ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 692 (2007) 4424–4435

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Reactivity of the metal–cyclopentadienyl (indenyl, fluorenyl and cycloheptatrienyl) bonds

Ruiting Liu, Xigeng Zhou *

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China

Received 1 April 2007; received in revised form 18 May 2007; accepted 18 May 2007
Available online 2 June 2007

Abstract

The focus of this review concerns the reactivity patterns of metal–cyclopentadienyl (indenyl, fluorenyl and cycloheptatrienyl) bonds. The advances in the metal–carbon(η^5) insertion chemistry have demonstrated that the π-bonding character provides additional reaction opportunities which are not shown by metal–alkyl compounds and these differences are highlighted.

Keywords: Insertion; Coupling reaction; Organometallic complexes; Cyclopentadienyl; Indenyl; Fluorenyl; Cycloheptatrienyl

1. Introduction

Since the landmark synthesis and characterization of ferrocene over 50 years ago [1], the cyclopentadienyl ligand has become one of the most versatile ligands in organometallic chemistry [2–4], and then related carbocyclic ligands, such as fluorenyl [5] and indenyl groups [6], have been studied increasingly, too. However, in most cases, these ligands play the role of a spectator that stabilizes and solubilizes but does not participate in organometallic reactions [2–6]. Insertion of an organic functional group into a metal–ligand bond represents a fundamental step for many metal-promoted functionalizations. Since the discovery of the first insertion into the metal–cyclopentadienyl bond in late 1970s [7], the reactivity chemistry based on the aromatic carbocycle anion ligands has experienced important development during the last three decades. A great deal of investigations have confirmed that the π-bonding modes between metal ions and anionic carbocyclic rings can impart organometallic complexes a unique reactivity and initiate the unexpected reaction sequence. Many compounds with unprecedented structures and reactivity patterns have been isolated from insertions of unsaturated substrates into the metal–carbocycle π bonds. It is realized that instead of being ancillary ligation the aromatic carbocycle anion ligands have the potential for some unique chemistry distinct from anything possible with other ligands.

The purpose of this review is to present a brief account of the developments in the insertion chemistry based on the cyclopentadienyl and related carbocyclic ligands during the last two decades. It will not review the elimination and modification of the cyclopentadienyl ligands since these topics have been reviewed elsewhere [4b]. Moreover, this paper does not include reaction chemistry of the metal–carbon π bonds based on the non-carbocyclic ligands, such as allyl and propargyl groups, although they possess many intriguing reactivities [8]. To provide some context to much of the current work, there is some overlap between this review and its predecessors [9,10].

2. Reactivity of the cyclopentadienyl ligands

Ligands are essential part of organometallic complexes, they impose a dominant control over both the physical and

---

* Corresponding author. Tel.: +86 21 65643769; fax: +86 21 65641740.
E-mail address: xgzhou@fudan.edu.cn (X. Zhou).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.05.033

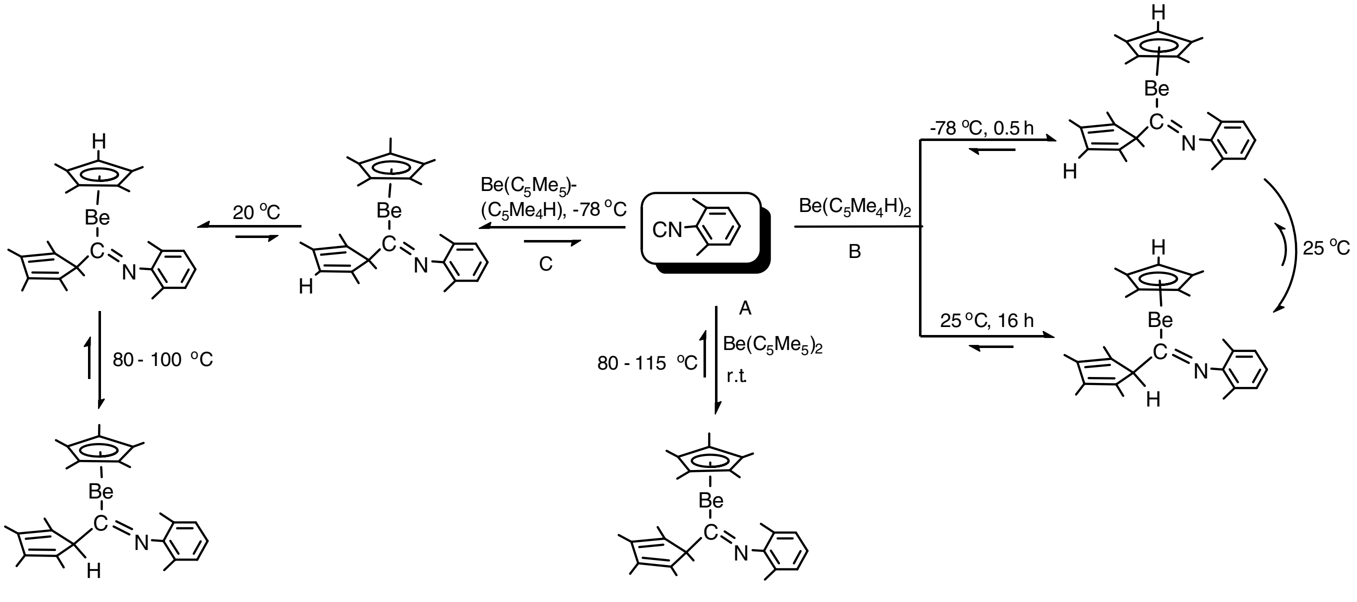
chemical properties of these complexes. Most of the chemistry so far has been based on the complexes containing cyclopentadienyl and modified cyclopentadienyl groups, which are excellent inert ancillary ligands and not involved in the bond formation and cleavage. However, more and more unprecedented participations of the cyclopentadienyl group in various reactions, such as formal coupling, insertion, and reduction reactions, have been observed recently, by which lots of novel organometallic complexes have been obtained.

2.1. Main group complexes

Extensive series of complexes involving one, two, or three π-bound cyclopentadienyl ligands are now known for most main group elements, enabling interesting comparisons and revealing some distinct reactivities [2]. Although the reactivity of the main metal–cyclopentadienyl bonds has been studied extensively, research efforts are primarily focused on the cyclopentadienyl exchange reactions, where the cyclopentadienyl groups are transferred to other metals or liberated as cyclopentadienes [2b]. Examples of insertions of unsaturated substrates into the M–C π bonds of metallocene complexes of main metals are rare [10].

Since the successful preparation of beryllocene [11], $Be(C_5H_5)_2$, the chemistry of beryllocene and substituted beryllocene complexes has remained undeveloped for a period of over 40 years with the exclusion of the synthesis of $Be(C_5H_5)(C_5Me_5)$ [12]. Recently, Carmona's group made many excellent contributions on synthesis, structures, and reactions of substituted beryllocenes [10,13–17]. It has been found that $Be(C_5Me_5)_2$, $Be(C_5Me_4H)_2$, and $Be(C_5Me_5)(C_5Me_4H)$ are highly fluxional molecules in solution, whose dynamic behavior has been explained as involving two very facile processes, ring exchange and a sigmatropic shift around the η^1 ring [13–15]. Both $Be(C_5Me_4H)_2$ and $Be(C_5Me_5)(C_5Me_4H)$ present η^5/η^1 geometries of the slip-sandwich type characterized by low temperatures X-ray crystallography. In the latter, the η^1-C_5Me_4H ring bonds to Be metal through the unique CH carbon atom, whereas $Be(C_5Me_5)_2$ exhibits an almost regular η^5/η^5 sandwich structure in solid state [13–15].

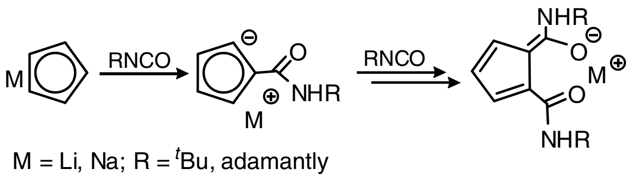
Significantly, this fluxionality of beryllocene structures can lead to various insertions of CNXyl (Xyl = C_6H_3-2,6-Me_2) into the beryllium–cyclopentadienyl bond [14,16,17]. The reaction of $Be(C_5Me_5)_2$ with CNXyl at room temperature forms the insertion product $Be(\eta^5–C_5Me_5)(C(NXyl)C_5Me_5)$. However, this reaction is reversible and the partial dissociation into reactants is observed when the latter is heated to 80–115 °C (Scheme 1, pathway A) [15,16]. The analogous reversible insertion reaction of $Be(C_5Me_4H)_2$ with CNXyl at room temperature gives complex $Be(\eta^5–C_5Me_4H)(C(NXyl)C_5Me_4H)$ from the coupling of CNXyl with the Be–η^1-C(H) σ bond (Scheme 1, pathway B) [14,16,17]. Interestingly, if the reaction is conducted at −78 °C, a different isomer, resulting from β-C(Me)–CNXyl coupling of the C_5Me_4H, is generated, which is stable at room temperature in the solid state but converts to the C(H)–CNXyl coupling isomer in solution (Scheme 1, pathway B). The treatment of $Be(C_5Me_5)(C_5Me_4H)$ with CNXyl has allowed the isolation of three different iminoacyl isomers [14]. $Be(C_5Me_5)(C_5Me_4H)$ reacts with CNXyl to yield the iminoacyl complex $Be(\eta^5$-$C_5Me_5)(C(NXyl)C_5Me_4H)$ which resulted from C–C coupling between the β-C(Me) unit of C_5Me_4H and CNXyl at low temperature, whereas at room temperature, an unusual conversion to isomer $Be(\eta^5$-$C_5Me_4H)(C(NXyl)C_5Me_5)$, through the formal extraction of CNXyl and subsequent reinsertion into the inverted $[Be(\eta^1$-$C_5Me_5)(\eta^5$-$C_5Me_4H)]$, takes place (Scheme 1, pathway C). Furthermore, it is found that the



Scheme 1.

thermodynamic isomer, containing an iminoacyl fragment that involves a coupling of Be–η^1-C(H) with CNXyl, is formed under prolonged heating at 80–100 °C (Scheme 1, pathway C). Apparently, these results indicate that the existence of isomeric structures of beryllocenes in solution can lead to variable insertion chemistry.

