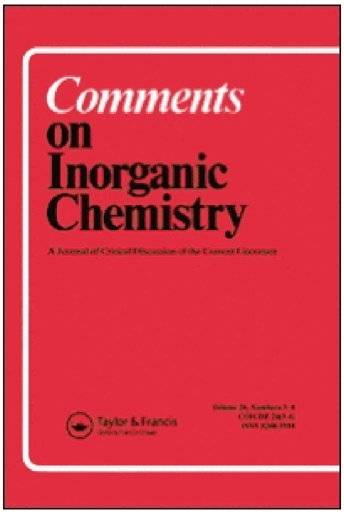

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Bifunctional Cyclopentadienyl Ligands in Organotransition Metal Chemistry

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Bifunctional Cyclopentadienyl Ligands in Organotransition Metal Chemistry

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The coordination chemistry of cyclopentadienyl ligands that contain an additional coördination site appended to the ring-periphery by a covalent bridge Z, C_5R_4-Z-X or C_5R_4-Z-L, is outlined. When transition metals are coordinated both to the cyclopentadienyl group C_5R_4 and the pendent donor site X or L (X = CH_2, NR′, O; L = HC=CH_2, NR'_2, PR'_2, OR′, SR′), the resulting complexes possess distinct properties due to the chelate effect. In such complexes the coordination sphere is defined by the nature of the bridge Z and the coordinating groups X and L and a series of metallacyclic complexes becomes available of which the chemistry is different from that of their non-bridged analogs.

Key Words: *functionalized cyclopentadienyl ligands, metallocene complexes, semilabile ligands, ligand design, chelate effect*

A. INTRODUCTION

More than forty years have elapsed since the serendipitous discovery of bis(η^5-cyclopentadienyl)iron or ferrocene[1] and its subsequent structural elucidation as the prototypical sandwich com-

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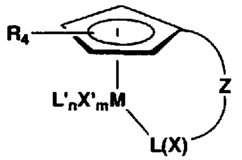
plex.[2,3] The introduction of the cyclopentadienyl ligand as a novel type of ancillary ligand in coordination chemistry[4] ushered in a period of explosive growth of organotransition metal chemistry. This development does not yet appear to have come to a halt. On the contrary, cyclopentadienyl transition metal complexes are increasingly finding application in catalysis and organic synthesis.[5] The most recent activities, such as employing bis(cyclopentadienyl) complexes of d- and f-block elements as catalyst components in homogeneous olefin polymerizations ("metallocene catalysts"[6]) as well as the use of chiral cyclopentadienyl complexes as reagents for stereoselective syntheses[7] emphasize the growing importance of this ligand.[8]

The present article focuses on transition metal complexes with cyclopentadienyl ligands that contain an additional coordinating site X or L tethered to the periphery of the five-membered ring via a bridge Z, where X is a one-electron, L a two-electron ligand (using the neutral ligand formalism), and Z a covalent bridge of appropriate length (Fig. 1). These bidentate ligands may give rise to chelate complexes in which the cyclopentadienyl group and the additional donor group X or L are both interacting with the metal center. To the best of our knowledge, the number of such transition metal complexes is still relatively small, in particular those ex-



Carbon:	$X = CH_2$, CO(acyl); $L = CH{=}CH_2$, $CH{=}CHCH{=}CH_2$, C_6H_5
Nitrogen:	X = NR', N; $L = NR'_2$, NC_6H_3(pyridyl)
Phosphorus:	X = PR'; $L = PR'_2$
Oxygen:	X = O; L = OR'
Sulfur:	L = SR'

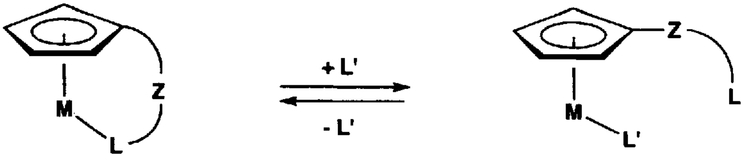
FIGURE 1 General formula for a metal complex containing a bifunctional cyclopentadienyl ligand. X and X′ denote one-electron, L and L′ two-electron ligands, following the neutral ligand formalism.

amples that had been designed rationally. We believe that such chelate complexes possess unique properties which differ significantly from those of the related cyclopentadienyl complexes without a link Z. They might offer new possibilities in rationally tailoring the coordination sphere around a reactive transition metal center. Also, by having an additional functionality L (or X) tethered to the cyclopentadienyl ligand it becomes possible to study intramolecular interaction of L with the metal center under conditions where substrate molecules similar to L would normally be reacting *inter*molecularly.

