catalyzed couplings with aryl halides in the presence of hindered phosphine ligands (Scheme 18) [113]. The reaction affords moderate control over the degree of arylation (e.g., **26** versus **27**). When Cp_2ZrCl_2 is used as the cyclopentadiene source [114], there is essentially



Scheme 17.



Scheme 18.

no control over the degree of arylation, but pentaarylcyclopentadienes (e.g., **27**) are typically formed in good yield (typically 50–80%).

2.7. Structural highlights

Cyclopentadienes bearing only perfluoroaryl substituents are typically crystalline solids, and several have been characterized by single-crystal X-ray diffraction. In the absence of vicinal substituents (Fig. 1), the aryl groups lie nearly in the same plane as the cyclopentadiene moiety, with typical Cp-aryl torsion angles of 5–10°. The overall structure of the cyclopentadiene is not significantly influenced by the identity of the perfluoroaryl substituent. With two or more vicinal aryl groups (Fig. 2), the compounds adopt propellar-type structures with larger torsion angles.

3. Synthesis of transition metal complexes bearing perfluoroaryl substituents

3.1. Titanium, zirconium, and hafnium complexes

The titanium half-metallocene complex **29** was prepared in 80% yield by the Me_3SiCl elimination route (Scheme 19) [115]. Even under forcing conditions using an excess of the starting silane (**28**, prepared from C_6F_5CpNa and Me_3SiCl in THF), only the half-metallocene was observed. Using the corresponding stannane (**30**, prepared from C_6F_5CpNa and Me_3SnCl in THF), the metallocene **31** was obtained in 51% yield [115].

In unpublished work in our own laboratories, we attempted to prepare **31** by metathesis reactions of $(C_6F_5Cp)Na$ with $TiCl_4(THF)_2$ or by reaction of $(C_6F_5Cp)Na$ with $TiCl_3(THF)_3$ followed by oxidative chlorination [116]. These reactions gave only intractible dark red solids. However a report of the synthesis of the bis(indenyl) complex **32** by analogous metathesis with the substituted indenyllithium appeared in a patent (Scheme 20) [117], albeit with neither analytical data nor assignment of

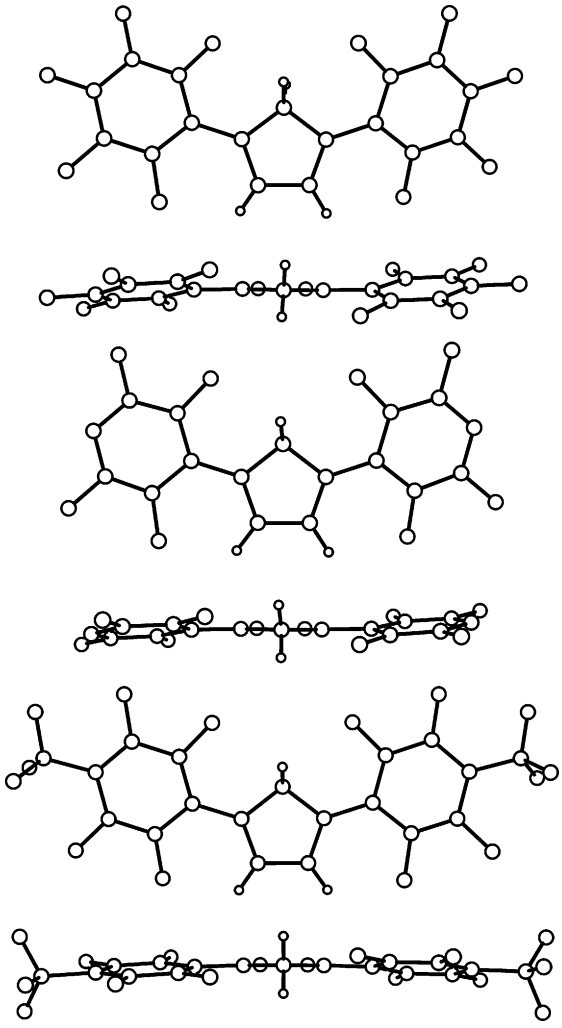


Fig. 1. Molecular structures of **2dCF** [94], **2dN** [99], and **2dCCF3** [98].

the product stereochemistry (*rac* versus *meso*). Other C_6F_5-substituted Cp titanium complexes that have been implicated as reactive intermediates but not isolated are described in Section 6.2.

Zirconocene and hafnocene derivatives bearing perfluoroaryl substituents are amenable to synthesis by metathesis of Zr–Cl or Hf–Cl bonds with [(perfluoroaryl)cyclopentadienyl]sodium compounds (Scheme 21). The C_6F_5-substituted compounds **33**–**36** and **40** are obtained quickly and in moderate to high yields as thermally stable, pale yellow crystalline solids. The triarylated complex **37** is obtained in lower yield and is also thermally unstable, a feature ascribed to the low basicity of the triarylated ligand. Analogous metallocene complexes bearing $C_6F_4CF_3$ (**38**) and C_5F_4N substituents (**39**) are obtained similarly. Additional complexes deriving from ligand substitutions and abstractions of group 4 metallocene wedge ligands are described in Section 6.3.

3.2. Molybdenum and tungsten complexes

Several Cp–Mo and Cp–W complexes bearing ring C_6F_5 substituents have been prepared. All of the synthetic work in this

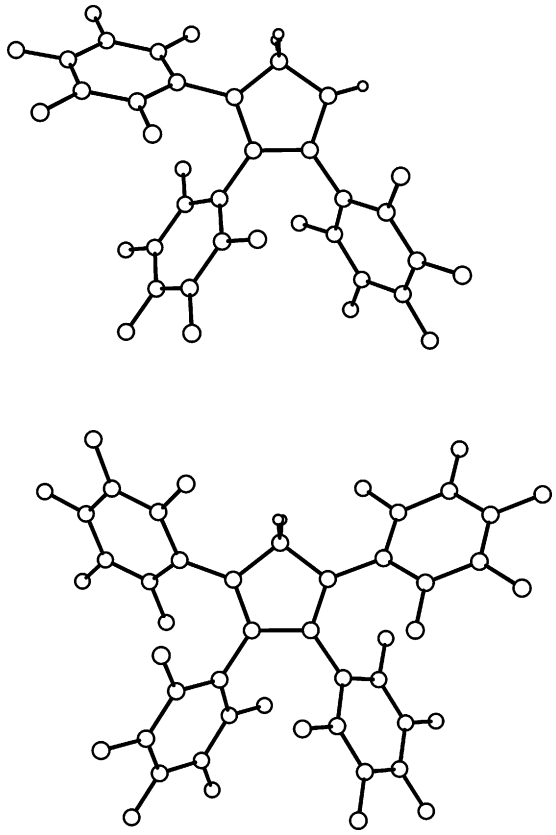
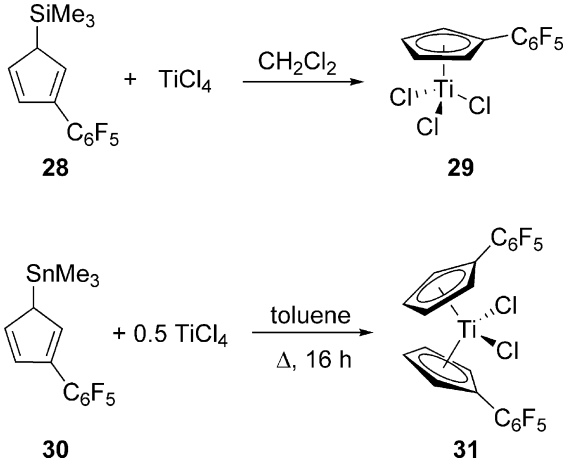
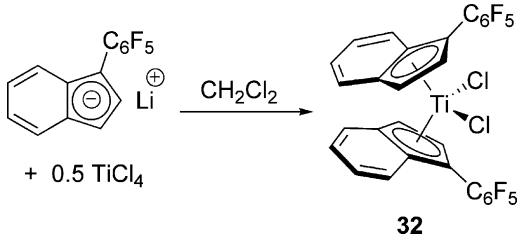


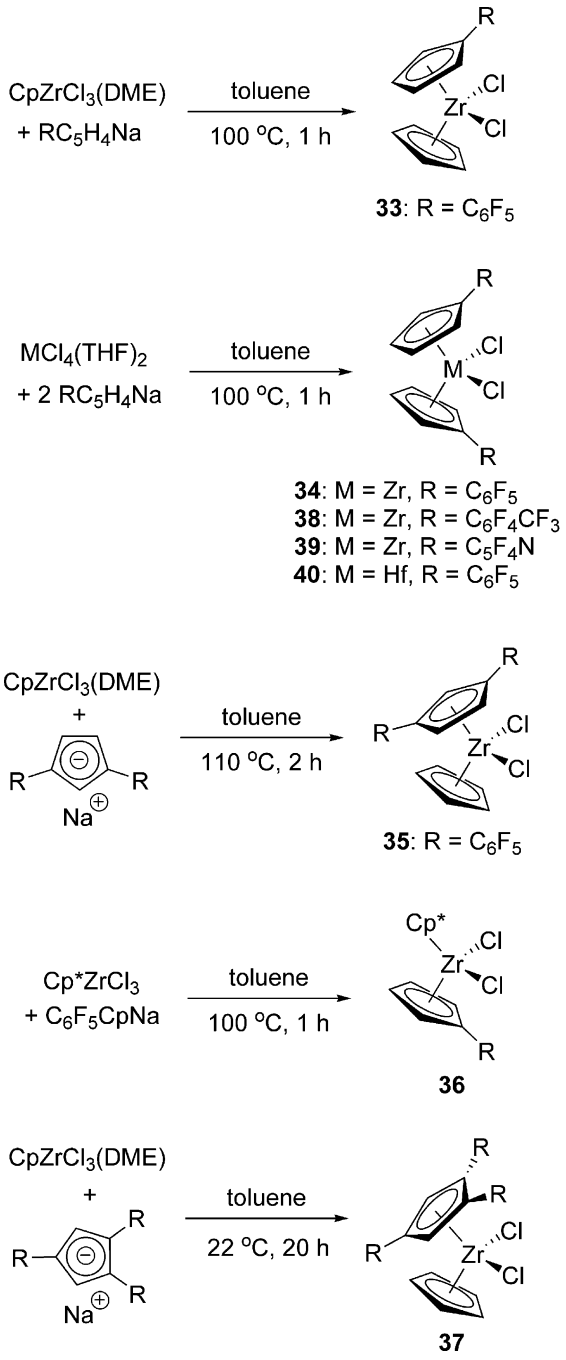
Fig. 2. Molecular structures of **3aCF** [94] and **4CF** [95].



Scheme 19.



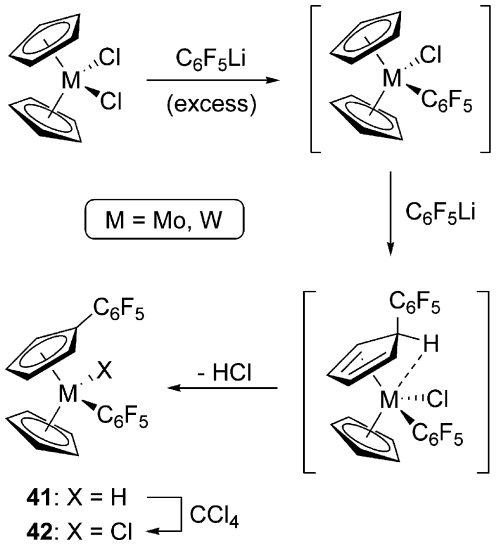
Scheme 20.



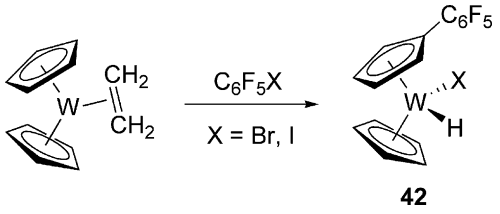
Scheme 21.

area to date has involved the attack of C_6F_5 synthons on Cp ligands already coordinated to Mo or W. Reactions of group 6 metallocene dichlorides with excess C_6F_5Li result in substitution at the Cp ligand and in the metallocene wedge (Scheme 22) [118,119], with concomitant formal hydride transfer to the metal center. The ^{19}F NMR spectrum of the hydride complex **41** (M = Mo) suggested a significant thermal barrier to M–C_6F_5 bond rotation.

A similar outcome is observed when starting with a W^{II} complex and with reversed charge at the C_6F_5 *ipso* carbon of the synthon (Scheme 23) [120]. Trapping experiments suggest that the halogen is initially transferred to the W center as X^+ (X = Br,



Scheme 22.



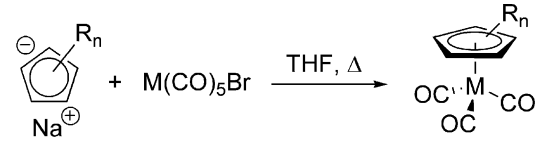
Scheme 23.