Reaction of main-metal cyclopentadienyl complexes with isocyanate has provided a convenient route to the carbamoyl-substituted cyclopentadienyl complexes. MCp (M = Li, Na) reacts with equivalent of alkylisocyanate to yield M[η^5-C_5H_4(CONHR)] admixing with the doubly functionalized M[C_5H_3-1,2-(CONHR)$_2$] (Scheme 2) [18]. The latter is much less reactive toward metal exchange reactions than the former. The strategy has been applied to synthesize other organometallic complexes with functionalized cyclopentadienyl ligands. For example, the treatment of Na[η^5-C_5H_4(CONHR)] with transition metal halides $FeCl_2$ and $CpTiCl_3$ gives the corresponding Fe[η^5-C_5H_4(CONHR)]$_2$ (R = ^{t}Bu) and Cp(η^5-C_5H_4CONHR)-$TiCl_2$ (R = adamantly), respectively [18]. Whereas reaction of NaCp with 2 equiv. of ^{t}BuNCO leads to the selective formation of Na[C_5H_3-1,2-(CONH^{t}Bu)$_2$] [19], the subsequent transmetalation reaction with metal halides of Group 8 leads to the formation of metallocene complexes M[η^5-C_5H_3-1,2-(CONH^{t}Bu)$_2$]$_2$ (M = Fe, Ru), but with metal halides of Group 4 giving the oxygen-coordinated complex Zr[κ^2-*O*,*O*-C_5H_3-1,2-(CONH^{t}Bu)$_2$]$_2$Cl$_2$ [18,20]. The coordination modes of the ligand depend strongly on the nature of the transition metal. The strongly oxyphilic metal ions typically favor the mode of κ^2-*O*,*O*-chelating coordination, while for the more soft metal ions the ligand trends to bond through carbon atoms.



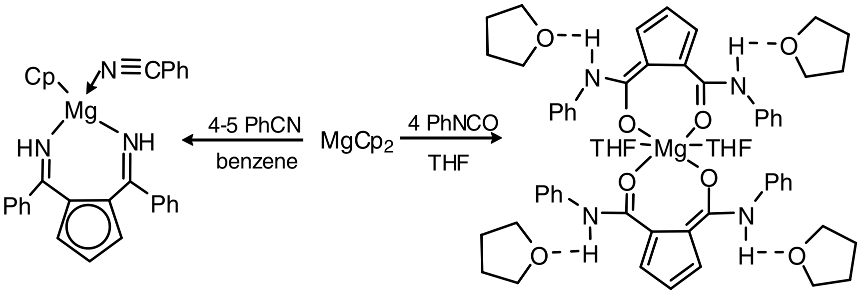
Scheme 2.

Similarly, the reaction of Cp_2Mg with 4 equiv. of PhNCO also gives the rare poly-isocyanate insertion product Mg[{κ^2-*O*,*O*-C_5H_3-1,2-(CONHPh)$_2$}(THF)]$_2$ · 4THF, as shown in Scheme 3. The structure of the resulting Mg complex is clearly determined by X-ray diffraction [21]. Moreover, insertion of benzonitrile into the Mg–C(Cp) π-bond of Cp_2Mg is also observed, giving 1,2-disubstituted cyclopentadienyl diimine product CpMg[κ^2-*N*,*N*-C_5H_3-1,2-(C(Ph)NH)$_2$](NCPh) with a extended π-ligand system, and thus offers an approach to enhance the electrophilic character of the metal center (Scheme 3) [22].

2.2. Transition metal complexes

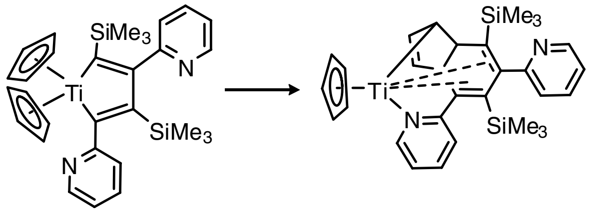
Transition metallocene complexes have been a cornerstone in the development of modern organometallic chemistry and continue to be a focus for structural and chemical studies [3]. In most cases, the cyclopentadienyl ligands are only typically ancillary ligands, since d-transition metals typically have a stronger binding affinity for the cyclopentadienyl groups. However, recent investigations demonstrate that, under proper conditions, the M–C(Cp) π-bond of transition metal complexes could be also expected to undergo some unique and versatile reactions regioselectively.

In contrast to the main metallocenes, examples of the η^1-Cp alkyl-like insertion of transition metallocenes are very rare. Generally, the η^5-Cp ligands bounded to transition metal trend to participate in a sequence of carbon–carbon bond forming reactions featuring partial removement of the Cp ligand from the metal η^5-coordination sphere. For example, intramolecular reactions of titanacyclopentadienyl units with Cp ligand are observed by Rosenthal et al. [23–25]. Unsymmetrically substituted titanacyclopentadiene Cp_2Ti[C($SiMe_3$)=C(Py)C($SiMe_3$)=C(Py)], generated in situ, is unstable at room temperature and rearranges with an intramolecular insertion of one bound Cp unit into the titanacyclopentadiene to produce the dihydroindenyl complex (Eq. (1)) [23]. In contrast, symmetrically substituted Cp_2Ti[C($SiMe_3$)=C(Py)C(Py)=C($SiMe_3$)] is stable and does not rearrange in this manner. Further studies show that diethyl substituted bicyclic titanacyclopentadiene rearranges to a tricyclic η^4:η^3-dihydroindenyl complex via the reduction elimination of one Cp ligand and one vinyl group and the sequent intramolecular insertion of the resultant pendent cyclopentadiene into the M–C σ-bond (Eq. (2)) [24]. A similar rearrangement product

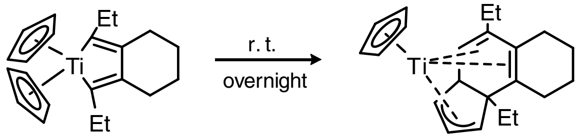


Scheme 3.

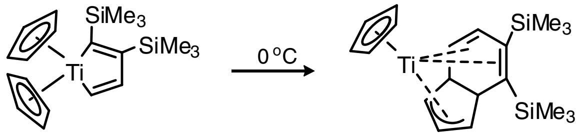
from $Cp_2Ti[CH{=}CHC(SiMe_3){=}C(SiMe_3)]$, dihydroindenyl complex, is formed around 0 °C (Eq. (3)) [25].



(1)



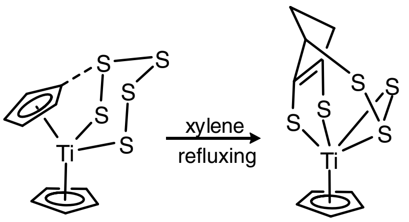
(2)



(3)

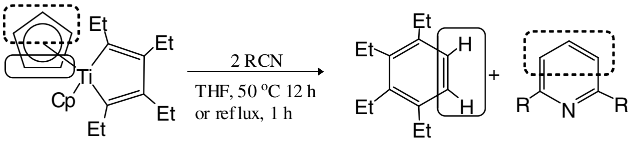
Reaction of oxatitanacyclopentane with ${}^tBuNC$ produces an unexpected complex which possesses a single η^5-Cp and an η^4-azadiene ligand characterized by an X-ray structure analysis (Scheme 4, pathway A) [26]. The azadiene ligand results from the coupling of ${}^tBuNC$ molecule with both the metallacycle ring and one of the Cp ligands. Acid-mediated hydrolysis of the mixed η^5-cyclopentadienyl/η^4-azadiene titanium complex produces lactol in high yield (Scheme 4, pathway A). Further investigations indicate that the N-substituents of isonitrile play an important role in directing the reaction pathway. The reaction of oxatitanacyclopentane with smaller isonitrile ${}^nBuNC$ followed by treatment with HCl affords a benzene derivative via a different reaction pathway from that of ${}^tBuNC$ (Scheme 4, pathway B). In the benzene derivative, the six carbons of the phenyl ring are derived from a Cp ligand and one molecule of ${}^nBuNC$, representing another unique mode of the reactivity of titanocenes.