Two distinct types of chelate complexes containing such ligands can be distinguished according to the nature of the pendent coordination site X or L:

1. In many reactions the cyclopentadienyl ligand acts as an inert supporting ligand for a reactive transition metal center by not actively participating in a given substrate transformation. However, under certain conditions, for example during catalytic cycles, the cyclopentadienyl ligand may be involved in irreversible chemical reactions or may even dissociate from the metal.[9] A second donor L or X tethered to the cyclopentadienyl ligand could stabilize the binding of the entire ligand framework by additionally "anchoring" the cyclopentadienyl ligand system to the metal, thus preventing decomposition reactions. In such cases L or X will be bound at least as firmly as the cyclopentadienyl ligand (preferentially also as a multiply bonding ligand) at the metal center in order to ensure such enhanced stability.

2. If the additional ligand X or L is a weakly bonding ligand, it becomes possible to design so-called semilabile ligands. In such ligand systems, the cyclopentadienyl ligand is assumed to remain



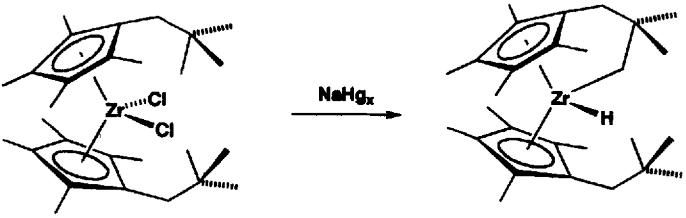
SCHEME 1 Semi-labile ligand based on cyclopentadienyl ligand where L is temporarily blocking a coordination site.

firmly coordinated at the reactive metal center, whereas the pendent ligand X or L could easily be displaced by an incoming substrate molecule, but at the same time should be able to protect the metal from deactivating through bimolecular aggregation reactions (Scheme 1). The weakly coordinating pendent group could be derived from solvent molecules such as ether groups. Phosphine-ether ligand systems have in fact been widely used as selective homogeneous catalysts,[10] demonstrating the validity of this concept.

By deliberately modifying the nature of each of the features C_5R_4, X, L, and Z in the cyclopentadienyl bifunctional ligand systems, a great potential for imparting novel properties to the resulting chelate complexes and for controlling the metal reactivity seems to emerge. What follows is an overview of some recent results, including our own.

B. LIGANDS BASED ON A CARBON FUNCTIONALITY

Alkyl substituted cyclopentadienyl ligands represent a somewhat special case of the bifunctional ligands, since an alkyl side chain would represent the most weakly "bonding" donor L for intramolecular complexation. To date an agostic bonding between the alkyl chain of a cyclopentadienyl ligand and a coordinatively unsaturated metal center does not appear to have been detected.[11] Such compounds would also be a useful model for the hitherto unknown metal alkane complex. Although saturated C–H and C–C bonds react intermolecularly with a transition metal center only with great difficulty,[11,12] it has been known that distal methyl groups of the pentamethylcyclopentadienyl ligand[13] can undergo a cyclometallation reaction to form so-called tucked-in complexes.[14] Formally, these compounds can be considered to be the first member of metallacyclic compounds where the metal center is coordinated to both the η^5-cyclopentadienyl and the η^1-alkyl group.[15] As demonstrated by Bercaw, intramolecular C–H activation through oxidative addition[16a] or sigma-bond metathesis[16b] occurs preferentially at the γ-position of the alkyl chain (Eq. (1)), leading to the formation of a five-membered metallacycle.



(1)

If the appended ligating group X represents another cyclopentadienyl ligand, the complexes derived from such linked bis(cyclopentadienyl) ligands are referred to as ansa-metallocenes or also as metallocenophanes. This class of complexes, in particular chiral ones, pioneered by Brintzinger,[7,17] have gained tremendous importance as homogeneous olefin polymerization catalysts. Although this rapidly growing field of substantial commercial potential cannot be included here,[6,7,17] it should be noted that many of these bridged cyclopentadienyl ligands have a number of properties in common with the bidentate functionalized cyclopentadienyl ligands.