I) to afford a W^{IV} intermediate and a C_6F_5 anion. Thus the chemistry in Schemes 22 and 23 is mechanistically consistent.

3.3. Manganese and rhenium complexes

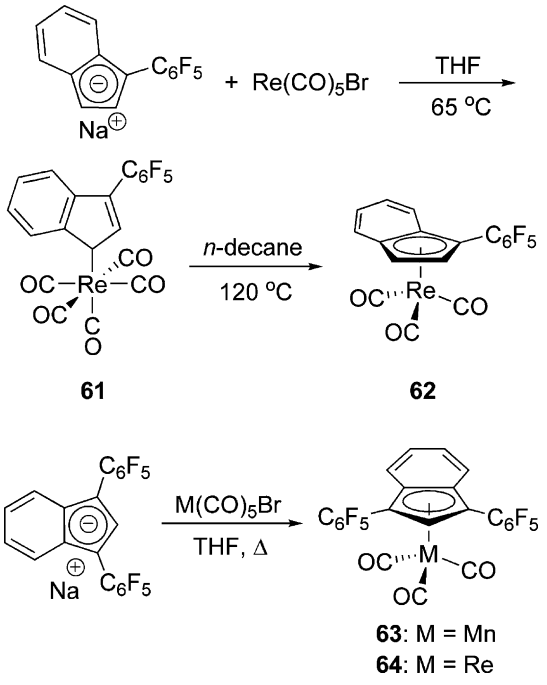
A series of piano stool complexes has been prepared by reactions of NaCp ligands bearing pentafluorophenyl [92,94,95], perfluoro-4-tolyl [98], and perfluoro-4-pyridyl [99] substituents (see Section 2) with a metal carbonyl halide precursor (Scheme 24).

Indenyl complexes bearing perfluoroaryl substituents have also been prepared by reactions of substituted indenylsodium



		substituent positions					
	R	1	12	13	123	124	1234
M = Mn	C_6F_5	**43**		**44**	**45**	**46**	**47**
	C_7F_7	**48**				**49**	
	C_5F_4N	**50**	**51**	**52**			
M = Re	C_6F_5	**53**		**54**	**55**	**56**	**57**
	C_5F_4N	**58**	**59**	**60**			

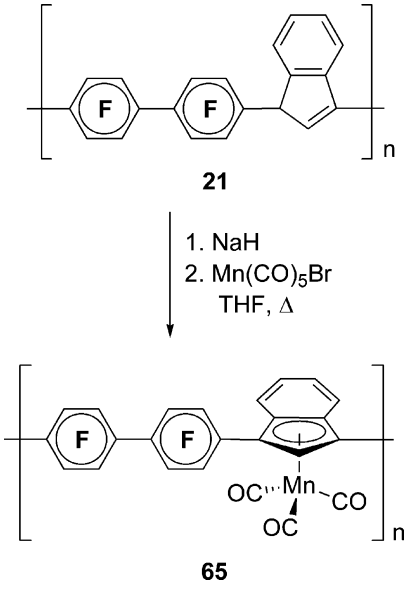
Scheme 24.



Scheme 25.

ligands and a metal carbonyl halide (Scheme 25) [101,110]. An η^1-indenylrhenium pentacarbonyl intermediate (**61**) was isolated and subsequently thermolyzed to afford the corresponding η^5-indenylrhenium tricarbonyl product (**62**). Intermediates of lower hapticity were not observed in reactions leading to the diarylated analogues (**63**, **64**).

Coordination of the $Mn(CO)_3$ fragment to oligo[1,3-indenylene-4,4′-octafluorobiphenylene] (**21**) gave a corresponding oligomeric species (**65**) in which about 85% of the indenyl units had reacted (Scheme 26) [110]. The infrared spectrum of the coordinated $Mn(CO)_3$ fragment compared favorably to the well-characterized model (**63**).



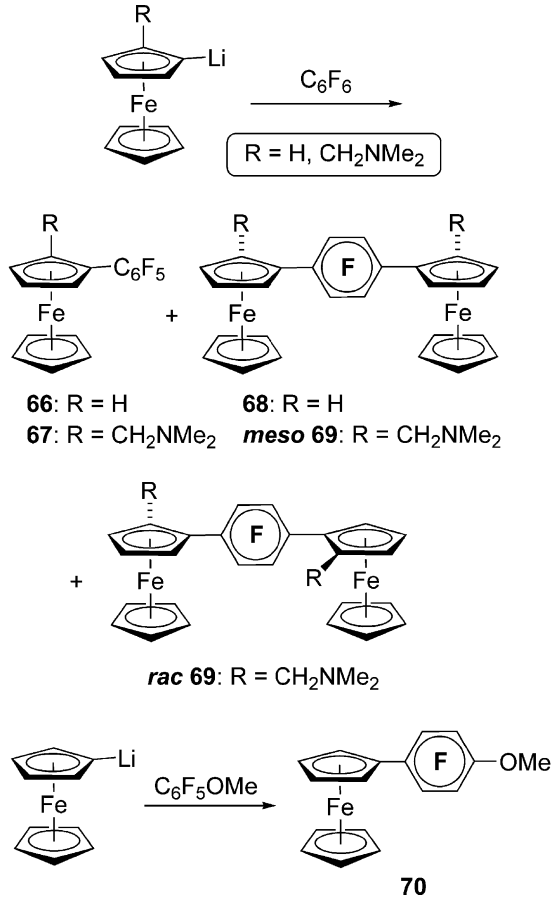
Scheme 26.

3.4. Iron and cobalt complexes

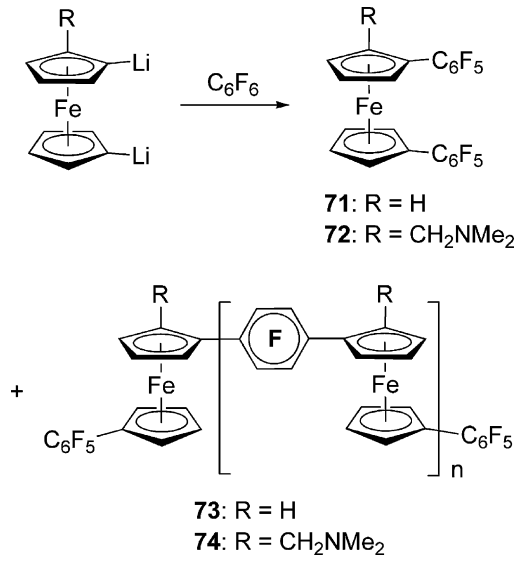
Although this section focuses on two primary methods of deliberate synthesis, the complex (C_6F_5Cp)CpFe has been reported as a byproducts on other occasions. Photolysis of iodoferrocene in the presence of C_6F_6 gave (C_6F_5Cp)CpFe in 32% yield (58% based on unrecovered iodoferrocene) [121]. The reaction of K[CpFe(CO)$_2$] with C_6F_5Br gave a complex mixture of products, from which (C_6F_5Cp)CpFe was isolated by silica gel chromatography in 12% yield [122].

3.4.1. Arylation of lithioferrocenes

Ferrocene undergoes metalation by either strong bases (e.g., *n*-BuLi) [123–129] or electrophilic reagents (e.g., mercuric acetate) [130]. Lithioferrocenes undergo direct nucleophilic substitution reactions with perfluoroarenes. The observed products depend on ratios of starting materials (Scheme 27, R = H). For example, the reaction of monolithioferrocene with C_6F_6 gives either the arylferrocene (**66**) or the diferrocenyltetrafluorobenzene (**68**) [131–133]. *N*,*N*-Dimethylaminomethylferrocene undergoes regioselective monolithiation (Scheme 27, R = CH_2NMe_2) and arylation with C_6F_6 to afford the analogous arylferrocene (**67**) and dimetallic complex (**69**). The diastereomers (*meso*-**69** and *rac*-**69**) were separated by selective extraction, and the structure of *meso*-**69** was confirmed by crystallographic analysis of the bis(methiodide) derivative. The preparation of **70** illustrates how formation of the dimetallic species can be prevented if the starting arene already bears one non-fluorine substituent [132].



Scheme 27.

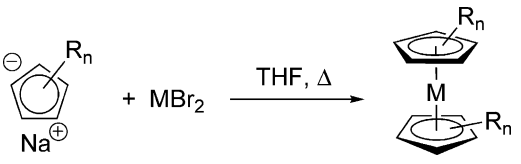


Scheme 28.

When dilithioferrocene reacts with C_6F_6, a mixture of products is obtained (Scheme 28, R = H). Using excess C_6F_6, the diarylated ferrocene (**71**) is the major product. Using 1 equiv. of C_6F_6, one obtains a mixture of ferrocenylene-tetrafluorophenylene oligomers (**73**). The initial difficulties encountered in assigning the structure of the diiron complex (**73**, $n = 1$) can probably be ascribed to the low solubility of the compound and probably also to the poor sensitivity of the NMR instrumentation available at the time [132]. Subsequent isolation, purification, and complete characterization of **73** ($n = 1$, see Section 4.2) confirmed the structure shown [134]. Looking back on the original NMR data [132], the signal arising from the *p*-tetrafluorophenylene group is slightly shifted and shows a "complex" coupling pattern, consistent with a mixture of the diiron complex and the next highest oligomer (**73**, $n = 1, 2$). The substituted oligomers (**74**) are sufficiently soluble in common solvents that their molecular weight ($M_n \sim 3500$; $n \sim 9$) is readily characterized by NMR spectroscopic end group analysis. The "electronic communication" between the ferrocenyl units in **68** and **73** ($n = 1$) is barely detectable by square wave voltammetry [133,134], in contrast to fairly strong electrochemical coupling observed in phenylene-linked diferrocenes [135].

3.4.2. Synthesis from perfluoroaryl-substituted cyclopentadienyl anions

Homoleptic ferrocenes and cobaltocenes are readily prepared by ligand substitution reactions of cyclopentadienyl anions with iron and cobalt halides. This method applies well to the synthesis of ferrocenes and cobaltocenes bearing perfluoroaryl groups (Scheme 29) [94]. The electron-withdrawing effects of the C_6F_5 groups (see Section 5.2 below) stabilize the substituted cobaltocenes toward oxidation. For example, **83** is an air-stable compound even in benzene solution and in the presence of dilute aqueous acid. Dissolution of the C_6F_5-substituted cobaltocenes



		substituent positions				
	R	1	12	13	123	124
M = Fe	C_6F_5	**74**		**75**	**76**	**77**
	C_7F_7	**78**				
	C_5F_4N	**79**	**80**	**81**		
M = Co	C_6F_5	**82**		**83**	**84**	**85**

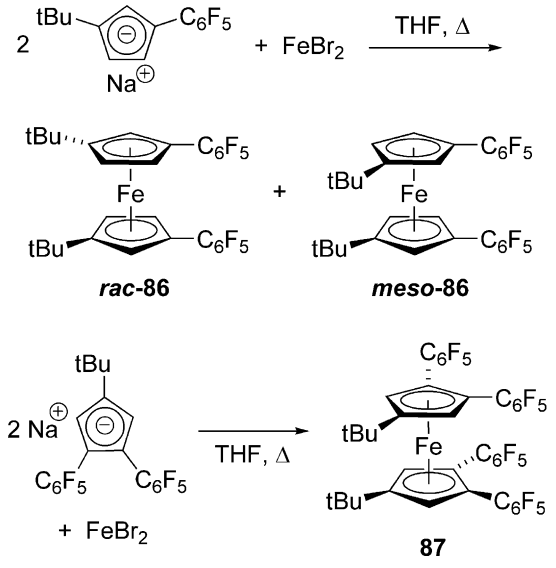
Scheme 29.

83–85 in D_2SO_4 affords orange solutions that exhibit ^1H and ^{19}F NMR spectra consistent with the corresponding diamagnetic cobaltocenium bisulfates. Oxidation of the diarylated cobaltocene **82** with air and dilute aqueous hydrochloric acid enabled isolation of the corresponding cobaltocenium ion as the air-stable hexafluorophosphate.

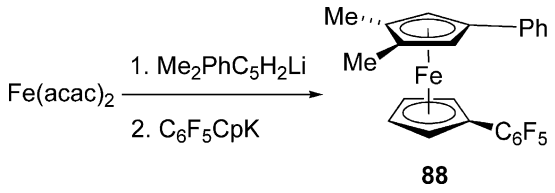
The presence of two different substituents on a Cp ligand leads, in general, to a diastereomeric mixture of homoleptic ferrocenes (Scheme 30). The butylated, arylated Cp ligand **6** afforded such a mixture (**86**), which was separated by fractional crystallization. The diarylated ligand **7** furnished the corresponding tetraarylated ferrocene **87** [97].

Mixed ferrocenes can sometimes be prepared by sequential addition of different cyclopentadienyl ligand sources to a suitable metal precursor (Scheme 31). This method led to the preparation of the mixed ferrocene **88** albeit as the minor product isolated by fractional crystallization [136].