Another aspect of Cp functioning as active substrate is the addition of S_5 unit to a Cp ligand (Eq. (4)) [27]. The thermally induced intramolecular rearrangement of Cp_2TiS_5, refluxing for 24 h in deoxygenated and dried xylenes, gives the double S insertion/isomerization product β-$C_{10}H_{10}S_5Ti$ via migration of a π-complexed organic ligand to inorganic sulfur atoms accompanying the hydrogen transfer.



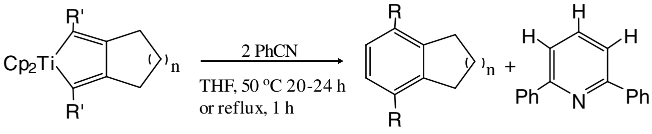
(4)

Recently, Xi and Takahashi et al. achieved a breakthrough in the areas of activation and functionalization of cyclopentadienyl ligands bonded to titanium centers, wherein intriguing carbon–carbon bond cleavage and formation involving the cyclopentadienyl ligand, one attractive target of organic chemistry, were observed [28–32]. In the presence of RCN (R = Ph, p-F-C_6H_4CN, p-Me-C_6H_4CN, Pr), one η^5-cyclopentadienyl ligand in $Cp_2Ti[C(Et){=}C(Et)C(Et){=}C(Et)]$ is torn into a two-carbon unit, which then reacts intramolecularly with the titanacyclopentadiene unit to form 1,2,3,4-teraethylbenzene, and a three-carbon unit that reacts with benzonitrile to afford 2,6-disubstituted pyridine derivative (Eq. (5)) [29,30]. Apparently, the two CH moieties in tetraethylbenzene and the three CH moieties in pyridine derivative result from the Cp ligand of the parent reagent. Moreover, Koga explores the mechanism of the reaction of $Cp_2Ti(C_4H_4)$ with MeCN to form benzene and pyridine using the density functional theory (DFT) method [32]. Bicyclic titanacyclopentadienes can react in similar manner. (Eq. (6)) [29,30].



R = Ph, p-F-C_6H_4CN, p-Me-C_6H_4CN, Pr

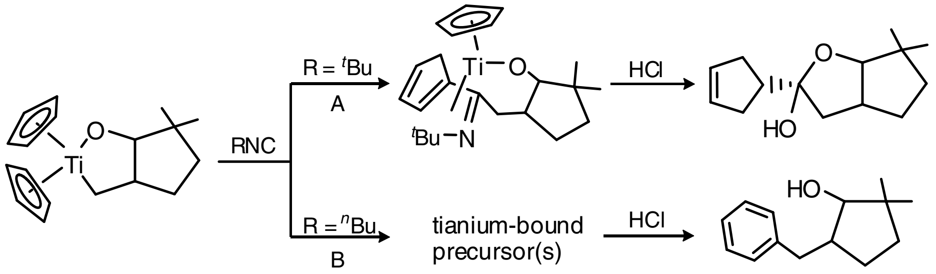
(5)



R' = Et, n = 2; R' = Pr, n = 1 and 2

(6)

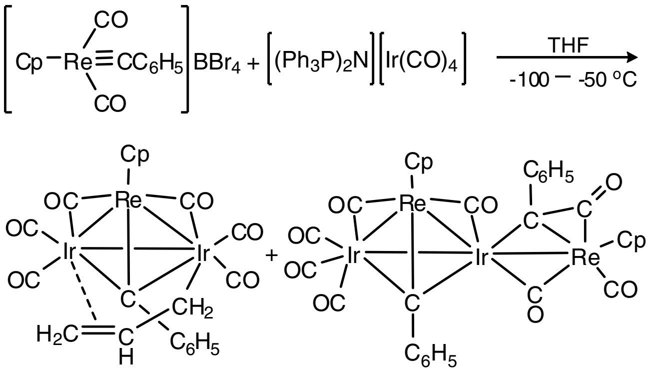
Furthermore, treatment of bis(cyclopentadienyl)titanacyclopentadienes with O_2 or organic halides as oxidants affords unusual indene derivatives without the need of nitriles [28]. In these final indene products, the substituent R^4 is



Scheme 4.

attached to the five-membered ring and only R^1, R^2, R^3 attached to the six-membered ring, which indicates that a novel alkyl group migration takes place in the formation of indene derivatives along with the carbon–carbon bond cleavage of cyclopentadienyl ligand. A possible reaction pathway is shown in Scheme 5, indicating that the intermediate is similar to the η^4:η^3-dihydroindenyl complex as shown in Eq. (2) [24].

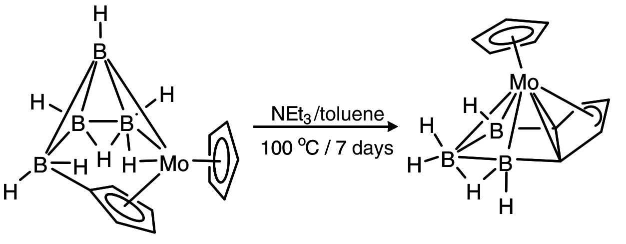
Another example of cyclopentadienyl ligand torn into two pieces is obtained in the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2ReCC_6H_5]BBr_4$ with $[(Ph_3P)_2N][Ir(CO)_4]$, affording Re_2Ir_2 mixed-tetrametal cluster $Re_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ and an unexpected Re–Ir_2 mixed-trimetal bridging carbyne complex with an allyl ligand, $[ReIr_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_3H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5H_5)]$ (Scheme 6) [33]. For the latter, the allyl group (C_3H_5) presumably comes from the cyclopentadienyl ligand of $[(\eta^5\text{-}C_5H_5)(CO)_2ReCC_6H_5]BBr_4$. In the course of the reaction, the cyclopentadienyl ligand is torn into a three-carbon unit (C_3H_3) and a two-carbon unit (C_2H_2), then the three CH moieties are trapped by reactants accompanied by the subsequent abstraction of two hydrogens from solvent THF to form an allyl ligand bonded to the two Ir atoms in η^2 and η^1 modes, respectively, to construct complex $[ReIr_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_3H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_2(CO)_4\,(\eta^5\text{-}C_5H_5)]$.



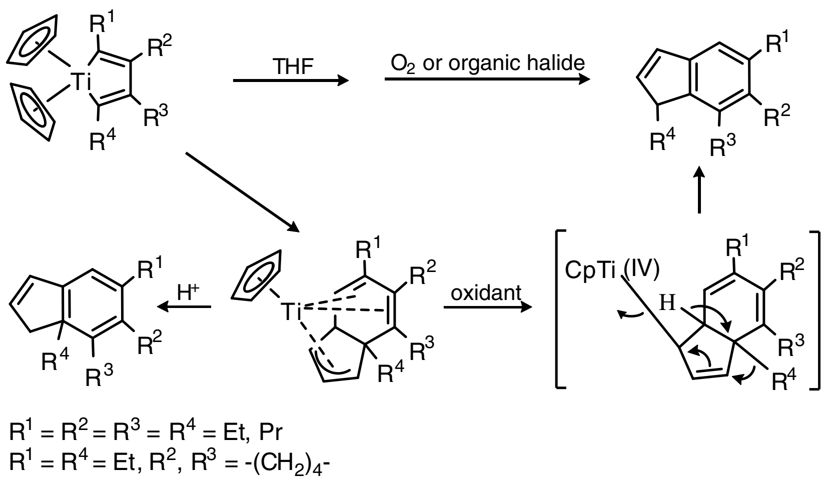
Scheme 6.

Noticeably, Dzwiniel and Stryker recently found that the cyclopentadienyl ligands could be transformed into η^5-cycloheptadienyl-type groups via an unusual tandem pronotation/ring expansion reaction, providing a new strategy to convert five-membered rings to seven-membered rings. Treatment of mixed cyclopentadiene/cyclopentadienyl cobalt complexes with excess 2-butyne at low temperature in the presence of $HBF_4 \cdot OEt_2$ results in the formation of mixed cyclopentadienyl/cycloheptadienyl complexes $(\eta^5\text{-}C_5Me_5)Co(\eta^5\text{-}2,3\text{-}Me_2\text{-}5\text{-}R\text{-}6\text{-}R'\text{-}C_7H_5)BF_4$ (R, R′ = H, Me, ^{t}Bu) (Scheme 7), indicating that one cyclopentadienyl is formally ring-opened and incorporated into alkyne to form cycloheptadienyl group [34]. The reaction depends strongly on the steric factor. For example, the ring expansion of $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_5H_5R)$ could not be generalized to other alkynes, arguably due to the limited steric accessibility of the metal center. Furthermore, the absence of substituents on cyclopentadiene and cyclopentadienyl rings also prevents the reaction, demonstrating that incorporation of at least one substituent into the system is needed.