The elegant design by Hawthorne of the highly active "one-armed bandit" hydrogenation catalyst based on a rhodium complex with the 1-(3-butenyl)-1,2-dicarbollide ligand[18] prompted us to investigate the coordination chemistry of ω-alkenyl functionalized cyclopentadienyl ligands in more detail. At the outset of our work several years ago, practically no such ligand was known, although some other ligand systems containing an ω-alkenyl function had been described in the literature which allowed the study of the intramolecular coordination of a C═C bond at a transition metal center.[15,19]

From inspection of molecular models, a 3-butenyl substituent was decided to have the appropriate chain length to enable the intramolecular coordination of the terminal olefin functionality at a metal center when attached to the cyclopentadienyl periphery. An allyl or a vinyl group[8b,8c] appeared to be too short for such an interaction, whereas a 4-pentenyl chain also seemed to have the right chain length, possibly with added conformational flexibility. Thus, 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene was synthesized by addition of 3-butenyl-Grignard reagent to 2,3,4,5-tetramethylcyclopenten-1-one,[21] following a methodology established previously for the synthesis of C_5Me_5H.[13b] One of the persistent synthetic obstacles, the dehydration of the intermediate carbinol, was overcome by the use of strongly acidic ion-exchange resins.[21g] ^1H and ^{13}C NMR spectra of THF-soluble $Li(C_5Me_4CH_2CH_2CH{=}CH_2)$ show that the anion has C_s symmetry and that the methyl groups of the ring and methylene protons of the side chain are pairwise enantiotopic. This NMR spectroscopic feature is diagnostic for all "open chain" complexes in which the olefinic bond does not interact strongly with the metal center and in which the metal center is not chiral.[22]

A number of transition metal derivatives of this ligand as well as the homologous 4-pentenyl system have been described, some of which could be converted into complexes containing intramolecular C=C bond coordination. This novel binding mode was demonstrated for cobalt,[21,22c] iridium,[22a] and nickel[22b] complexes (Fig. 2). These chelate complexes represent a new class of chiral organometallic complexes in which the asymmetry arises from a quasi-helical arrangement of the entire ligand framework rather than from a distinct chiral center, resembling the C_2-symmetric ansa-metallocenes[17] and the resolvable D_3-symmetric (all-trans-cyclododecatriene) nickel.[23]

As shown by NMR spectroscopic studies, the chelate complexes of cobalt(I) appear to be conformationally fairly rigid. The temperature independence of the ^1H NMR spectrum of $Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(CO)$ in the range -80–$+80$°C, for instance, suggests that no fluxional behavior such as ring inversion processes are occurring. The chelate ring is obviously also without much strain, since all the dihedral angles of the 3-butenyl chain

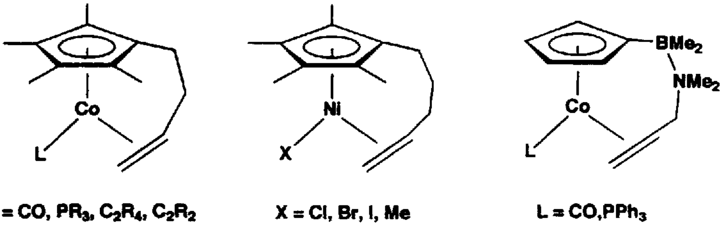


FIGURE 2 Examples of cyclopentadienyl complexes containing intramolecularly coordinated ω-alkenyl appendage [Co (Refs. 21a and 21c), Ni (Ref. 22b)].

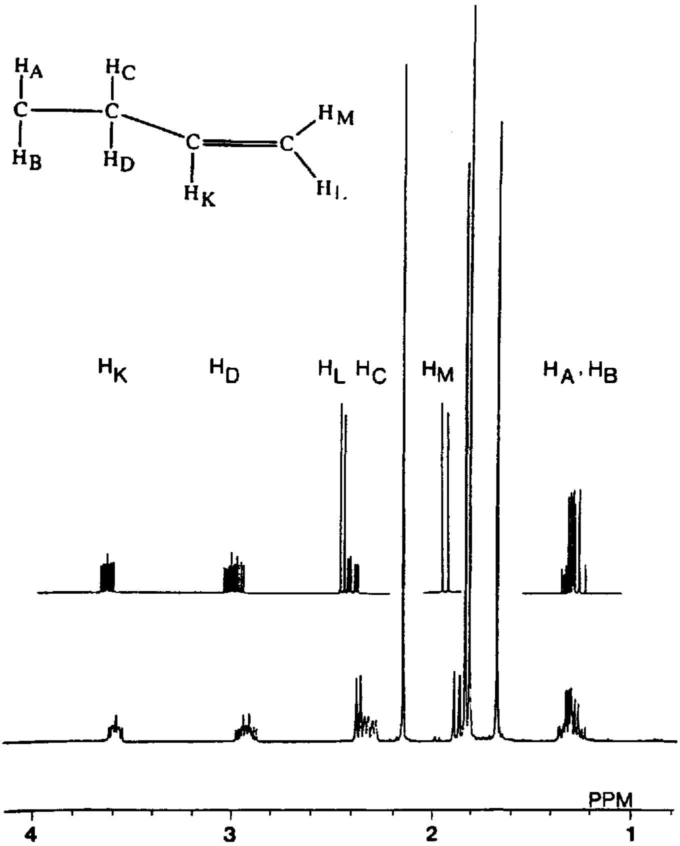
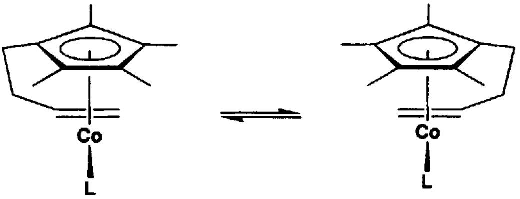