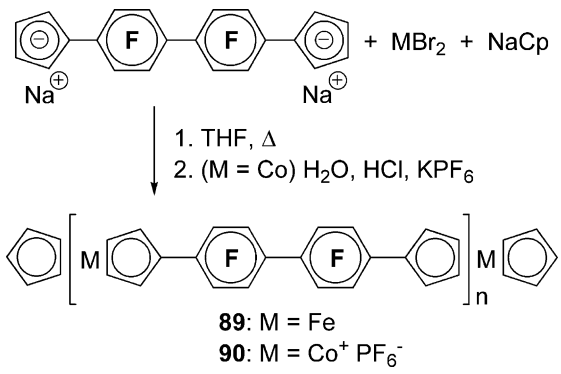
Reactions of an octafluorobiphenylene-linked bis(cyclopentadienyl) ligand (**17**) with Fe^{II} and Co^{II} sources give oligomeric species (Scheme 32) [108]. NaCp is added as a "capping" ligand, enabling dimetallic and trimetallic species (**89**, **90**;



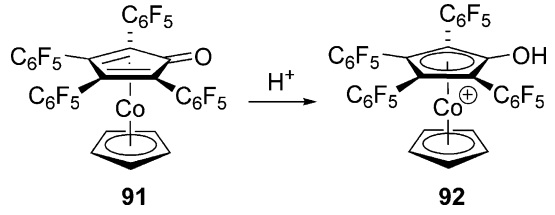
Scheme 30.



Scheme 31.



Scheme 32.



Scheme 33.

$n = 1, 2$) to be separated from the otherwise intractable product mixtures by liquid chromatography. The cobalt derivatives are isolated as the corresponding cobaltocenium hexafluorophosphates (**90**).

Tetracyclone complexes are beyond the scope of this review, even though several highly fluorinated examples (e.g., **91**) have been prepared. These complexes are mentioned here only to make the point that their conjugate acids can be viewed formally as hydroxy(tetraaryl)cyclopentadiene complexes, as in the case of the "mixed cobaltocene" **92** (Scheme 33) [137].

4. Structure and dynamics

Table 1 presents the published record of perfluoroarylated Cp complexes that have been crystallographically characterized. Instead of displaying each of these structures here, cross-cutting themes are introduced and illustrated in the following four sections.

4.1. General structural features

Attachment of perfluoroaryl groups to Cp ligands ordinarily has no significant effect on the *general* structural features of Cp complexes. Because of the relatively small amount of

Table 1
Crystallographically characterized perfluoroarylated Cp complexes

Complex	CSD code	References
(η^5-$CF_3C_6F_4C_5H_4)_2ZrCl_2$ (**38**)		[98]
[η^5-1,2,4-$(C_6F_5)_3C_5H_2$]$CpZrCl_2$ (**37**)	EYUSOG	[164]
(η^5-$C_6F_5C_5H_4)_2Hf(CH_3)_2$ (**100**)	EYUSUM	[164]
[η^5-1,2,4-$(C_6F_5)_3C_5H_2$]$Mn(CO)_3$ (1/2 C_6D_6) (**46**)	ACEDUH	[94]
[η^5-1,2,3,4-$(C_6F_5)_4C_5H$]$Mn(CO)_3$ (**47**)	MICRUL	[95]
(η^5-$CF_3C_6F_4C_5H_4$)$Mn(CO)_3$ (**48**)		[98]
[η^5-1,2,4-$(CF_3C_6F_4)_3C_5H_2$]$Mn(CO)_3$ (**49**)		[98]
[η^5-1,3-$(C_5F_4N)_2C_5H_3$]$Mn(CO)_3$ (**52**)		[99]
[η^5-1,3-$(C_6F_5)_2C_5H_3$]$Re(CO)_3$ (**54**)	ACEFAP	[94]
[η^5-1,2,4-$(C_6F_5)_3C_5H_2$]$Re(CO)_3$ (**55**)	ACEFET	[94]
[η^5-1,2,3,4-$(C_6F_5)_4C_5H$]$Re(CO)_3$ (**56**)	MICSAS	[95]
[η^5-$(C_5F_4N)C_5H_4$]$Re(CO)_3$ (**58**)		[99]
[η^1-3-$(C_6F_5)C_9H_6$]$Re(CO)_3$ (**61**)	QEWVAP	[101]
[η^5-1-$(C_6F_5)C_9H_6$]$Re(CO)_3$ (**62**)	QEWVET	[101]
[η^5-1,3-$(C_6F_5)_2C_9H_5$]$Re(CO)_3$ (**64**)	QEWVIX	[101]
[η^5-$(C_6F_5)C_5H_4$]$_2$Fe (**71**)	LOTDAZ	[136]
[η^5-$(C_6F_5)C_5H_4$][η^5-1-(C_6F_5)-2-$(Me_2NCH_2)C_5H_3$]Fe (**72**)	XEQKEJ	[134]
(η^5-$(C_6F_5)C_5H_4$)(η^5-1-Ph-3,4-$Me_2C_5H_2$)Fe (**58**)	LOTCUS	[136]
[η^5-1-(C_6F_5)-2-$(Me_2NCH_2)C_5H_3$]CpFe (**67**)	XEQKAF	[134]
[η^5-1,2,4-$(C_6F_5)_3C_5H_2$]$_2$Fe (4 C_6H_6) (**77**)	ACEDIV	[94]
rac-[η^5-1-(C_6F_5)-3-^{t}BuC_5H_3]$_2$Fe (*rac*-**86**)	ADIQAF	[97]
meso-[η^5-1-(C_6F_5)-3-^{t}BuC_5H_3]$_2$Fe (*meso*-**86**)	ADIQEJ	[97]
[η^5-1,2-$(C_6F_5)_2$-4-^{t}BuC_5H_2]$_2$Fe ($CDCl_3$) (**87**)	ADIQAF	[97]
[1,4-{CpFe[η^5-2-$(Me_3NCH_2)C_5H_3$-1-]}$_2C_6F_4$]I_2 (3 $CHCl_3$) (**69**.2MeI)	XEQKIN	[134]
CpFe[η^5-C_5H_4-(4,4′-$C_6F_4C_6F_4$)-η^5-C_5H_4]FeCp (**89**, $n=1$)	QANZEK	[108]
[η^5-$(C_6F_5)C_5H_4$]Fe[η^5-C_5H_4-(1,4-C_6F_4)-η^5-C_5H_4]Fe[η^5-C_5H_4 (C_6F_5)] (**73**, $n=1$)	XEQJUY	[134]
[η^5-1,2,3-$(C_6F_5)_3C_5H_2$]$_2$Co (**55**)	ACEDOB	[94]

available structural data, exceptions are often limited to single examples. For $CpM(CO)_3$ complexes (M = Mn, Re), unchanged parameters include M–Cp(centroid) distances, M–CO and C–O distances, and OC–M–CO angles. In the complex (4-$CF_3C_6F_4C_5H_4$)$Mn(CO)_3$ (**48**), the C–C distances of the Cp ligand exhibited a slight alternation with the longest bond opposite the substituent [98], but the corresponding perfluoro-4-pyridyl substituted $CpRe(CO)_3$ did not exhibit this feature [99]. $CpM(CO)_3$ complexes (M = Mn, Re) bearing four C_6F_5 groups showed slight (0.02–0.04 Å) elongation in the M–Cp(centroid) distances, a distortion that could be ascribed to either a steric or electronic effect (e.g., M–Cp bond becoming "ionic") [95]; however the $M(CO)_3$ tripods were undistorted.

For ferrocenes and cobaltocenes, unchanged parameters include the Fe–Cp(centroid) distances and the linear Cp–Fe–Cp (axial) angle. Even in the highly hindered complex **87** the axial angle is distorted only about 6° from linear. For group 4 metallocene complexes, unchanged parameters include the M–Cp(centroid) distances, the Cp(centroid)-M–Cp(centroid) angle, and the distances and angles among the wedge ligands. The most "extreme" example to date is the zirconocene dichloride **37**, which shows a lengthening (0.09 Å) of the Cp–Zr bond for the substituted ligand and a slight widening (about 2°) in the Cp–Zr–Cp angle. Otherwise the triarylated Cp ligand in **37** is neither distorted nor "slipped." To recapitulate, perfluoroaryl groups do not cause significant distortions in Cp complexes, a point that becomes important in understanding electronic substituent effects (see Section 5).

4.2. Arene stacking

Fluoroaromatic and non-fluorinated aromatic systems often engage in arene stacking [138]. This phenomenon is sufficiently general and parametrically reliable that one can envision using arene stacking in the three-dimensional design of organic materials (i.e., "crystal engineering"). For the present discussion, two structural parameters are particularly useful. The intercentroid distance is the distance between the respective centroids of the two C_6 rings. The centroid-plane distance is the distance between the centroid of one C_6 ring and the least squares plane defined by the second C_6 ring. When these two distances are identical, then the stacked arenes are "aligned;" if not, they are "slipped." The first perfluoraryl-substituted Cp complexes demonstrating arene stacking phenomena were the ferrocenes **71** and **72** (Fig. 3) [136]. In the homoleptic ferrocene **72**, the transannular stacking arrangement is a "slipped stack," with an intercentroid distance of 3.58 Å and a centroid-plane distance of 3.28 Å. In the mixed ferrocene **72**, the arrangement is not closer, but it is better aligned, with an intercentroid distance of 3.54 Å and a centroid-plane distance of 3.38 Å. While stacking is to be expected in the mixed ferrocene, its occurrance in the homoleptic ferrocene warrants rationalization. The "slipped stack" minimizes the distances between 2-, 3-, 5-, and 6-carbons of the C_6F_5 groups with fluorines on the opposite ring, a simple but compelling electrostatic model [136].

Subsequently numerous other perfluoroaryl-substituted Cp complexes have revealed two general types of arene stacking behavior in the crystalline state: (1) intramolecular stacking of

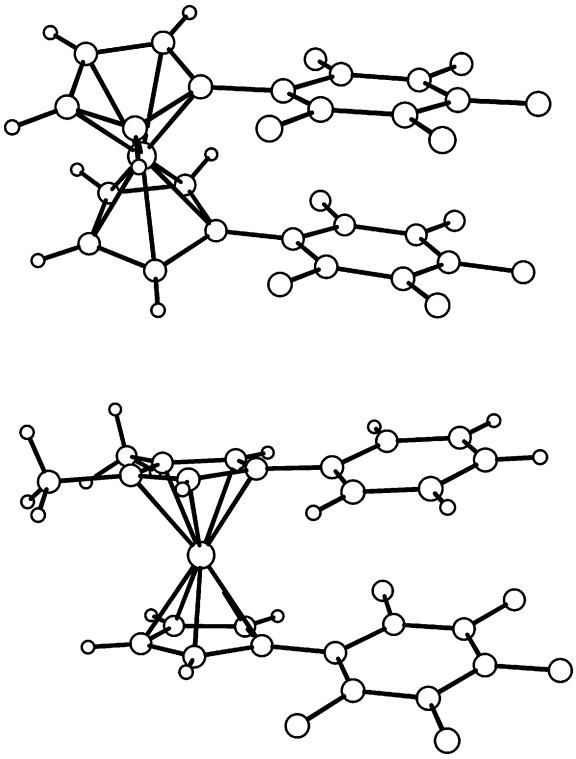


Fig. 3. Molecular structures of **71** (top) and **88** [136] showing arene stacking phenomena.

C_6F_5 groups; (2) stacking of C_6F_5 groups with solvent (typically benzene) or with Cp ligands. In principle, intermolecular C_6F_5/C_6F_5 stacking is also possible but has not been reported, although unpublished results from our laboratory have revealed intermolecular stacking in $(CH_3C_6F_4C_5H_4)_2Fe$ [116].

With the diastereomeric butylated complexes *rac*-**86** and *meso*-**86**, mutual repulsion of the *tert*-butyl groups allows arene stacking in the *rac* isomer, but in the *meso* isomer, alignment of the C_6F_5 groups would also require eclipsing the *tert*-butyl groups, and stacking does not occur [97]. The diiron complex **73** exhibits "double decker" arene stacking about the central tetrafluorophenylene group (Fig. 4) [134]. The stacking parameters are similar to those observed for the diarylferrocenes **71** and **72**.

The triarylated $CpMn(CO)_3$ complex **46** crystallizes with a molecule of C_6D_6 sandwiched between two C_6F_5 groups (Fig. 5) [94]. The solvent is somewhat disordered, but on the other hand, the adduct was stable enough to collect data on a point-detector instrument at room temperature. These arene stacking phenomena are not limited to metal complexes; the tetraarylated cyclopentadiene **4CF** also crystallizes with $1/2C_6H_6$ in a manner similar to that shown for **46**.

The hexaarylated ferrocene **77** crystallizes with four molecules of C_6H_6. The molecular structure includes *two* transannular C_6F_5/C_6F_5 stacks, and the packing diagram reveals stacking chains comprising one instance of intramolecular C_6F_5/C_6F_5 stacking and the benzene solvate [94]. This composition is highly labile toward desolvation (Fig. 6).