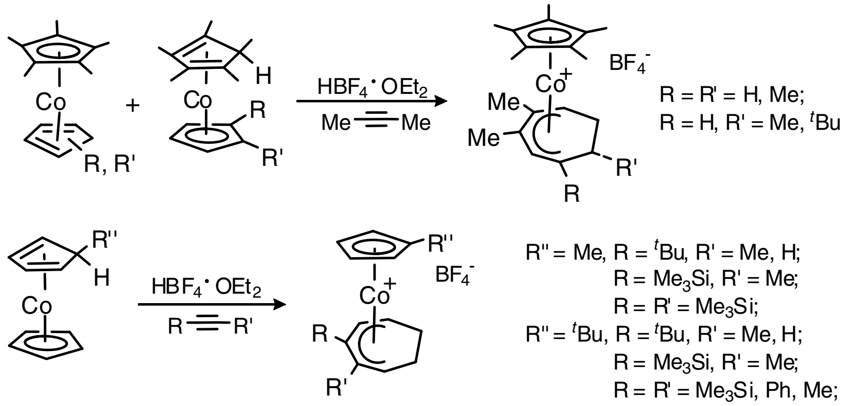
The synthesis and reactivity of metallacarbaborane attract currently an increasing attention [35]. It is worth noting that the transformation of Cp ligands can provide a new way to the synthesis of metallacarbaborane [36]. Reaction of *arachno*-2-$[Mo(\eta^5\text{-}Cp)(\eta^5\text{:}\eta^1\text{-}C_5H_4)B_4H_7]$ with NEt_3 gives *nido*-1-$[Mo(\eta^5\text{-}Cp)(\eta^3\text{:}\eta^2\text{-}C_3H_3)C_2B_3H_5]$ via the removal of a $\{BH_3\}$ unit by Lewis base NEt_3 and partial incorporation of a cyclopentadienyl ligand into the molybdaborane framework (Eq. (7)). In nido-1-$[Mo(\eta^5\text{-}Cp)(\eta^3\text{:}\eta^2\text{-}C_3H_3)C_2B_3H_5]$, two-carbon atoms of the $\{C_2B_3H_5\}$ fragment are from the η^5:η^1-C_5H_4 unit of molybdaborane.



(7)

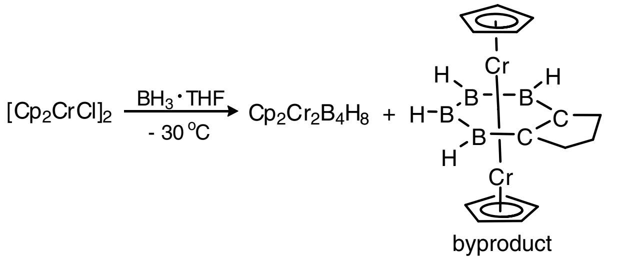


Scheme 5.

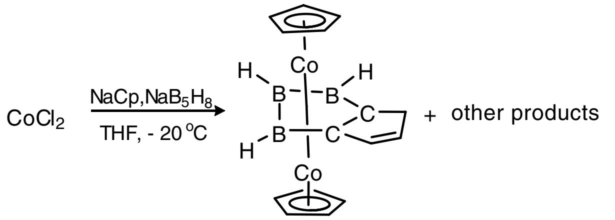


Scheme 7.

In the series works to synthesize metallaboranes, Fehlner and coworkers obtained $(C_5Me_5)_2Cr_2B_4H_8$ [37]. Significantly, when the C_5Me_5 is replaced by C_5H_5, a new metallacarbaborane byproduct $[(\eta^5\text{-Cp})Cr]_2[\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)]$ is also isolated in low yield except for the analogous $Cp_2Cr_2B_4H_8$ in the reaction of $[Cp_2CrCl]_2$ with $BH_3 \cdot HCl$ (Eq. (8)) [38]. The formation of $[(\eta^5\text{-Cp})Cr]_2[\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)]$ may be attributed to the formal insertion of a cyclopentadienyl ligand into a metallaborane framework. Miller and coworkers found that the reaction of NaB_5H_8 with NaCp and $CoCl_2$ could lead to the formation of a five-membered carbaborane complex $[(\eta^5\text{-Cp})Co]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(\mu\text{-}1,2\text{-}C_3H_4\text{-}1,2\text{-}C_2B_3H_3)]$ via the formal coupling reaction of the cyclopentadienyl group with the borane ligand (Eq. (9)) [7].



(8)



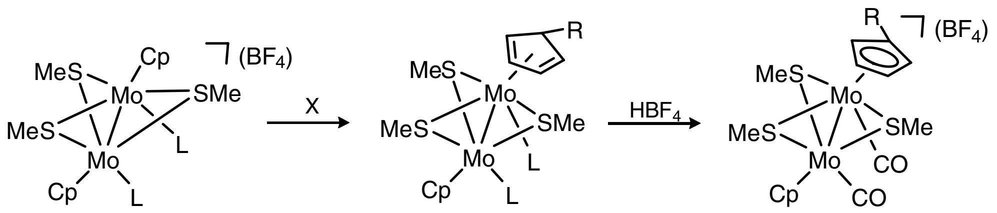
(9)

Recently, Schollhammer's group examined the reaction of thiolato-bridged binuclear molybdenum complexes $[Mo_2Cp_2L_2(\mu\text{-SMe})_3](BF_4)$ (L = XylNC, CO, Bu^t) with a base and anionic reagents, and found that the regioselectivity of nucleophilic reaction remarkably depends on the nature of the co-ligands and anionic reagents [39–41]. When L is a good π-acceptor, the anion attacks at the carbon atoms of the Cp favorably, leading to the occurrence of the regioselective protonation or alkylation of the Cp ligand. However, in the case of L for a poor π-acceptor, the formation of μ-formimidoyl molybdenum complexes is favored. $[Mo_2Cp_2L_2(\mu\text{-SMe})_3](BF_4)$ reacts with the anionic reagents to give $[Mo_2Cp(\eta^4\text{-}C_5H_5R)L_2(\mu\text{-SMe})_3]$ (L = XylNC. X = $LiBu^n$, $NaBH_4$, R = H; L = CO. X = $NaBH_4$, R = H; X = RMgCl, R = Me, Pr^i, Bu^n, Ph; X = LiR, R = Me, Bu^n) [39]. The deprotonation of $Mo_2(\eta^5\text{-Cp})(\eta^4C_5H_5R)(CO)_2(\mu\text{-SMe})_3$ affords the functionalized cyclopentadienyl complexes $[Mo_2(\eta^5\text{-Cp})(\eta^5\text{-}C_5H_4R)(CO)_2(\mu\text{-SMe})_3](BF_4)$ (R = Me, Bu^n, Ph) (Scheme 8).

Very recently, Xie and coworkers found that the bridged cyclopentadienyl ligand could also undergo some unique regioselective transformations. Ruthenium-mediated coupling/cycloaddition of the cyclopentadienyl ligand with alkynes gives tricyclic complexes [42]. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCMe)_2$ with 3 equiv. of ArC≡CH affords $[\eta^4{:}\sigma\text{-}Me_2C(C_{11}H_7Ar_3)(C_2B_{10}H_{10})]Ru(NCMe)$ (Ar=Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$), in which H1, H2, and H3 come from the alkyne. A possible reaction pathway is given in Scheme 9, which contains three stages: oxidative coupling of the two alkyne ligands, stepwise migration of the newly formed diene unit to the Cp ring, and oxidative coupling between a newly coordinated alkyne and the coordinated double bond of the cyclohexadiene unit followed by reductive elimination.

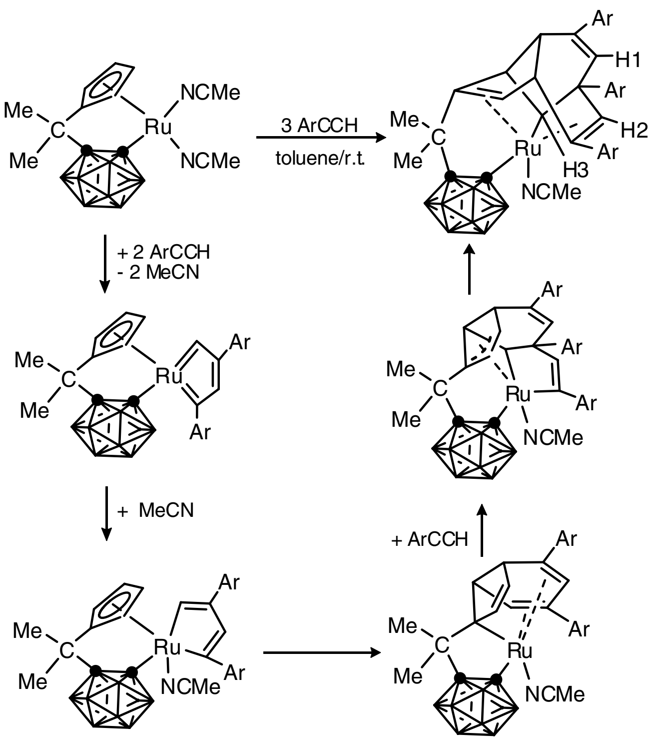
Moreover, in the course of synthesizing complexes containing doubly linked ligand, an unusual intramolecular coupling reaction of *o*-carboranyl with cyclopentadienyl has been established [43]. Reactions of $[Me(R^1)A(C_5H_3R^2)(C_2B_{10}H_{10})]Li_2$ with one equivalent of $RuCl_2(PPh_3)_3$ afford $[\eta^5\text{-}Me(R^1)A(C_5H_2R^2)(C_2B_{10}H_{10})]RuH(PPh_3)_2$ (A = C, R^1 = H, Me, R^2 = H; A = C, $R^1 = R^2$ = Me; A = Si, R^1 = Me, R^2 = H). However, the reaction of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with $RuCl_2[PPh_2(OEt)]_3$, or $RuCl_2(PPh_3)_3$/dppe under the same conditions affords only $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]RuL_2$ (L = $PPh_2(OEt)$, dppe). These results show that such intramolecular coupling reactions are driven by steric factors. A possible reaction pathway for the formation of ruthenium(II) hydride complexes is shown in Scheme 10.