The diarylated ferrocene **71** shows, in addition to intramolecular C_6F_5/C_6F_5 stacking (see above), intermolecular stacking of C_6F_5 groups with neighboring Cp groups (Fig. 7).

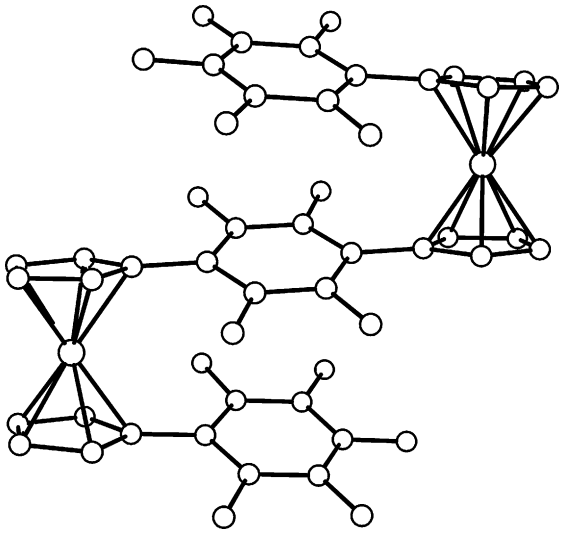


Fig. 4. Molecular structure of **73** showing arene stacking [134].

4.3. Conformational properties

4.3.1. Cp-aryl torsional angles

The Cp-aryl torsional angle is a soft parameter with preferences that are perhaps on the same order as crystal packing forces. Unhindered Cp-aryl torsions typically lie in the 0–50° range, and there are no clear trends, for instance, as a function of early-versus-late transition metals. However, when two perfluoroaryl groups occupy vicinal sites on a Cp ligand, the torsional angles become larger to minimize the vicinal repulsions. For example, the two Cp–C_6F_5 interplanar torsional angles in **54** are 23° and 39°; both torsions are unhindered. In **55** the "isolated" Cp–C_6F_5 torsional angle is 42°, whereas the torsional angles for the two *vicinal* Cp–C_6F_5 groups are 66° and 51°. In **56** the "inner" Cp–C_6F_5 torsional angles are 61° and 57°, while the "outer" angles are 36° and 49°. None of the latter three structures have solvents of crystallization. Comparison of the first and last examples shows that even this *vicinal* versus non-*vicinal* trend is rather weak.

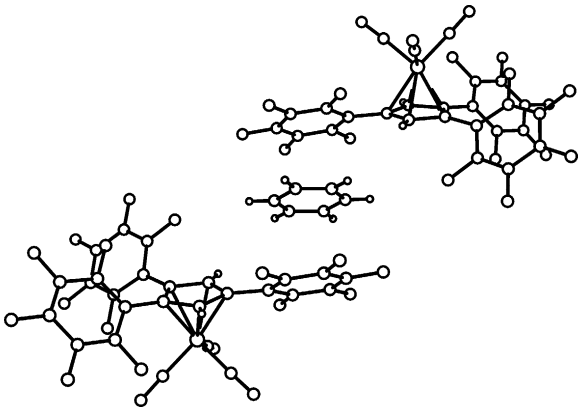


Fig. 5. Partial packing diagram of crystalline **46** showing C_6D_6 solvate [94].

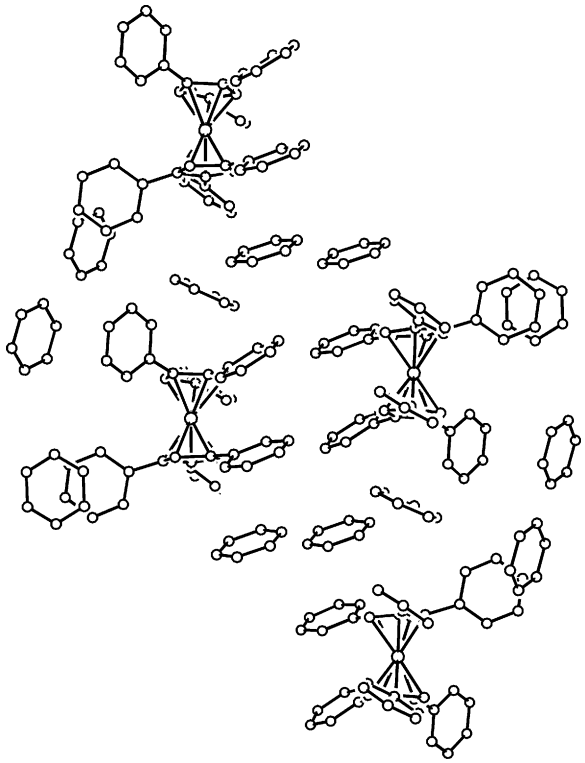


Fig. 6. Partial packing diagram of crystalline **77** showing C_6H_6 solvates [94].

Cp-aryl torsions have also been analyzed in solution using dynamic NMR spectroscopy. Perfluoroaryl groups are easier to analyze than phenyl groups, because the inherent dispersion of ^{19}F NMR gives rise to a much wider kinetic window [94]. In piano stool complexes, rotations of *vicinal* Cp–C_6F_5 bonds have been measured in several cases. In **55** for example, the "isolated" Cp–C_6F_5 torsion is still in fast exchange at −90 °C, whereas decoalescence of the *ortho* fluorines occurs below −50 °C. The rate of Cp–C_6F_5 bond rotation at −50 °C was about 11 kHz, and an Eyring analysis afforded an enthalpy of activation ($\Delta H^{\ddagger}$) of 9(1) kcal mol^{-1}. For the both of the tetraarylated complexes (**47** and **57**), the barriers to rotation of the "outer" Cp–C_6F_5 groups was 8(1) kcal mol^{-1}, while the "inner" Cp–C_6F_5 were fixed at all temperatures [95]. In comparison, the barrier to rotation of the "inner" Cp–C_6H_5 groups in (η^5-Ph_4C_5H) complexes is about 9 kcal mol^{-1} [139]. None of the perfluoroarylated piano stool complexes showed evidence of restricted rotation of the Cp ligand with respect to the $M(CO)_3$ tripod.

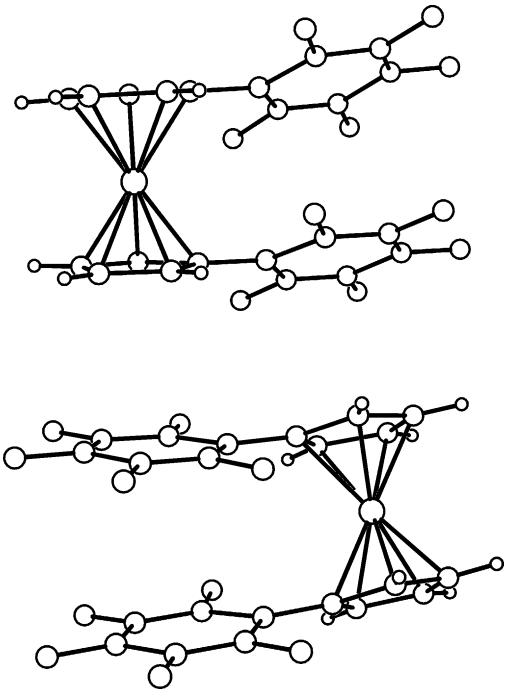


Fig. 7. Partial packing diagram of crystalline **71** showing intramolecular Cp–C_6F_5 stacking [136].

4.3.2. Axial conformations of parallel metallocene

Most of the conformational effects in parallel metallocenes are based on analyses of ferrocenes and cobaltocenium ions bearing bulky, roughly isotropic groups such as *tert*-butyl or trimethylsilyl [140]. One might expect aryl-substituted ferrocenes to differ for two main reasons. First, aryl groups are flat, not spherical. Transannular conformational preferences might couple with Cp-aryl preferences giving rise to correlated or geared motions [139,141]. Finally with perfluoroaryl substituents there is the additional issue of *attractive* forces arising from arene stacking. Again ^{19}F NMR is a useful tool because its high intrinsic dispersion facilitates signal-counting and symmetry-based ground-state structural assignment in the slow-exchange regime, which in ideal cases can be compared to crystallographic data.

Fig. 8 presents a typical analysis carried out on the hexaarylated ferrocene **77**. The rotamer diagram presents the ten canonical conformations and their point group symmetries, including the four pairs of enantiomers (**b/j**, **c/i**, **d/h**, and **e/g**). Filled circles are the C_6F_5 substituents, and open circles are hydrogens. Eclipsed and staggered conformers (**e** and **s**, respectively) are assigned enthalpies (subscripts) based on an arbitrary scale in which each eclipsing interaction equals +1 and each gauche interaction equals +0.5 [140]. In this analysis, the most stable conformer is **c/i** (one eclipsing interaction), which is the observed structure with six trimethylsilyl substituents [142]. With six C_6F_5 substituents, the crystal structure (Fig. 6) adopts the **e/g** structure, albeit with four molecules of benzene also present in the unit cell. At this point one will observe that there is no simple enthalpic "cost per interaction" for eclipsing C_6F_5/C_6F_5 groups that will predict the **e/g** conformer as the ground state. Moreover if the complex adopts the **e/g** ground state structure in solution, the rotamer diagram suggests that the barrier to racemization (via the staggered conformer **f**) should be negligible. The observed barrier (based on dynamic ^1H NMR spectroscopic analysis) is 11(2) kcal mol^{-1}, exactly the same barrier observed for the [1,2,4-$(Me_3Si)_3C_5H_2]_2Fe$ [142]. However replacing the "isolated" C_6F_5 groups of **77** with *tert*-butyl groups (i.e., complex **87**) results in a significantly higher axial rotational barrier of 17(2) kcal mol^{-1} and a solid state structure that is closest to the staggered conformer **d/h**. This increase can be rationalized as follows. Based on Fig. 8, racemization of any enantiomeric pair of rotamers proceeds through rotamer **f**. In

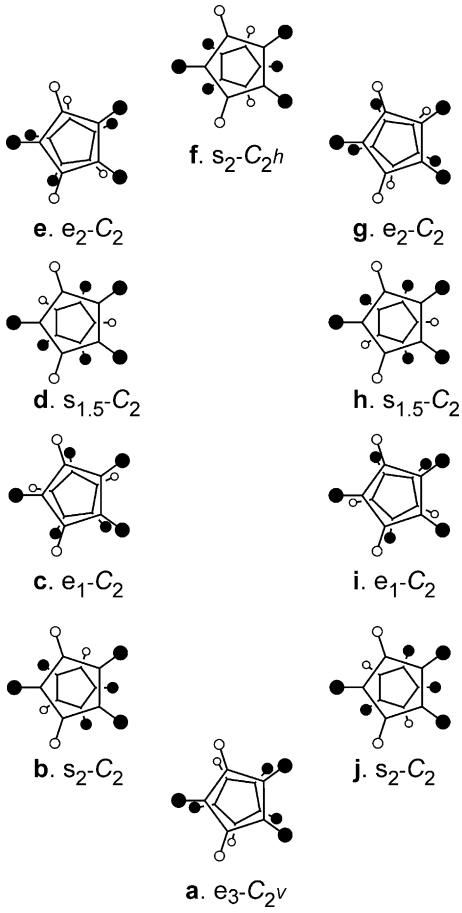


Fig. 8. Rotamer diagram for **77**. Notation is defined in the text.

77, the "isolated" C_6F_5 group can rotate to accomodate the pair of C_6F_5 groups opposite, which are more constrained by vicinal interactions. But in **87**, the "isolated" group is a *tert*-butyl group which the opposing pair of C_6F_5 groups cannot so easily straddle. Clearly, a much more complex model is needed to account for the dynamic behavior of perfluoroaryl-substituted metallocenes. Unfortunately, the Cp–C_6F_5 barriers in **77** were not determined; comparison to the barrier observed in the rhenium piano stool **55** would be instructive.

5. Physicochemical analyses of perfluoroaryl substituent effects

Numerous techniques have been applied to determine the intrinsic electronic effects of Cp substituents on coordinated metal ions and metal-containing molecular fragments. This section focuses on two techniques that have been used to analyze the effects of perfluoroaryl groups in particular.

5.1. Infared spectroscopy

IR spectroscopy is particularly useful for analyzing electronic effects in Cp complexes that also contain carbonyl ligands. In many cases detailed studies have been conducted over wide ranges of substituents with correlations to other physicochemical parameters, reaction kinetics, and so on [143]. Examples include but are not limited to $Cp_2Ti(CO)_2$ [37,144], $Cp_2Zr(CO)_2$ [145], $CpFe(CO)(PPh_3)I$ [30] $[CpRu(CO)]_2(\mu\text{-}CO)_2$ $CpMn(CO)_3$ [63,146], $CpRe(CO)_3$ [147], $CpCo(CO)_2$ [148], $CpRh(CO)_2$ [149], and $CpIr(CO)(PPh_3)$ [150]. Within a structurally homologous series of compounds, a higher stretching "frequency" (usually reported as a wavenumber) for a particular normal mode indicates a more electron-deficient metal center.

Group 7 piano stool complexes – substituted congeners of $CpM(CO)_3$ (M = Mn, Re) – have been analyzed using IR spectroscopy. Table 2 presents all of the published data on perfluoroaryl-substituted complexes, along with selected data from the literature to frame the data in a quantitative context. The trends are illustrated graphically (Fig. 9) using M = Mn, for which there are more examples, but it is clear from the

Table 2
Carbonyl stretching wavenumbers for perfluoroarylated Cp complexes

Entry	Complex	Wavenumbers[a]						References
		M = Mn			M = Re			
		A	*E*		*A*	*E*		
1	$CpM(CO)_3$	2028	1944		2031	1939		[94]
2	$[\eta^5\text{-}(C_6F_5)C_5H_4]M(CO)_3$	2032	1954		2034	1947		[94]
3	$[\eta^5\text{-}1,3\text{-}(C_6F_5)_2C_5H_4]M(CO)_3$	2035	1966	1960	2038	1953		[94]
4	$[\eta^5\text{-}1,2,3\text{-}(C_6F_5)_3C_5H_2]M(CO)_3$	2041	1975	1963	2043	1965	1954	[94]
5	$[\eta^5\text{-}1,2,4\text{-}(C_6F_5)_3C_5H_2]M(CO)_3$	2040	1973	1965	2042	1963	1957	[94]
6	$[\eta^5\text{-}1,2,3,4\text{-}(C_6F_5)_4C_5H]M(CO)_3$	2044	1980	1970	2047	1970	1959	[94]
7	$[\eta^5\text{-}(CF_3C_6F_4)C_5H_4]Mn(CO)_3$	2034	1957					[98]
8	$[\eta^5\text{-}1,2,4\text{-}(CF_3C_6F_4)_3C_5H_2]Mn(CO)_3$	2044	1979	1972				[98]
9	$[\eta^5\text{-}(C_5F_4N)C_5H_4]M(CO)_3$	2035	1959		2037	1951		[99]
10	$[\eta^5\text{-}1,2\text{-}(C_5F_4N)_2C_5H_3]M(CO)_3$	2041	1972	1965	2043	1964	1956	[99]
11	$[\eta^5\text{-}1,3\text{-}(C_5F_4N)_2C_5H_3]M(CO)_3$	2041	1974	1968	2043	1964	1961	[99]
12	$[\eta^5\text{-}(CF_3)C_5H_4]Mn(CO)_3$	2030	1942					[34]
13	$[\eta^5\text{-}Cl_5C_5]Mn(CO)_3$	2048	1982					[171]
14	$[\eta^5\text{-}(CH_3)_5C_5]Mn(CO)_3$	2017	1928					[172]

[a] Recorded in alkane solvent except for $[\eta^5\text{-}(CF_3)C_5H_4]Mn(CO)_3$ (neat liquid).

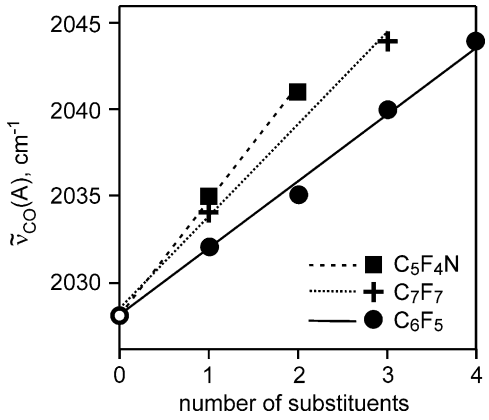


Fig. 9. Carbonyl stretching wavenumbers (A band) for substituted $CpMn(CO)_3$ complexes.

data in Table 2 that the substituent shifts in the rhenium analogues are essentially identical. These data demonstrate that substituent electron-withdrawing strength decreases in the order $CF_3 > C_5F_4N > C_6F_4CF_3 > C_6F_5 = Cl > H$.

5.2. Solution voltammetry

The oxidation potentials of substituted ferrocenes and cobaltocenes are useful probes of electronic substituent effects of ring substituents [151]. Electrochemical techniques such as cyclic voltammetry or square wave voltammetry are intrinsically invasive: a chemical reaction occurs at an electrode. Thus electrochemical data can be more difficult to obtain than infrared spectra. Substituent shifts are considered more reliable if the electrochemical couple is fully reversible. Decomposition of the ferrocenium or cobaltocene species on the time-scale of a cyclic voltammogram can be detected in the loss of current in the return wave. Although most substituted ferrocenes are stable, the corresponding ferrocenium ions can be subject to internal attack by Lewis-basic substituents such as acetamido [152] or by the supporting solvent/electrolyte [123]. The same is true when determining the reduction potential of a cobaltocenium ion—the 19-electron cobaltocene may be unstable. With complexes that are only sparingly soluble, achieving reversibility in the presence of trace adventitious impurities such as water and oxygen can be difficult.

Ferrocenes and cobaltocenium hexafluorophosphates bearing only perfluoroaryl substituents typically exhibit reversible electrochemical behavior in deoxygenated dichloromethane or acetonitrile solutions using tetra-*n*-butylammonium hexafluorophosphate as the electrolyte and activated alumina as an internal desiccant. Tables 3 and 4 present the body of published data, along with selected data from the literature to enable the effects of perfluoroaryl substituents to be placed in a quantitative context. The trends are illustrated graphically (Fig. 10), and the trends are consistent with those obtained using infrared

Table 4
Oxidation potentials of perfluoroarylated ferrocenes relative to $Cp_2Co|Cp_2Co^+$

Complex	$E_{1/2}$ (ox) (mV)[a]	References
Cp_2Co	(0)	
$[\eta^5\text{-}(C_6F_5)C_5H_4]_2Co$	400	[94]
$[\eta^5\text{-}1,3\text{-}(C_6F_5)_2C_5H_4]_2Co$	760	[94]
$\{CpCo[\eta^5\text{-}C_5H_4\text{-}(4,4'\text{-}C_6F_4C_6F_4)\text{-}\eta^5\text{-}C_5H_4]CoCp\}(PF_6)_2$	232	[108]

[a] Recorded in acetonitrile solution using 0.1 M *n*-Bu_4NPF_6 as the electrolyte.

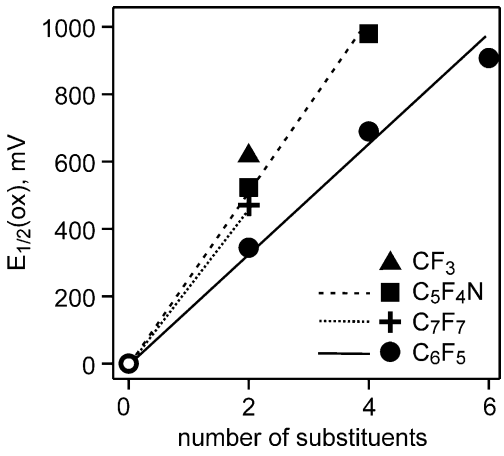


Fig. 10. $Fe^{II}|Fe^{III}$ half-wave potentials for substituted ferrocenes.

Table 3
Oxidation potentials of perfluoroarylated ferrocenes relative to $Cp_2Fe|Cp_2Fe^+$

Complex	$E_{1/2}$ (ox) (mV)[a]	References
Cp_2Fe	(0)	
$[\eta^5\text{-}(C_6F_5)C_5H_4]_2Fe$	345	[92]
$[\eta^5\text{-}1,3\text{-}(C_6F_5)_2C_5H_4]_2Fe$	678	[92]
$[\eta^5\text{-}1,2,3\text{-}(C_6F_5)_3C_5H_2]_2Fe$	951	[94]
$[\eta^5\text{-}1,2,4\text{-}(C_6F_5)_3C_5H_2]_2Fe$	940	[94]
$[\eta^5\text{-}(CF_3C_6F_4)C_5H_4]_2Fe$	465	[98]
$[\eta^5\text{-}(C_5F_4N)C_5H_4]_2Fe$	520	[99]
$[\eta^5\text{-}1,3\text{-}(C_5F_4N)_2C_5H_4]_2Fe$	985	[99]
$CpFe[\eta^5\text{-}C_5H_4\text{-}(4,4'\text{-}C_6F_4C_6F_4)\text{-}\eta^5\text{-}C_5H_4]FeCp$	200	[108]
$Cp\{Fe[\eta^5\text{-}C_5H_4\text{-}(4,4'\text{-}C_6F_4C_6F_4)\text{-}\eta^5\text{-}C_5H_4]\}_2FeCp$	180(2), 372	[108]
$Cp\{Fe[\eta^5\text{-}C_5H_4\text{-}(4,4'\text{-}C_6F_4C_6F_4)\text{-}\eta^5\text{-}C_5H_4]\}_3FeCp$	192, 382	[108]
$[\eta^5\text{-}(C_6F_5)C_5H_4]Fe[\eta^5\text{-}C_5H_4\text{-}(1,4\text{-}C_6F_4)\text{-}\eta^5\text{-}C_5H_4]Fe[\eta^5\text{-}C_5H_4\ (C_6F_5)]$	323, 349	[108]
$[\eta^5\text{-}(CF_3)C_5H_4]_2Fe$	640	[34]

[a] Recorded in dichloromethane solution using 0.1 M *n*-Bu_4NPF_6 as the electrolyte.

spectroscopy. Note especially that the $Co^{II}|Co^{III}$ couple is more sensitive to the substituents than the $Fe^{II}|Fe^{III}$ couple.

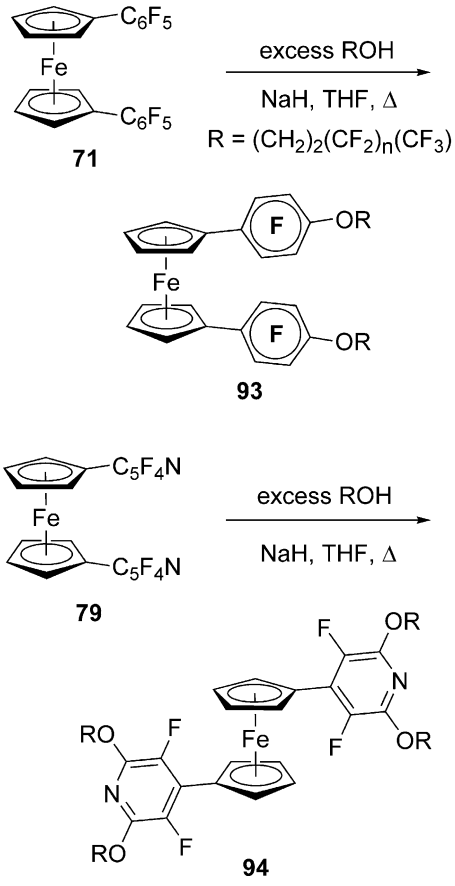
6. Reactions of perfluoroaryl-substituted cyclopentadienylmetal complexes

6.1. Nucleophilic aromatic substitution

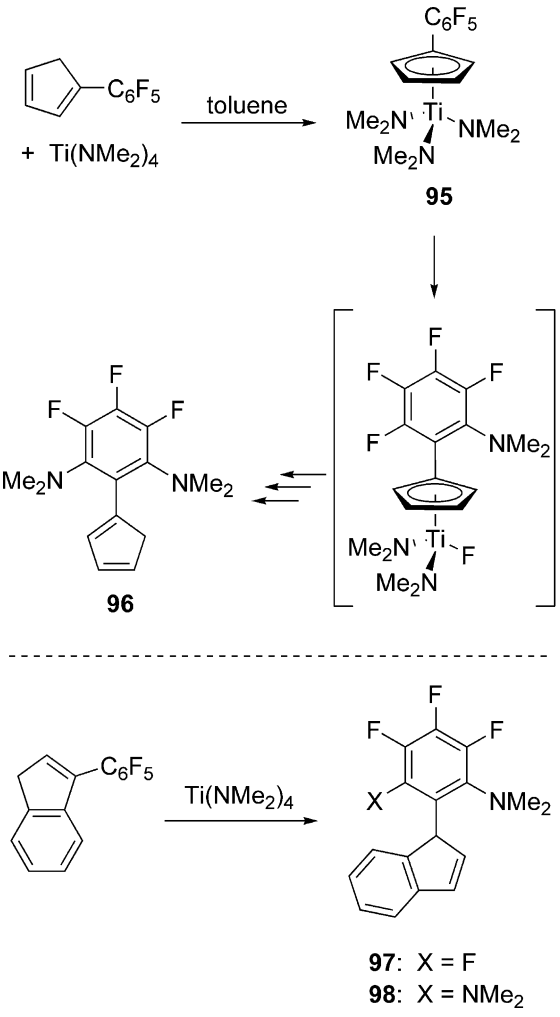
Although stable toward most electrophiles, perfluoroaryl substituents, especially C_6F_5 and C_5F_4N, are susceptible to attack by strong nucleophiles (Scheme 34). The products **93** and **94** are obtained in moderate yields after purification by silica gel chromatography. This chemistry has appeared so far only in conference abstracts [153,154], but the nucleophilic substitution technique holds promise as an alternative method of attaching "fluorous ponytails" (and likely other moieties) to ferrocene.