$[Pd(\eta^5\text{-}C_5HPh_4)(\mu\text{-RNC})]_2$ reacts with isocyanide to yield the ketenimine compound, $Ph_4C_4C{=}C{=}NR$ (R =

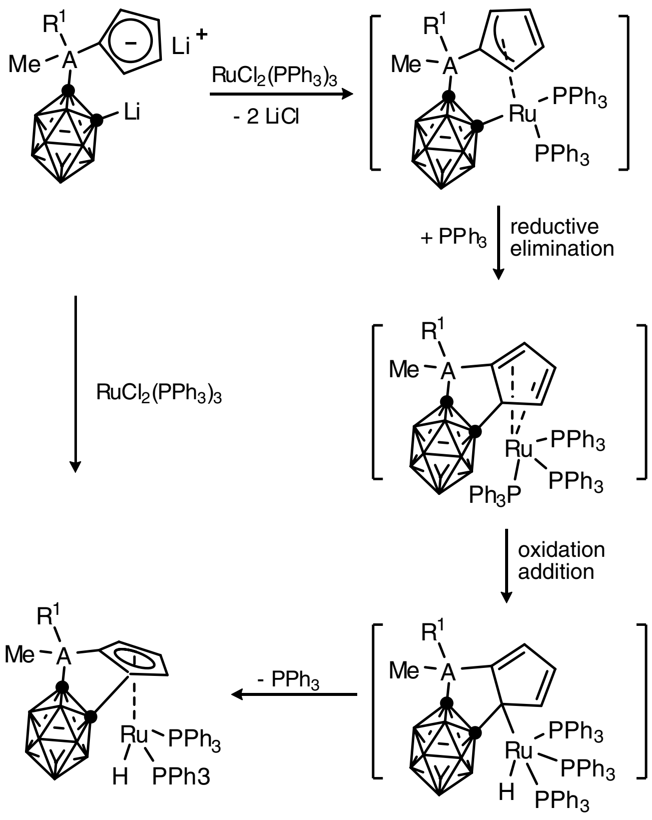


L = XylNC, X = LiBu^n,N aBH$_4$,R = H;
L= CO. X = NaBH$_4$.R = H;
X=R MgCl. R = Me, Pr^i,B u^n,P h;
L = CO. X = LiR. R = Me, Bu^n.
L= CO; R = Me, Bu^n,P h

Scheme 8.

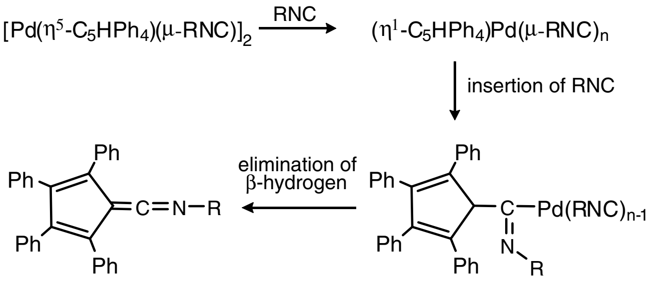


Scheme 9.



A = C, Si; R^1 = H, Me

Scheme 10.



R = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$

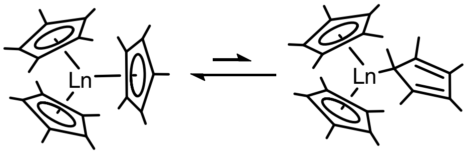
Scheme 11.

2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$), a possible mechanism involves an initial $\eta^5 \rightleftharpoons \eta^1$ interconversion of C$_5$HPh$_4$ ligand followed by an insertion of isocyanide into a Pd–C σ-bond, and the subsequent elimination of a β-hydrogen atom (Scheme 11) [44].

2.3. Rare earth complexes

Cyclopentadienyl ligands are generally inert to lanthanide-based reaction chemistry except elimination reaction [4]. Only recently, Evans and coworkers demonstrated that bulky substituted cyclopentadienyl lanthanide complexes, such as (C$_5$Me$_5$)$_3$Ln, offer a scaffold for interesting metal–cyclopentadienyl bond reactivity [9]. Namely, the C$_5$Me$_5$ ring of organolanthanide complexes adopts uncharacteristic reactivity patterns and displays high reactivity with a variety of substrates when the C_5Me_5 ligand is placed in sufficiently congested coordination environments. Depending on the substrate encountered, $(C_5Me_5)_3Ln$ can react in two reaction modes: (1) as if they were bulky alkyl complexes $(\eta^5\text{-}C_5Me_5)_2Ln(\eta^1\text{-}C_5Me_5)$ or (2) as if they were the zwitterions $[(C_5Me_5)_2Ln]^+C_5Me_5]^-$ in which the $[C_5Me_5]^-$ ligand is functioning as a one-electron reductant. The order of reactivity of $(C_5Me_5)_3Ln$ (Ln = La, Ce, Pr, Nd, Sm) is $(C_5Me_5)_3Sm > (C_5Me_5)_3Nd > (C_5Me_5)_3Pr > (C_5Me_5)_3Ce > (C_5Me_5)_3La$, suggesting that the reactivity increases with the decreasing size of the metal.

The alkyl-like reactivity of the $(C_5Me_5)_3Ln$ complexes without elimination of pentamethylcyclopentadienyl group has been investigated with CO [45–47], THF [47–51], PhCN [51], PhNCO [51], and CO_2 [47]. In these reactions, $(C_5Me_5)_3Ln$ can react initially as if an $\eta^5\text{-}C_5Me_5 \rightleftharpoons \eta^1\text{-}C_5Me_5$ equilibrium occurs as shown in Eq. (10), which leads to sterically less crowded $(C_5Me_5)_2Ln(\eta^1\text{-}C_5Me_5)$ and thus features $\eta^1\text{-}C_5Me_5$ alkyl-like reactivity.



(10)

$(C_5Me_5)_3Sm$ reacts with CO to form an unexpected thermally stable carbocationic complex $(C_5Me_5)_2Sm(O_2C_7Me_5)$ via double insertion of CO into Sm–C(C_5Me_5) unit (Scheme 12) [45]. Spectral analyses indicate that the reaction of $(C_5Me_5)_3Ln$ (Ln = Ce, Pr, Nd) with CO gives the analogous compounds $(C_5Me_5)_2Ln(O_2C_7Me_5)$. However, only at 50 °C and longer reaction time does the formation of $(C_5Me_5)_2La(O_2C_7Me_5)$ has been examined [46,47]. In remarkable contrast to the insertion chemistry of $(C_5Me_5)_3Ln$, addition of CO to $(C_5Me_5)_3U$ affords only an uranium carbonyl adduct product $(C_5Me_5)_3U(CO)$ [46].

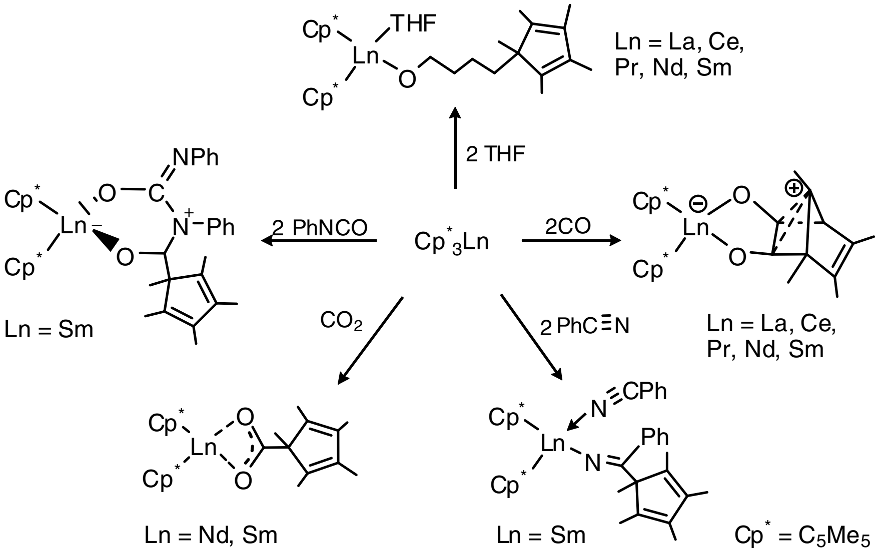
All the lanthanides $(C_5Me_5)_3Ln$ (Ln = La, Ce, Pr, Nd, Sm) react with THF to form the ring-opened products $(C_5Me_5)_2Ln[O(CH_2)_4C_5Me_5](THF)$ but more rigorous conditions are required for increasing the size of the metal complex (Scheme 12) [47–51]. $(C_5Me_5)_2Ln(\eta^1\text{-}C_5Me_5)$(THF) is initially formed and then the coordinated THF could be Lewis acid-activated to nucleophilic attack by the adjacent C_5Me_5 group.

$(C_5Me_5)_3Sm$ reacts with 2 equiv of PhCN to form $(C_5Me_5)_2Sm[NC(Ph)C_5Me_5](NCPh)$ (Scheme 12). In the insertion base adduct, one benzonitrile has been inserted into a Sm–C(C_5Me_5) unit while another coordinates to samarium atom [51].