6.2. C–F ortho-activation

Nucleophilic substitution methods (Section 6.1) can afford aryl substituents with nucleophiles that have been introduced in the *para* and *meta* positions. Reactions of cyclopentadiene or indene bearing one C_6F_5 group have recently been shown to undergo *ortho* displacement of fluoride by dimethylamino upon treatment with $Ti(NMe_2)_4$ (Scheme 35) [155]. Solution NMR measurements conducted on reaction mixtures suggested



Scheme 34.

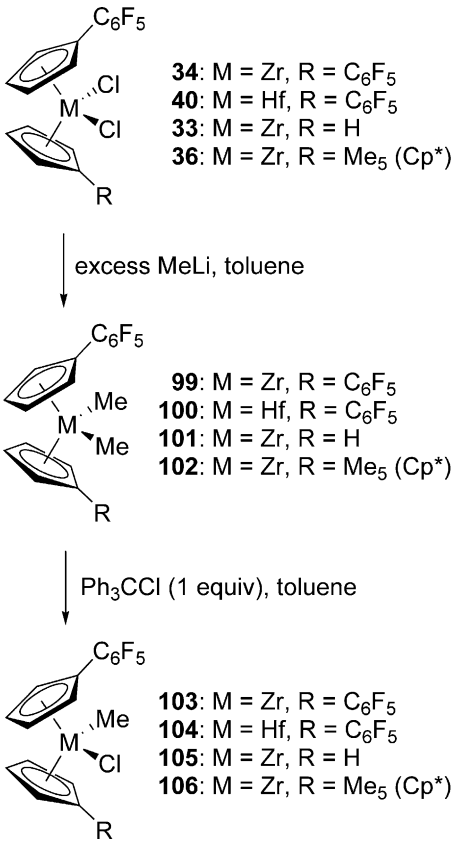


Scheme 35.

a mechanism in which the cyclopentadiene (or indene) coordinates to Ti (probably in an η^5 fashion), followed by an intramolecular nucleophilic displacement of fluoride. In the case of the substituted indene, the reaction was optimized on a preparative scale to give either the monoamine (**97**) or the diamine (**98**) selectively. The use of the diaminated cyclopentadiene **96** as a ligand was demonstrated by preparing the corresponding substituted ferrocene $\{\eta^5\text{-}[2,6\text{-}(Me_2N)_2C_6F_3]C_5H_4\}_2Fe$ [155].

6.3. Wedge ligand substitution and abstraction in group 4 metallocene complexes

The wedge ligands of bent metallocenes are commonly known to undergo facile nucleophilic substitution and electrophilic exchange. Although reactions of group 4 metallocene complexes derived from perfluoroaryl-substituted Cp ligands are generally similar to those of the unsubstituted metallocene complexes, there are occasionally important differences. For example, while Cp_2ZrCl_2 reacts with methyllithium in diethyl ether solution to afford $Cp_2Zr(CH_3)_2$ [156], the analogous reaction of perfluoroaryl-substituted zirconocene dichlorides (Scheme 36) must be carried out in a hydrocarbon suspension using methyl-



Scheme 36.

lithium that is scrupulously free of ether, otherwise the *para* fluorines will undergo some substitution by methyl groups [157]. These methylation reactions must also be carried out in the dark, otherwise only intractible black solids are obtained. Once the metallocene is dimethylated, one methyl group can be selectively replaced with chlorine using trityl chloride (Scheme 37) [158].

Dimethylmetallocenes also undergo electrophilic ligand abstraction using either Brønsted acids or strong organo-Lewis acids including alumoxanes [159]. Abstraction of a single methyl group is quantitative using 1 equiv. of the strong Lewis-acidic reagent tris(pentafluorophenyl)borane [160]. The resulting quasi-ionic species are useful as catalysts for the polymerization of ethylene and other olefins [159]. The preparative chemistry extends smoothly to dimethylmetallocenes

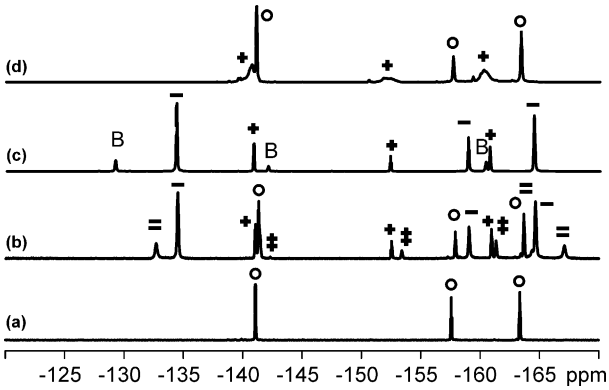
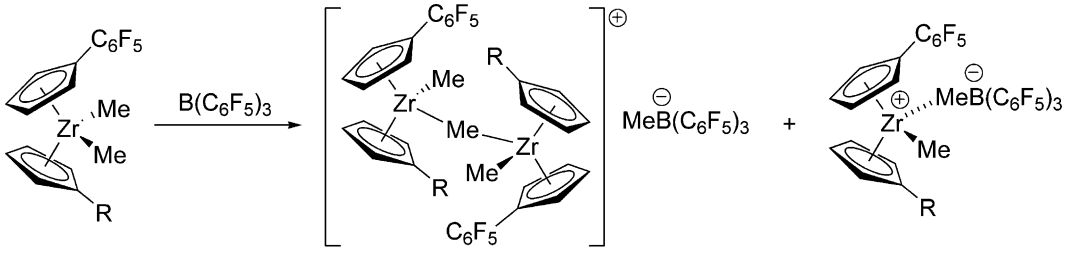


Fig. 11. ^{19}F NMR spectra (376 MHz) showing the progress of methyl anion abstraction from **101** in C_6D_6. (a) **101**; (b) **101** + 0.5 equiv. of $B(C_6F_5)_3$; (c) **101** + excess $B(C_6F_5)_3$; (d) **101** + 10 equiv. of MAO. Legend: (◯) **101**; (B) $B(C_6F_5)_3$; (+/−) mononuclear cation and tightly bound borate anion, respectively, of **110**; (‡/=) dinuclear cation and loosely bound borate anion, respectively, of **108**.

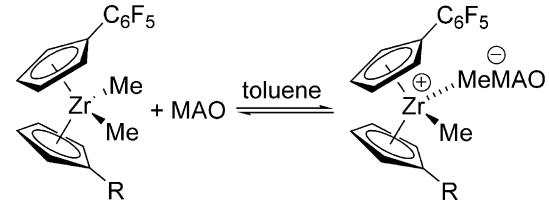
bearing perfluoroaryl substituents (Scheme 37) [157]. Less than 1 equiv. of $B(C_6F_5)_3$ affords a mixture of mononuclear and dinuclear ion-paired species (**107** and **109**, respectively), whereas an excess of $B(C_6F_5)_3$ results in complete conversion to the mononuclear species. The reaction is readily followed using ^{19}F NMR (Fig. 11a–c), whereas corresponding ^{1}H NMR spectra are not sufficiently resolved for quantitative speciation of the reaction mixtures.

Comparison of the unsubstituted [161], monoarylated, and diarylated reaction systems (Scheme 37) reveals a respective decrease in the tendency to form the (μ-CH_3)-bridged dinuclear complex **107** as compared to **108**. The zirconocenium species **109**, with the additional C_6F_5 substituent, would be more electrophilic than **110**, which could result in a preference for bonding **109** to the $MeB(C_6F_5)_3$ anion (forming the mononuclear ion-paired species) rather than to the unreacted neutral $ZrMe_2$ species **99** (forming the dinuclear cation **107**). On the other hand, in these systems it is difficult to rule out subtle steric and solvation effects [159].

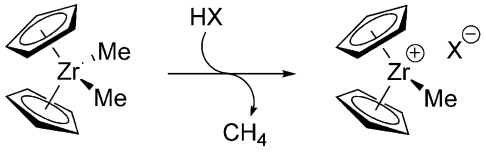
Methylalumoxane (MAO, a complex mixture obtained by partial hydrolysis of trimethylaluminum) is often used as the organo-Lewis acid in methyl anion abstractions from the group 4 metallocene complexes [159]. Complete conversion to the ionic species requires a large excess (200–1000-fold) of the alumoxane component. With C_6F_5-substituted metal-



Scheme 37.



Scheme 38.

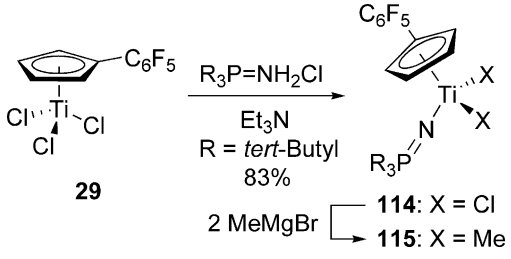


Scheme 39.

locenes (Scheme 38), the abstraction event can be monitored using ^{19}F NMR spectroscopy (Fig. 11d) [157]. Titration studies revealed that the propensity to undergo methyl anion abstraction with MAO decreased in order of increased metal-centered electrophilicity: $(C_6F_5Cp)CpZr(CH_3)_2$ (**101**) > $(C_6F_5Cp)_2Zr(CH_3)_2$ (**99**) > $(C_6F_5Cp)_2Hf(CH_3)_2$ (**100**).

Electron-withdrawing substituents increase the carbon acidity of cyclopentadienes [162]. Bronsted acids (HX) can serve as protonolytic activators for group 4 metallocene dimethides (Scheme 39), because if the conjugate base (X^-) is sufficiently weak it should not serve as a catalyst poison [159]. The use of (perfluoroaryl)cyclopentadienes (e.g., **4CF**, **5**, **15**, and **16**) as components of group 4 metallocene catalyst activators for ethylene polymerization has been claimed in patents [96,107]. None of the putative zirconocenium poly(perfluoroaryl)cyclopentadienide salts has been isolated.

Half-sandwich group 4 complexes also undergo nucleophilic substitutions. The titanium half-metallocene complex **29** undergoes further ligand substitution by phosphinimides (Scheme 40) to afford a quasi-metallocene (**114**) which can be activated toward olefin polymerization catalyst [163].



Scheme 40.

Table 5
Ethylene polymerization using C_6F_5-substituted, MAO-activated group 4 metallocene catalysts

Entry	Pre-catalyst	Al:M	T_p (°C)	A^a	References
1	$[\eta^5\text{-}(C_6F_5)C_5H_4]_2TiCl_2$ (**31**)	4000	20	0.41	[115]
2	$[\eta^5\text{-}(C_6F_5)C_5H_4]_2TiCl_2$ (**31**)	4000	50	0.15	[115]
3	Cp_2TiCl_2	4000	20	11	[115]
4	Cp_2TiCl_2	4000	50	13	[115]
5	$[\eta^5\text{-}(C_6F_5)C_5H_4]_2ZrCl_2$ (**34**)	4000	20	3.0	[115]
6	$[\eta^5\text{-}(C_6F_5)C_5H_4]_2ZrCl_2$ (**34**)	4000	50	31	[115]
7	Cp_2ZrCl_2	4000	20	41	[115]
8	Cp_2ZrCl_2	4000	50	35	[115]
9	Cp_2ZrCl_2	2300	50	53	[164]
10	$[\eta^5\text{-}(C_6F_5)C_5H_4]_2ZrCl_2$ (**34**)	2300	50	14	[164]
11	$[\eta^5\text{-}(Ph)C_5H_4]_2ZrCl_2$	2300	50	53	[164]

[a] Polymerization activity in (Mg PE) (mol Ti or Zr)$^{-1}$ [ethylene]$^{-1}$ (h)$^{-1}$; average of two or three runs. Reaction times varied widely.

6.4. Olefin polymerization catalyzed by group 4 metallocene complexes

Olefin polymerization by group 4 metallocenes requires prior or in situ activation (abstraction of a wedge ligand), which is achieved using various electrophilic co-catalysts [159]. Ethylene is polymerized more rapidly than other olefins and to higher molecular weights. Table 5 presents the results of ethylene homopolymerizations carried out using C_6F_5-substituted group 4 metallocenes. $(C_6F_5Cp)_2TiCl_2$ (**31**) shows low activity compared to its unsubstituted counterpart (entries 1–4), which is ascribed to more facile deactivation of the arylated catalyst by reduction to Ti^{III} [115]. A solution of **31** treated with activator (MAO) changed color rapidly and exhibited a clear EPR spectrum ($g = 1.988$, doublet, splitting = 7.2 G). $(C_6F_5Cp)_2ZrCl_2$ (**34**) is only slightly less active than Cp_2ZrCl_2 (entries 5–10) at 50 °C, but at 20 °C the decrease in activity is more dramatic. Similar results are obtained when triisobutylaluminum (TIBA) and triphenylcarbenium tetrakis(pentafluorophenyl)borate were used as the activator component in polymerizations carried out at 0 °C [115]. Direct comparison of C_6F_5- and C_6H_5-substituted catalysts (entries 10–11) argues against attributing the lower activity of the C_6F_5-substituted complexes to a simple steric effect [164].

Table 6 presents the results of ethylene-1-hexene copolymerizations using aryl-substituted zirconocene dichlorides [164]. As a general trend, the electron-deficient catalysts (entries 1–3 versus entries 5–6) exhibit lower activities while incorporating more comonomer, although it is important to note that the trend is not particularly striking and that opposite trends have been observed in other systems [165,166].

Titanium half-metallocene complexes are useful as catalysts for styrene polymerization [167–169]. In general, electron-releasing substituents are found to enhance polymerization activity [170]. However, an opposite effect is observed with a C_6F_5-substituted catalyst (Table 7) [115]. The observed rate increase is ascribed to greater electrophilicity in the putative Ti^{III} intermediate formed upon reaction of the half-metallocene precursor and the co-catalytic activator methylalumoxane (MAO). A mixture of $(C_6F_5Cp)TiCl_3$ and MAO gave a green solution

Table 6
Ethylene-1-hexene co-polymerization using C_6F_5-substituted, MAO-activated metallocenes[a]

Entry	Pre-catalyst	A[b]	M_w[c]	M_w/M_n[c]	%H[d]
1	[η^5-$(C_6F_5)C_5H_4$]$CpZrCl_2$ (**33**)	12	114	3.1	7
2	[η^5-$(C_6F_5)C_5H_4]_2ZrCl_2$ (**34**)	10	38	2.6	13
3	[η^5-1,3-$(C_6F_5)_2C_5H_3$]$CpZrCl_2$ (**35**)	7	17	2.4	19
4	Cp_2ZrCl_2	26	130	2.5	6
5	[η^5-$(Ph)C_5H_4]_2ZrCl_2$	26	230	3.0	7
6	[η^5-1,3-$(Ph)_2C_5H_3$]$CpZrCl_2$	26	265	31	5

[a] [1-Hexene] = 0.4 M; T_p = 50 °C; Al:Zr = 2300. $P(C_2H_4)$ = 1.0 atm. Reaction time = 5 min. Data represents averages from three separate polymerization experiments. Data from Ref. [164].
[b] Polymerization activity in (Mg PE) (mol Zr)$^{-1}$ [ethylene]$^{-1}$ (h)$^{-1}$.
[c] Weight- and number-averaged molecular weights (M_w and M_n) in kD determined by GPC.
[d] Mol% hexene incorporation in polymer determined by ^{13}C NMR spectroscopy.

Table 7
Styrene polymerization using C_6F_5-substituted, MAO-activated titanium complexes[a]

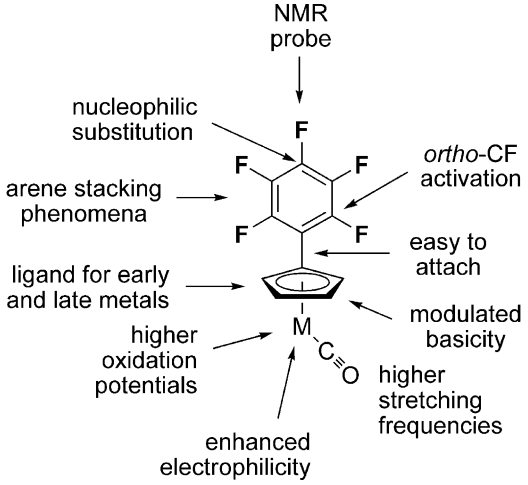
Entry	Pre-catalyst	T_p	A[b]	T_m[c]	%S[d]
1	[η^5-$(C_6F_5)C_5H_4$]$TiCl_3$ (**29**)	20	9.8	275	95
2	[η^5-$(C_6F_5)C_5H_4$]$TiCl_3$ (**29**)	50	86	277	98
3	$CpTiCl_3$	20	6.3	262	94
4	$CpTiCl_3$	50	14	264	96

[a] [Styrene] = 0.8 M, Al:Zr = 4000, toluene solvent. Reaction times varied. Data represents averages from two separate polymerization experiments. Data from Ref. [115].
[b] Polymerization activity in (Mg PS) (mol Ti)$^{-1}$ [styrene]$^{-1}$ (h)$^{-1}$.
[c] Melting temperature determined by DSC.
[d] Percentage of syndiotactic (2-butanone insoluble) polymer.

from which an EPR signal was obtained (g = 2.0045, doublet, splitting = 7.4 G).

7. Closing remarks

With the advent of convenient procedures for attaching perfluoroaryl groups to cyclopentadienes and indenes, the door is opened to the exploration of their electron-withdrawing effects in catalysis by transition metal Cp complexes. We already know that certain catalytic processes are accelerated by perfluoroaryl groups while others are retarded. Perfluoroaryl groups are stable enough to withstand the conditions of olefin polymerization catalysis by group 4 metallocenes, an important test of stability toward strong electrophiles. At the same time, emerging research shows that the perfluoroaryl Cp substituents can also serve as scaffolds for the attachment of other functionalities to metallocene cores by nucleophilic substitution. These findings suggest that perfluoroaryl-substituted Cp complexes are poised to find utility not only in catalysis but more broadly in organometallic and materials chemistry (Scheme 41).



Scheme 41.

References

[1] F.A. Cotton, J. Organomet. Chem. 637–639 (2001) 18.
[2] P.L. Pauson, J. Organomet. Chem. 637–639 (2001) 3.
[3] E.O. Fischer, R. Jira, J. Organomet. Chem. 637–639 (2001) 7.
[4] M. Rosenblum, J. Organomet. Chem. 637–639 (2001) 13.
[5] I.R. Butler, Organomet. Chem. 31 (2004) 394.
[6] W. Kaminsky, J. Polym. Sci. A Polym. Chem. 42 (2004) 3911.
[7] T.P. Hanusa, Organometallics 21 (2002) 2559.
[8] P. Jutzi, Pure Appl. Chem. 75 (2003) 483.
[9] S. Arndt, J. Okuda, Chem. Rev. 2002 (2002) 1953.
[10] B.E. Bursten, R.J. Strittmatter, Angew. Chem. Intl. Ed. 30 (1991) 1069.
[11] P.G. Gassman, C.H. Winter, Organometallics 10 (1991) 1592.
[12] J.A. Pool, P.J. Chirik, Can. J. Chem. 83 (2005) 286.
[13] G.W. Coates, Chem. Rev. 100 (2000) 1223.
[14] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.
[15] M.L. Hays, D.J. Burkey, J.S. Overby, T.P. Hanusa, S.P. Sellers, G.T. Yee, V.G. Young, Organometallics 17 (1998) 5521.
[16] J.A. Gladysz, B.J. Boone, Angew. Chem. Intl. Ed. 36 (1997) 551.
[17] J.S. Overby, T.P. Hanusa, S.P. Sellers, G.T. Yee, Organometallics 18 (1999) 3561.
[18] R.L. Halterman, Chem. Rev. 92 (1992) 965.
[19] A.H. Hoveyda, J.P. Morken, Angew. Chem. Intl. Ed. 35 (1996) 1262.
[20] T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988.
[21] M.R. Douglass, M. Ogasawara, S. Hong, M.V. Metz, T.J. Marks, Organometallics 21 (2002) 283.
[22] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.
[23] P.J. Shapiro, Coord. Chem. Rev. 231 (2002) 67.
[24] J.C. Green, Chem. Soc. Rev. 27 (1998) 263.
[25] R.B. King, Coord. Chem. Rev. 20 (1976) 155.
[26] G.T. Yee, J.S. Miller, in: J.S. Miller, M. Drillon (Eds.), Magnetism: Molecules to Materials V, Wiley-VCH, Weinheim, Germany, 2005, p. 223.
[27] P.C. Möhring, N.J. Coville, J. Mol. Catal. A Chem. 96 (1995) 181.
[28] C. Janiak, U. Versteeg, K.C.H. Lange, R. Weimann, E. Hahn, J. Organomet. Chem. 501 (1995) 219.
[29] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.
[30] P.C. Möhring, N. Vlachakis, N.E. Grimmer, N.J. Coville, J. Organomet. Chem. 483 (1994) 159.
[31] T.H. Lowry, K.S. Richardson, Mechanism and Theory in Organic Chemistry, 3rd ed., Harper, New York, 1987, p. 144.
[32] R. Leino, P. Lehmus, A. Lehtonen, Eur. J. Inorg. Chem. 16 (2004) 3201.
[33] S. Aldridge, C. Bresner, Coord. Chem. Rev. 244 (2003) 71.
[34] P.G. Gassman, C.H. Winter, J. Am. Chem. Soc. 108 (1986) 4228.
[35] T. Olsson, O. Wennerström, Acta Chem. Scand. B 32 (1978) 293.
[36] R.P. Hughes, H.A. Trujillo, Organometallics 15 (1996) 286.
[37] E.J. Parsons, P.G. Gassman, J. Coord. Chem. 35 (1995) 41.