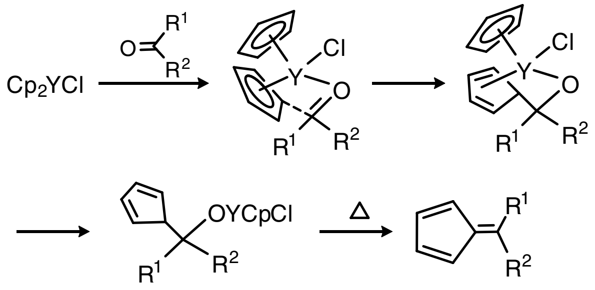
$(C_5Me_5)_3Sm$ reacts with PhNCO in a 1:2 molar ratio to form a more complicated product $(C_5Me_5)_2Sm[OC(C_5Me_5)N(Ph)C(NPh)O]$ (Scheme 12). The formation of the observed product can be rationalized by a C–N coupling between a coordinated PhNCO and a PhNCO unit initially inserted into a Sm–C_5Me_5 bond via the intermediate $(C_5Me_5)_2Sm[OC(C_5Me_5)NPh](OCNPh)$, an analogue to the above-mentioned $(C_5Me_5)_2Sm[NC(Ph)C_5Me_5](NCPh)$, which contains a nucleophilic nitrogen adjacent to the carbon atom of the coordinated isocyanate, a position that is electrophilic [51].

Studies on the reactivity of $(C_5Me_5)_3Ln$ toward CO_2 are scarce [47]. $(C_5Me_5)_3Ln$ (Ln = Nd, Sm) reacts with CO_2 in toluene to give the products from formal CO_2 insertion into a Sm-($\eta^1\text{-}C_5Me_5$) unit, $(C_5Me_5)_2Ln(O_2CC_5Me_5)$ (Scheme 12).

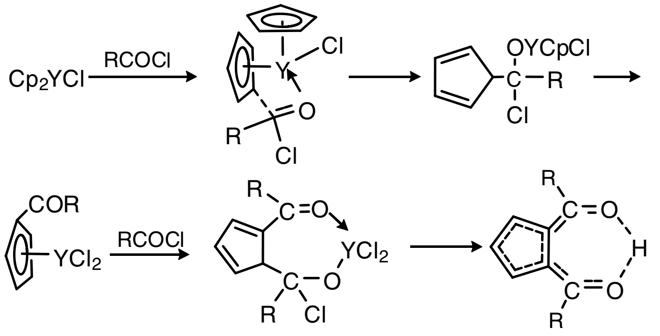
In the reactions of Cp_2YCl with aldehydes and ketones, the insertion of carbonyl into the Y–Cp π-bond generates fulvenes at 80 °C, whereas at lower temperature affording, after hydrolysis, cyclopentadienyl substituted alcohols. A possible reaction pathway for the formation of fulvenes is shown in Scheme 13 [52]. Evidence for another interesting insertion of carbonyl into the Ln–Cp π-bond is indirectly



Scheme 12.



Scheme 13.



Scheme 14.

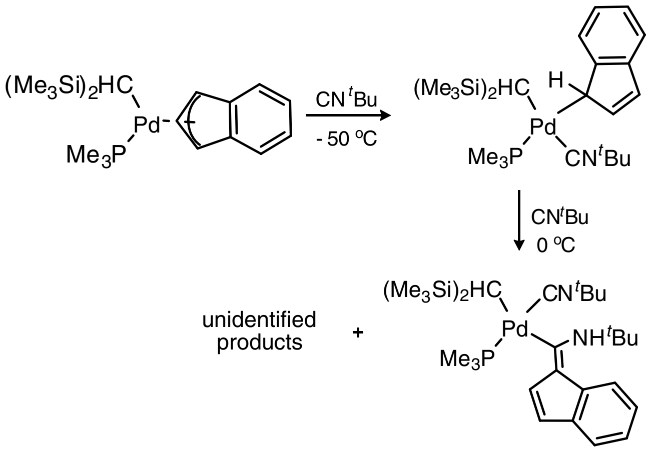
obtained in the reaction of Cp_2YCl with RCOCl, which affords 1,5-diacylcyclopentadienes and $RCO_2(CH_2)_4Cl$, an acylative ring-opening product of tetrahydrofuran (Scheme 14) [53].

3. Reactivity of the fluorenyl ligand

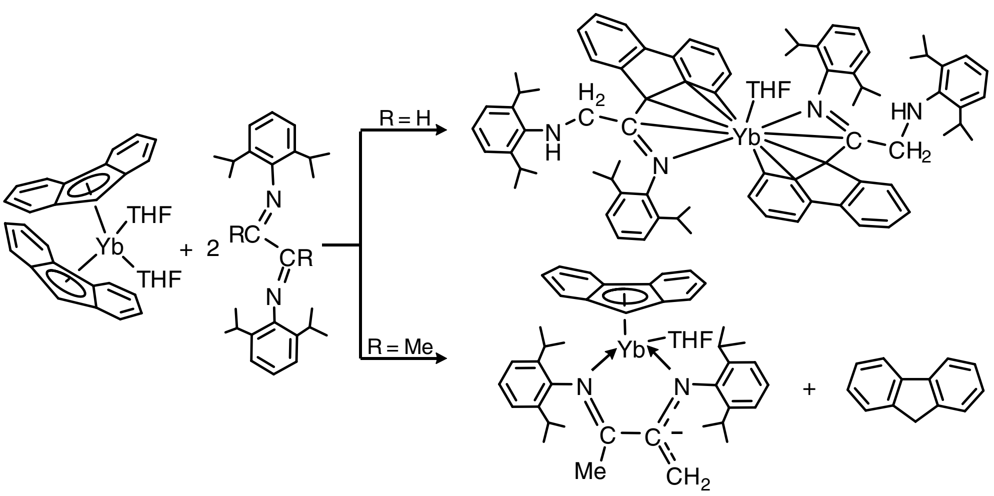
Compared with the corresponding cyclopentadienyl counterparts, studies on the reactivity of fluorenyl complexes are relatively scarce [5], and there are fewer examples involving the fluorenyl ligand. $Yb(C_{13}H_9)_2(THF)_2$ reacts with 2 equiv. of $(2,6\text{-}{}^iPr_2C_6H_3)N{=}CHCH{=}N(2,6\text{-}{}^iPr_2\text{-}C_6H_3)$ to form $Yb\{\eta^5\text{-}C_{13}H_8C({=}N[2,6\text{-}{}^iPr_2C_6H_3])CH_2NH\text{-}C_6H_3(2,6\text{-}{}^iPr_2C_6H_3)\}_2(THF)$ by the coupling of the fluorenyl and 1,4-disubstituted diazadienes (DAD) fragments [54]. However, the reaction pathway can be dramatically changed by modification of the substituent R on the carbon atom of the imino group in DAD. Reaction of $Yb(C_{13}H_9)_2(THF)_2$ with $(2,6\text{-}{}^iPr_2C_6H_3)N{=}CMeCMe{=}N(2,6\text{-}{}^iPr_2C_6H_3)$ under the same conditions leads to the formation of $Yb(\eta^5\text{-}C_{13}H_9)\{2,6\text{-}{}^iPr_2C_6H_3N{=}CMeC(CH_2){=}NC_6H_3{}^iPr_2\text{-}2,6\}(THF)$ and fluorine by proton abstraction from the DAD molecule (Scheme 15).

4. Reactivity of the indenyl ligand

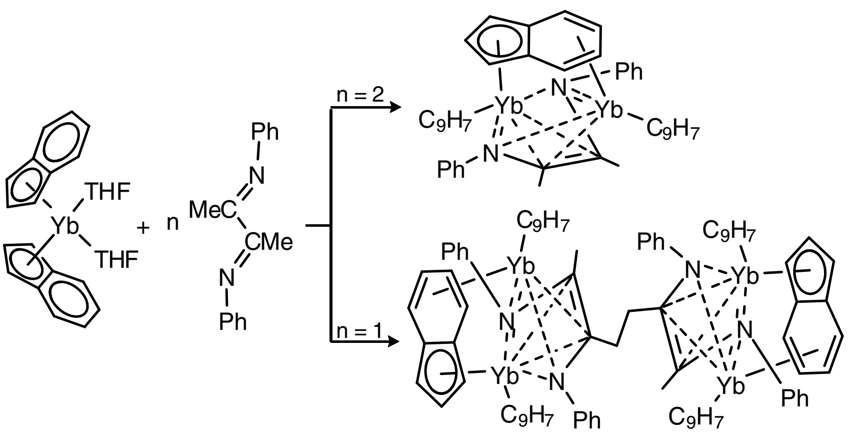
The higher reactivity of indenyl complexes in comparison to their Cp counterparts has been demonstrated convincingly in a number of reactions. Surprisingly, the reactions based on the indenyl ligands have remained little explored so far. The Pd(II) complex $(\eta^3\text{-Ind})Pd[CH$



Scheme 16.



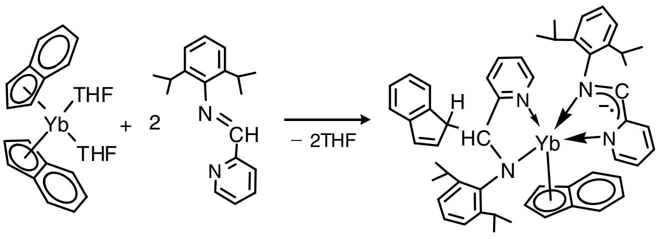
Scheme 15.



Scheme 17.

$(SiMe_3)_2](PMe_3)$ reacts with 2 equiv. of ${}^tBuNC$ to give an palladabenzofulvene $Pd[C(NH^tBu){=}C(C_8H_6)][CH(SiMe_3)_2](CN^tBu)(PMe_3)$ along with unidentified products [55]. Carrying out this reaction at low temperature and with only 1 equiv. of ${}^tBuNC$ has allowed the detection of an intermediate bearing an η^1-Ind species $Pd(\eta^1\text{-}C_9H_7)[CH(SiMe_3)_2](CN^tBu)(PMe_3)$, while the CN^tBu inserts into the Pd–η^1-Ind bond to give the palladabenzofulvene complex in the presence of another equivalent of ${}^tBuNC$ and with a higher temperature (about 0 °C) (Scheme 16).

Insertion of imine into the η^5-Yb-C_9H_7 bond is observed in the reaction of 2-((2,6-diisopropylphenylimino)methyl)pyridine with $(C_9H_7)_2Yb(THF)_2$, affording the Yb(III) derivative $[Yb(\eta^5\text{-}C_9H_7)\{N(2,6\text{-}{}^iPr_2C_6H_3)CH(C_9H_7)(C_5H_4N)\}\{2,6\text{-}{}^iPr_2C_6H_3NCH(C_5H_4N)^{\cdot-}\}]$ (Eq. (11)) [56]. Chelating effects and electron-accepting properties of imino compounds dramatically influence the insertion process, for example, imine $2,6\text{-}{}^iPr_2C_6H_5N{=}CHC_6H_5$ and iminothiophene $2,6\text{-}{}^iPr_2C_6H_5N{=}CHC_4H_4S$ do not react with $(C_9H_7)_2Yb(THF)_2$ even at more rigorous conditions. Moreover, both steric hindrance in the coordination sphere of the metal atom and the coordination capacities of the π-aromatic ligands bound to ytterbium also play a crucial influence on the reactivity pathway of ytterbocenes towards 2-(((2,6-diisopropylphenyl)imino)methyl)pyridine. For the complexes $L_2Yb(THF)_2$ ($L = C_{13}H_9$, C_5Me_5), the same reaction results in an oxidative cleavage of the η^5 Yb-L ($L = C_{13}H_9$, C_5Me_5) bond and formation of $[Yb\{2,6\text{-}{}^iPr_2C_6H_5NCH(C_5H_4N)^{\cdot-}\}_3]$ and $[Yb(C_5Me_5)\{2,6\text{-}{}^iPr_2C_6H_3NCH(C_5H4N)^{\cdot-}\}_2]$, respectively.

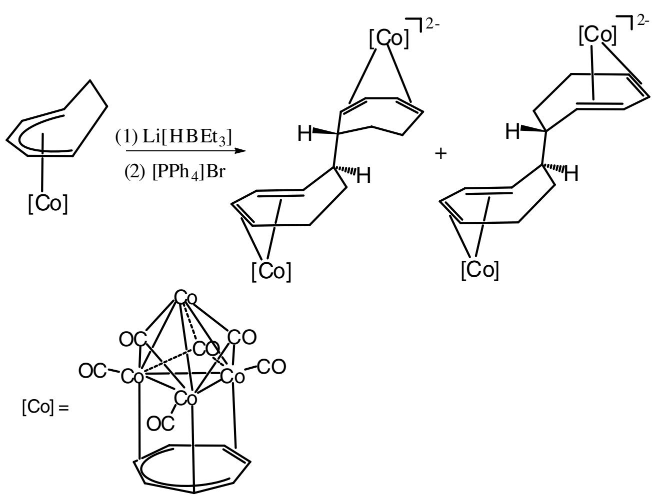


(11)

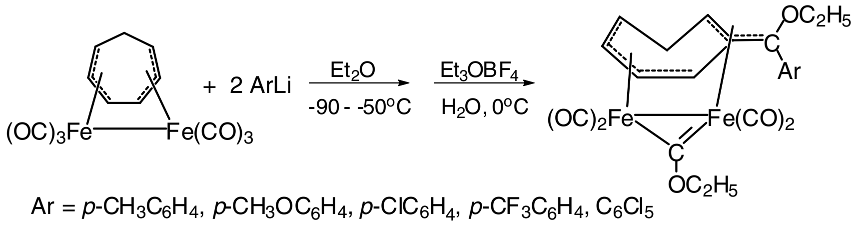
$Yb(C_9H_7)_2(THF)_2$ reacts with $PhN{=}C(Me)C(Me){=}NPh$ to give mixed-valent $Yb_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)_2\{\mu\text{-}\eta^4{:}\eta^4\text{-}PhNC(Me){=}C(Me)NPh\}$ with a μ-$\eta^5{:}\eta^4$- indenyl bridge or the coupling product of DAD ligands, $[Yb_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)_2\{\mu\text{-}\eta^4{:}\eta^4\text{-}PhNC(CH_2){=}C(Me)NPh\}]_2$, depending on the molar ratio of the reactants (Scheme 17) [57].

5. Reactivity of the cycloheptatrienyl ligand

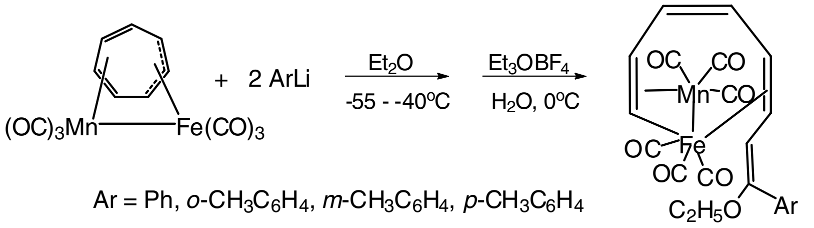
Treatment of tetracobalt cluster complex $Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ with $Li[HBEt_3]$, followed by addition of $[PPh_4]Br$, gives the complex $[\{Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_7H_7)\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-}(C_7H_9)_2)]^{2-}$ as a mixture of two diastereomers (Scheme 18) [58]. The coupling of carbon–carbon bond occurs exclusively at the carbon atoms in the enylic positions, adjacent to the unsaturated π-system of the C_7H_9 ligand, which indicates that the formation of $[\{Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_7H_7)\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-}(C_7H_9)_2)]^{2-}$ is regiospecific but not stereospecific.



Scheme 18.



Scheme 19.



Scheme 20.

(Cycloheptatriene)diiron hexacarbonyl $Fe_2(C_7H_8)(CO)_6$ reacts with 2 equiv. of aryllithium reagents, ArLi (Ar = p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-$CF_3C_6H_4$, C_6Cl_5), and then the resulting mixture is treated with Et_3OBF_4 in aqueous solution to afford isomerized bridging carbyne complexes, $Fe_2(CO)_4(\{\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7C(OC_2H_5)\text{-}Ar\}[\mu\text{-}C(OC_2H_5)])$ (Scheme 19) [59]. But the μ-(1-3-η: 4-7-cycloheptatrienyl)tricarbonylirontricarbonylmanganese $Mn(CO)_3Fe(CO)_3(C_7H_7)$ reacts with aryllithium reagents, ArLi (Ar = Ph, o-, m-, p-MeC_6H_4), under analogous conditions to yield ring-opened polyene complexes $[Mn(CO)_3\text{-}Fe(CO)_3]\{C_8H_7(OEt)Ar\}$ (Scheme 20) [60].

6. Conclusions

Recently there have been significant advances in the reaction chemistry of the M–C(η^5) bond. Reactivities that were believed challenging are now well documented. Nevertheless, much remains to be accomplished. It is clear that the aromatic carbocycle anion π-ligands can be reactive species rather than the spectator in some cases. Studies on the reaction chemistry of M–C(η^5) have potential for generating novel reactivity patterns and forming interesting organometallic derivatives in the future, since these reactions are sensitive to the electronic and steric characteristics of both the substrates and carbocyclic anion ligands.

The advances in the metal–carbon(η^5) insertion chemistry have demonstrated that reactivity patterns for metal complexes with the aromatic carbocycle anion ligand can be different to those shown by metal–alkyl, allyl and propargyl complexes and these differences are highlighted. For example, $(C_5Me_5)_3Sm$ reacts with CO to form an unusual thermally stable carbocationic complex $(C_5Me_5)_2Sm(O_2C_7Me_5)$ via double insertion of CO into Sm-C (C_5Me_5) unit, which is impossible for alkyl complexes. Therefore, further study of the reactivity chemistry based on aromatic carbocycle anion ligands can be expected to provide more detailed understanding and contributions to the development of organometallic chemistry.

Acknowledgements

We thank the NNSF of China, NSF of Shanghai, and Research Fund of Young Teacher of Fudan University for financial support.