[38] W.C. Finch, E.V. Anslyn, R.H. Grubbs, J. Am. Chem. Soc. 110 (1988) 2406.
[39] P.G. Gassman, J.W. Mickelson, J.R. Sowa, J. Am. Chem. Soc. 114 (1992) 6942.
[40] L.P. Barthel-Rosa, J.R. Sowa, P.G. Gassman, J. Fischer, B.M. McCarty, S.L. Goldsmith, M.T. Gibson, J.H. Nelson, Organometallics 16 (1997) 1595.
[41] J.K. Evju, K.R. Mann, Organometallics 21 (2002) 993.
[42] J.A. Brinkman, T.T. Nguyen, J.R. Sowa, Org. Lett. 2 (2000) 981.
[43] P.G. Gassman, J.A. Ray, P.G. Wenthold, J.W. Mickelson, J. Org. Chem. 56 (1991) 5143.
[44] E.P. Janulis, A.J. Arduengo, J. Am. Chem. Soc. 105 (1983) 3563.
[45] E.D. Laganis, D.M. Lemal, J. Am. Chem. Soc. 102 (1980) 6634.
[46] R.D. Chambers, M.P. Greenhall, Chem. Commun. (1990) 1128.
[47] M.J. Burk, A.J. Arduengo, J.C. Calabrese, R.L. Harlow, J. Am. Chem. Soc. 111 (1989) 8938.
[48] J.W. Mickelson, Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, USA, 1992, p. 91.
[49] O.W. Webster, J. Am. Chem. Soc. 88 (1965) 3046.
[50] O.W. Webster, J. Am. Chem. Soc. 87 (1965) 1820.
[51] E. Herdtweck, F.H. Köhler, R. Mölle, Eur. J. Inorg. Chem. (2005) 952.
[52] A.N. Nesmeyanov, N.E. Kolobova, K.N. Anisimov, Y.N. Makarov, Izv. Akad. Nauk SSSR Ser. Khim. 4 (1967) 953.
[53] R.E. Christopher, L.M. Venanzi, Inorg. Chim. Acta 7 (1973) 219.
[54] R.E. Christopher, L.M. Venanzi, Inorg. Chim. Acta 7 (1973) 489.
[55] O.W. Webster, J. Am. Chem. Soc. 88 (1966) 4055.
[56] Y.X. Lei, G. Cerioni, Z. Rappoport, J. Org. Chem. 65 (2000) 4028.
[57] M.I. Bruce, A.H. White, Aust. J. Chem. 43 (1990) 949.
[58] M.S. Blais, M.D. Rausch, J. Organomet. Chem. 502 (1995) 1.
[59] M.D. Rausch, J.F. Lewison, W.P. Hart, J. Organomet. Chem. 358 (1988) 161.
[60] J. Martin, C. Moise, J. Organomet. Chem. 232 (1982) C55.
[61] W.P. Hart, D.W. Macomber, M.D. Rausch, J. Am. Chem. Soc. 102 (1980) 1196.
[62] T.E. Bitterwolf, S. Gallagher, A.L. Rheingold, G.P.A. Yap, J. Organomet. Chem. 545–546 (1997) 27.
[63] C. Arsenault, P. Bougeard, B. Sayer, S. Yeroushalmi, M.J. McGlinchey, J. Organomet. Chem. 265 (1984) 283.
[64] F.X. Kohl, E. Schlüter, P. Jutzi, J. Organomet. Chem. 243 (1983) C37.
[65] G. Wulfsberg, R. West, J. Am. Chem. Soc. 93 (1971) 4085.
[66] B.G. Conway, M.D. Rausch, Organometallics 4 (1985) 688.
[67] M. Arthurs, J.C. Bickerton, M. Kirkley, J. Palin, C. Piper, J. Organomet. Chem. 429 (1992) 245.
[68] T. Cuenca, P. Royo, Coord. Chem. Rev. 193–195 (1999) 447.
[69] D. Hazafy, M. Sobocikova, P. Stepnicka, J. Ludvik, M. Kotora, J. Fluorine Chem. 124 (2003) 177.
[70] H. Grubert, K.L. Rinehart, Tetrahedron Lett. (1959) 16.
[71] K. Sünkel, D. Steiner, J. Organomet. Chem. 368 (1989) 67.
[72] Y.H. Han, M.J. Heeg, C.H. Winter, Organometallics 13 (1994) 3009.
[73] S.A. Kur, M.J. Heeg, C.H. Winter, Organometallics 13 (1994) 1865.
[74] L.V. Dinh, F. Hampel, J.A. Gladysz, J. Organomet. Chem. 690 (2005) 493.
[75] M.D. Rausch, Y.P. Wang, J. Organomet. Chem. 413 (1991) 111.
[76] A. Shafir, M.P. Power, G.D. Whitener, J. Arnold, Organometallics 19 (2000) 3978.
[77] C. Zou, M.S. Wrighton, J. Am. Chem. Soc. 112 (1990) 7578.
[78] L.V. Dinh, J.A. Gladysz, Chem. Commun. (2004) 998.
[79] R.P. Hughes, T.L. Husebo, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, Organometallics 16 (1997) 5.
[80] J. Kvicala, T. Briza, O. Paleta, K. Auerova, J. Cermak, Tetrahedron 58 (2002) 3847.
[81] T. Briza, J. Kvicala, O. Paleta, J. Cermak, Tetrahedron 58 (2002) 3841.
[82] J. Cermák, L. St'astná, J. Sykora, I. Císarová, J. Kvícala, Organometallics 23 (2004) 2850.
[83] R. Knapp, M. Rehahn, J. Organomet. Chem. 452 (1993) 235.
[84] J.A. Gamboa, A. Sundararaman, L. Kakalis, A.J. Lough, F. Jäkle, Organometallics 21 (2002) 4169.
[85] P.A. Deck, T.S. Fisher, J.S. Downey, Organometallics 16 (1997) 1193.
[86] G.A.M. Munro, P.L. Pauson, J. Organomet. Chem. 160 (1978) 177.
[87] O.J. Curnow, R.P. Hughes, J. Am. Chem. Soc. 114 (1992) 5895.
[88] R.P. Hughes, X.M. Zheng, C.A. Morse, O.J. Curnow, J.R. Lomprey, A.L. Rheingold, G.P.A. Yap, Organometallics 17 (1998) 457.
[89] R. Wahren, J. Organomet. Chem. 57 (1973) 415.
[90] A. Roloff, K. Meier, M. Reidiker, Pure Appl. Chem. 58 (1986) 1267.
[91] B. Klingert, A. Roloff, B. Urwyler, J. Wirz, Helv. Chim. Acta 71 (1988) 1858.
[92] P.A. Deck, W.F. Jackson, F.R. Fronczek, Organometallics 15 (1996) 5287.
[93] P.A. Deck, Inorg. Synth., in press.
[94] M.P. Thornberry, C. Slebodnick, P.A. Deck, F.R. Fronczek, Organometallics 19 (2000) 5352.
[95] M.P. Thornberry, C. Slebodnick, P.A. Deck, F.R. Fronczek, Organometallics 20 (2001) 920.
[96] S. Becke, U. Denninger, S. Kahlert, W. Obrecht, C. Schmid, H. Windisch, PCT Intl. Appl. WO (1999), 99/15534.
[97] P.A. Deck, C.E. Kroll, G.W. Hollis, F.R. Fronczek, J. Organomet. Chem. 637 (2001) 107.
[98] P.A. Deck, B.D. McCauley, C. Slebodnick, Unpublished results.
[99] A.D. Warren, P.A. Deck, C. Slebodnick, Unpublished results.
[100] P.A. Deck, K.F. Tetterton, Unpublished results.
[101] P.A. Deck, F.R. Fronczek, Organometallics 19 (2000) 327.
[102] V.R. Sinyakov, T.V. Mezhenkova, V.M. Karpov, V.E. Platonov, J. Fluorine Chem. 125 (2004) 49.
[103] A.F. Andrews, R.K. Mackie, J.C. Walton, J. Chem. Soc., Perkin Trans. 2 (1980) 96.
[104] F.G. Bordwell, J.C. Branca, J.E. Bares, R. Filler, J. Org. Chem. 1988 (1988) 780.
[105] G.A. Artamkina, I.P. Beletskaya, Zhurn. Org. Khim. 31 (1995) 1044.
[106] R. Filler, A.E. Fiebig, Chem. Commun. (1970) 546.
[107] A. Sommazzi, F. Masi, G. Borsotti, A. Proto, R. Santi, US Patent 6,596,891 (2003).
[108] C.B. Hollandsworth, W.G.J. Hollis, C. Slebodnick, P.A. Deck, Organometallics 18 (1999) 3610.
[109] J.B. Price, C. Slebodnick, P.A. Deck, J. Org. Chem. (2005).
[110] P.A. Deck, C.R. Maiorana, Macromolecules 34 (2001) 9.
[111] T.E. Bitterwolf, Polyhedron 7 (1998) 409.
[112] L.G. Greifenstein, J.B. Lambert, R.J. Nienhuis, H.E. Fried, G.A. Pagani, J. Org. Chem. 46 (1981) 5125.
[113] M. Miura, S. Pivsa-Art, G. Dyker, J. Heiermann, T. Satoh, N. Masakatsu, Chem. Commun. (1998) 1889.
[114] G. Dyker, J. Heiermann, M. Miura, J.I. Inoh, S. Pivsa-Art, T. Satoh, M. Nomura, Chem. Eur. J. 6 (2000) 3426.
[115] R.J. Maldanis, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 599 (2000) 107.
[116] P.A. Deck, Unpublished results, 2005.
[117] E.J.M. De Boer, B. Hessen, A.A. Van der Huizen, W. De Jong, A.J. Van Der Linden, B.J. Ruisch, L. Schoon, H.J.A. De Smet, F.H. Van Der Steen, H.C.T. Van Strien, A. Villena, J.J.B. Walhof, EP Eur. Pat. Appl. EP795564A1 (1997).
[118] W.E. Lindsell, J. Chem. Soc., Dalton Trans. (1975) 2548.
[119] M.L.H. Green, W.E. Lindsell, J. Chem. Soc. (1969) 2215.
[120] R.P. Hughes, S.M. Maddock, I.A. Guzei, L.M. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 123 (2001) 3279.
[121] C. Imrie, D.C. Nonhebel, P.L. Pauson, J. Chem. Soc., Perkin Trans. I 10 (1991) 2555.
[122] V.A. Ivushkin, P.K. Sazanov, G.A. Artamkina, I.P. Beletskaya, J. Organomet. Chem. 597 (2000) 77.
[123] P.G. Gassman, J.R. Sowa, M.G. Hill, K.R. Mann, Organometallics 14 (1995) 4879.
[124] M. Rausch, M. Vogel, H. Rosenberg, J. Org. Chem. 22 (1957) 900.
[125] R. Sanders, U.T. Mueller-Westerhoff, J. Organomet. Chem. 512 (1996) 219.
[126] S.I. Goldberg, L.H. Keith, T.S. Prokopov, J. Org. Chem. 28 (1963) 850.
[127] D.W. Slocum, T.R. Engelmann, C. Ernst, C.A. Jennings, W. Jones, B. Koonsvitsky, J. Lewis, P. Shenkin, J. Chem. Educ. 46 (1969) 144.

[128] M.D. Rausch, D.J. Ciappenelli, J. Organomet. Chem. 10 (1967) 127.
[129] D. Guillaneux, H.B. Kagan, J. Org. Chem. 60 (1995) 2502.
[130] C.H. Winter, K.N. Seneviratine, A. Bretschneider-Hurley, Comm. Inorg. Chem. 19 (1996) 1.
[131] H. Rosenberg, US Patent 3,422,130 (1969).
[132] M.I. Bruce, M.J. Melvin, J. Chem. Soc. (1969) 2107.
[133] W.G. Hollis, T.F. Bonsall, V.L. Cuba, P.A. Deck, F.R. Fronczek, Transit. Met. Chem. (2005).
[134] P.A. Deck, M.J. Lane, J.L. Montgomery, C. Slebodnick, F.R. Fronczek, Organometallics 19 (2000) 1013.
[135] E.E. Bunel, P. Campos, J. Ruz, L. Valle, I. Chadwick, M. Santa Ana, G. Gonzalez, J.M. Manriquez, Organometallics 7 (1988) 474.
[136] M.D. Blanchard, R.P. Hughes, T.E. Concolino, A.L. Rheingold, Chem. Mater. 12 (2000) 1604.
[137] J.E. Sheats, W. Miller, M.D. Rausch, S.A. Gardner, P.S. Andrews, F.A. Hibgie, J. Organomet. Chem. 96 (1975) 115.
[138] C.E. Smith, P.S. Smith, R.L. Thomas, E.G. Robins, J.C. Collings, C. Dai, A.J. Scott, S. Borwick, A.S. Batsanov, S.W. Watt, S.J. Clark, C.H. Viney, J.A.K. Howard, W. Clegg, T.B. Marder, J. Mater. Chem. 14 (2004) 413.
[139] M.P. Castellani, J.M. Wright, S.J. Geib, A.L. Rheingold, W.C. Trogler, Organometallics 5 (1986) 1116.
[140] J. Okuda, Top. Curr. Chem. 160 (1991) 97.
[141] S. Brydges, L.E. Harrington, M.J. McGlinchey, Coord. Chem. Rev. 233–234 (2002) 75.
[142] J. Okuda, E. Herdtweck, Chem. Ber. 121 (1988) 1899.
[143] B.E. Bursten, M.R. Green, Prog. Inorg. Chem. 36 (1998) 393.
[144] G.T. Palmer, F. Basolo, L.B. Kool, M.D. Rausch, J. Am. Chem. Soc. 108 (1986) 4417.
[145] C.E. Zachmanoglou, A. Docrat, B.M. Bridgewater, G. Parkin, C.G. Brandow, J.E. Bercaw, C.N. Jardine, M. Lyall, J.C. Green, J.B. Keister, J. Am. Chem. Soc. 124 (2002) 9525.
[146] M. Cais, N. Narkis, J. Organomet. Chem. 3 (1965) 269.
[147] I.R. Lyatifov, G.I. Gulieva, V.N. Babin, R.B. Materikova, P.V. Petrovskii, E.I. Fedin, J. Organomet. Chem. 326 (1987) 93.
[148] Y. Wakatsuki, H. Yamazaki, T. Kobayashi, Y. Sugawara, Organometallics 6 (1987) 1191.
[149] P.B. Graham, M.D. Rausch, K. Taschler, W. Vonphilipsborn, Organometallics 10 (1991) 3049.
[150] M.S. Blais, M.D. Rausch, Organometallics 13 (1994) 3557.
[151] W.E. Britton, R. Kashyap, M. El-Hashash, M. El-Kady, M. Herberhold, Organometallics 5 (1986) 1029.
[152] D.W. Hall, C.D. Russell, J. Am. Chem. Soc. 89 (1967) 2316.
[153] M.D. Wolter, W.G. Hollis, P.A. Deck, C. Slebodnick, Proceedings of the ACS National Meeting Abstracts, vol. 227, CHED 821, 2004.
[154] M.G. Poferl, W.G. Hollis, P.A. Deck, Proceedings of the ACS National Meeting Abstracts, vol. 227, CHED 807, 2004.
[155] P.A. Deck, M.M. Konaté, B.V. Kelly, C. Slebodnick, Organometallics 23 (2004) 1089.
[156] E. Samuel, M.D. Rausch, J. Am. Chem. Soc. 95 (1973) 6263.
[157] E.J. Hawrelak, P.A. Deck, Organometallics 22 (2003) 3558.
[158] E.J. Hawrelak, P.A. Deck, Organometallics 23 (2003) 9.
[159] E.Y.X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.
[160] X.M. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623.
[161] S. Beck, M.H. Prosenc, H.H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, J. Mol. Catal. A Chem. 111 (1996) 67.
[162] F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456.
[163] E.G. Ijpeij, H.J. Arts, G.H.J. Van Doremaele, F.H. Beijer, EP Patent 1,506,974 (2005).
[164] M.P. Thornberry, N.T. Reynolds, P.A. Deck, F.R. Fronczek, A.L. Rheingold, L.M. Liable-Sands, Organometallics 23 (2004) 1333.
[165] A. Yano, S. Hasegawa, T. Kaneko, M. Sone, M. Sato, A. Akimoto, Macromol. Chem. Phys. 200 (1999) 1542.
[166] F.J. Karol, S.C. Kao, New J. Chem. 18 (1994) 97.
[167] B. Hessen, J. Mol. Catal. A Chem. 213 (2004) 129.
[168] J. Schellenberg, N. Tomotsu, Prog. Polym. Sci. 27 (2002) 1925.
[169] W. Kaminsky, Adv. Catal. 46 (2001) 89.
[170] N. Ishihara, M. Kuramoto, M. Uoi, Macromolecules 21 (1988) 3356.
[171] K.J. Reimer, A. Shaver, Inorg. Chem. 14 (1975) 2707.
[172] R.B. King, A. Efraty, J. Am. Chem. Soc. 94 (1972) 3773.