References

[1] P.L. Pauson, T.J. Kealy, Nature 168 (1951) 1039.
[2] (a) P. Jutzi, N. Burfold, Chem. Rev. 99 (1999) 969;
(b) T.P. Hanusa, Organometallics 21 (2002) 2559;
(c) M.A. Beswick, J.S. Palmer, D.S. Wright, Chem. Soc. Rev. 27 (1998) 225.
[3] (a) S. Harder, Coord. Chem. Rev. 176 (1998) 17;
(b) J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307;
(c) K.E. Torraca, L. McElwee-White, Coord. Chem. Rev. 206–207 (2000) 469.
[4] (a) X.G. Zhou, M. Zhu, J. Organomet. Chem. 647 (2002) 28;
(b) H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865;
(c) H.C. Aspinall, Chem. Rev. 102 (2002) 1807;
(d) S. Arndt, J. Okuda, Chem. Rev. 102 (2002) 1953.
[5] (a) E. Kirillov, J.-Y. Saillard, J.-F. Carpentier, Coord. Chem. Rev. 249 (2005) 1221;
(b) M. Stradiotto, M.J. McGlinchey, Coord. Chem. Rev. 219–221 (2001) 311.
[6] D. Zargarian, Coord. Chem. Rev. 233–234 (2002) 157.
[7] V.R. Miller, R. Weiss, R.N. Grimes, J. Am. Chem. Soc. 99 (1977) 5646.
[8] (a) E. Klei, J.H. Teuben, H.J. de Liefde Meijer, E.J. Kwak, J. Organomet. Chem. 224 (1982) 327;
(b) P.W. Jolly, Acc. Chem. Res. 29 (1996) 544;
(c) C.M. Older, R. McDonald, J.M. Stryker, J. Am. Chem. Soc. 127 (2005) 14202;
(d) C.M. Older, J.M. Stryker, Organometallics 19 (2000) 3266;
(e) L.T. Dzwiniel, N. Etkin, J.M. Stryker, J. Am. Chem. Soc. 121 (1999) 10640;

(f) N. Etkin, T.L. Dzwiniel, K.E. Schweibert, J.M. Stryker, J. Am. Chem. Soc. 120 (1998) 9702;
(g) K.E. Schwiebert, J.M. Stryker, Organometallics 12 (1993) 600.
[9] W.J. Evans, B.L. Davis, Chem. Rev. 102 (2002) 2119.
[10] R. Fernández, E. Carmona, Eur. J. Inorg. Chem. (2005) 3197.
[11] E.O. Fischer, H.P. Hofmann, Chem. Ber. 92 (1959) 482.
[12] S.J. Pratten, M.K. Cooper, M.J. Aroney, J. Organomet. Chem. 381 (1990) 147.
[13] M.M. Conejo, R. Fernández, E. Gutiérrez-Puebla, A. Monge, C. Ruiz, E. Carmona, Angew. Chem., Int. Ed. 39 (2000) 1949.
[14] M.M. Conejo, R. Fernández, D. del Río, E. Carmona, A. Monge, C. Ruiz, Chem. Commun. (2002) 2916.
[15] M.M. Conejo, R. Fernández, D. Del Río, E. Carmona, A. Monge, C. Ruiz, A.M. Márquez, J.F. Sanz, Chem. Eur. J. 9 (2003) 4452.
[16] M.M. Conejo, R. Fernández, E. Carmona, R.A. Andersen, E. Gutiérrez-Puebla, A. Monge, Chem. Eur. J. 9 (2003) 4462.
[17] M.M. Conejo, R. Fernández, E. Carmona, Organometallics 20 (2001) 2434.
[18] M. Oberhoff, L. Duda, J. Karl, R. Mohr, G. Erker, R. Fröhlich, M. Grehl, Organometallics 15 (1996) 4005.
[19] K. Klaß, R. Fröhlich, G. Erker, J. Chem. Soc., Dalton Trans. (1999) 4457.
[20] K. Klaß, L. Duda, N. Kleigrewe, G. Erker, R. Fröhlich, E. Wegelius, Eur. J. Inorg. Chem. (1999) 11.
[21] R.A. Layfield, S.M. Humphrey, Organometallics 24 (2005) 6063.
[22] N. Etkin, C.M. Ong, D.W. Stephan, Organometallics 17 (1998) 3656.
[23] U. Rosenthal, C. Lefeber, P. Arndt, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov, J. Organomet. Chem. 503 (1995) 221.
[24] A. Tillack, W. Baumann, A. Ohff, C. Lefeber, A. Spannenberg, R. Kempe, U. Rosenthal, J. Organomet. Chem. 520 (1996) 187.
[25] D. Thomas, N. Peulecke, V.V. Burlakov, B. Heller, W. Baumann, A. Spannenberg, R. Kempe, U. Rosenthal, Z. Anorg. Allg. Chem. 624 (1998) 919.
[26] W.E. Crowe, A.T. Vu, J. Am. Chem. Soc. 118 (1996) 5508.
[27] D.M. Giolando, T.B. Rauchfuss, J. Am. Chem. Soc. 106 (1984) 6455.
[28] T. Takahashi, Y. Kuzuba, F. Kong, K. Nakajima, Z.F. Xi, J. Am. Chem. Soc. 127 (2005) 17188.
[29] Z.F. Xi, K. Sato, Y. Gao, J.M. Lu, T. Takahashi, J. Am. Chem. Soc. 125 (2003) 9568.
[30] Z.F. Xi, F.Z. Kong, W.X. Zheng, W.X. Zhang, Chinese. J. Org. Chem. 25 (2005) 229.
[31] R. Kempe, Angew. Chem., Int. Ed. Engl. 43 (2004) 1463.
[32] C.H. Suresh, N. Koga, Organometallics 25 (2006) 1924.
[33] L. Zhang, N. Xiao, Q. Xu, J. Sun, J.B. Chen, Organometallics 24 (2005) 5807.
[34] T.L. Dzwiniel, J.M. Stryker, J. Am. Chem. Soc. 126 (2004) 9184.
[35] B. Štíbr, Chem. Rev. 92 (1992) 225.
[36] M.L.H. Green, J.B. Leach, M.A. Kelland, J. Organomet. Chem. 691 (2006) 1295.
[37] (a) H. Hashimoto, M. Shang, T.P. Fehlner, Organometallics 15 (1996) 1963;
(b) H. Hashimoto, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 118 (1996) 8164.
[38] K. Kawamura, M.Y. Shang, O. Wiest, T.P. Fehlner, Inorg. Chem. 37 (1998) 608.
[39] N. Cabon, F.Y. Pétillon, P.-Y. Orain, P. Schollhammer, J. Talarmin, K.W. Muir, J. Organomet. Chem. 690 (2005) 4583.
[40] N. Cabon, E. Paugam, F.Y. Pétillon, P. Schollhammer, J. Talarmin, Organometallics 22 (2003) 4178.
[41] W.-S. Ojo, E. Paugam, F.Y. Pétillon, P. Schollhammer, J. Talarmin, Organometallics 25 (2006) 4009.
[42] Y. Sun, H.-S. Chan, H.T. Zhao, Z.Y. Lin, Z.W. Xie, Angew. Chem., Int. Ed. 45 (2006) 5533.
[43] Y. Sun, H.-S. Chan, Z.W. Xie, Organometallics 25 (2006) 4188.
[44] T. Tanase, T. Fukushima, T. Nomura, Y. Yamamoto, Inorg. Chem. 33 (1994) 32.
[45] W.J. Evans, K.J. Forrestal, J.W. Ziller, J. Am. Chem. Soc. 117 (1995) 12635.
[46] W.J. Evans, S.A. Kozimor, G.W. Nyce, J.W. Ziller, J. Am. Chem. Soc. 125 (2003) 13831.
[47] W.J. Evans, K.J.M. Perotti, S.A. Kozimor, T.M. Champagne, B.L. Davis, G.W. Nyce, C.H. Fujimoto, R.D. Clark, M.A. Johnston, J.W. Ziller, Organometallics 24 (2005) 3916.
[48] W.J. Evans, K.J. Forrestal, J.T. Leman, J.W. Ziller, Organometallics 15 (1996) 527.
[49] W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller, D. Alvarez, Organometallics 9 (1990) 2124.
[50] H. Schumann, M. Glanz, H. Hemling, F.H. Görlite, J. Organomet. Chem. 462 (1993) 155.
[51] W.J. Evans, K.J. Forrestal, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 9273.
[52] C.T. Qian, A. Qiu, Tetrahedron Lett. 29 (1988) 6931.
[53] C.T. Qian, A. Qiu, Y. Huang, W. Chen, J. Organomet. Chem. 412 (1991) 53.
[54] A.A. Trifonov, E.A. Fedorova, G.K. Fukin, N.O. Druzhkov, M.N. Bochkarev, Angew. Chem., Int. Ed. 43 (2004) 5045.
[55] F.M. Alías, T.R. Belderraín, M. Paneque, M.L. Poveda, E. Carmona, Organometallics 17 (1998) 5620.
[56] A.A. Trifonov, E.A. Fedorova, I.A. Borovkov, G.K. Fukin, E.V. Baranov, J. Larionova, N.O. Druzhkov, Organometallics 26 (2007) 2488.
[57] A.A. Trifonov, E.A. Fedorova, G.K. Fukin, E.V. Baranov, N.O. Druzhkov, M.N. Bochkarev, Chem. Eur. J. 12 (2006) 2752.
[58] H. Wadepohl, S. Gebert, H. Pritzkow, D. Osella, C. Nervi, J. Fiedler, Eur. J. Inorg. Chem. (2000) 1833.
[59] Y. Yu, J.B. Chen, Organometallics 12 (1993) 4131.
[60] B.H. Wang, R.H. Li, J. Sun, J.B. Chen, Chem. Commun. (1998) 631.