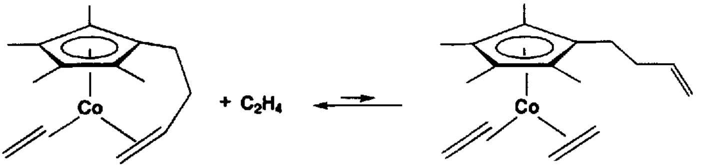
FIGURE 3 A portion of the ^1H NMR spectrum of (400 MHz, C_6D_6, 25°C) Co(η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)(CO).

show unexceptional values estimated from the ^nJ(H,H) coupling constants using the Karplus equation. Moreover, the configurational stability of the chelate complexes in solution is documented by the observation that prochiral groups such as the four methylene protons of the 3-butenyl chain in these complexes remain diastereotopic in the ^1H NMR spectrum (Fig. 3). A racemization process according to Eq. (2) therefore has to be slow on the NMR time scale.[21a,b,d]



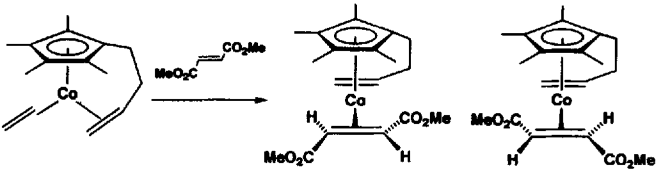
(2)

High-pressure NMR studies using the easily accessible ethylene complex $Co(\eta^5:\eta^2-C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2-C_2H_4)$ demonstrated that the equilibrium according to Eq. (3) lies significantly on the side of the chelate complex. Since the difference between the ligand dissociation enthalpy of ethylene and that of the olefinic side chain is expected to be marginal, the apparent stability of $Co(\eta^5:\eta^2-C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2-C_2H_4)$ versus the open-chain complex $Co(\eta^5-C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2-C_2H_4)_2$ has to be ascribed to the chelate effect.[21f]



(3)

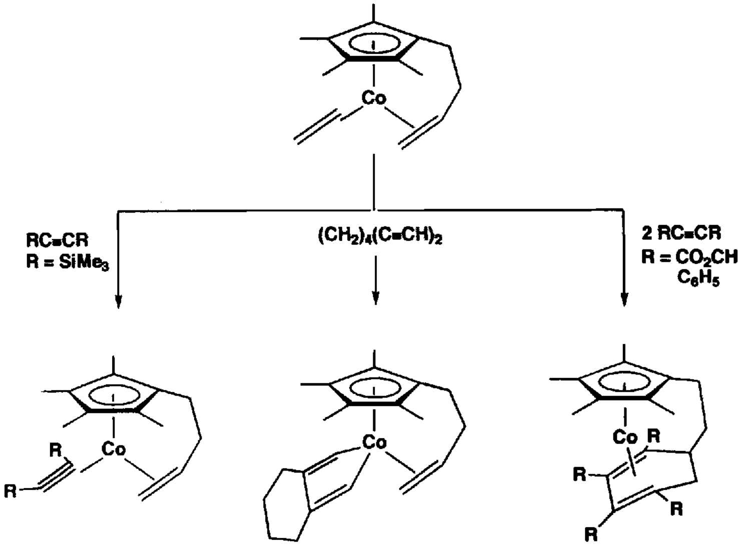
The ethylene complex indeed serves as a useful source for the 16-electron fragment $Co(\eta^5:\eta^2-C_5Me_4CH_2CH_2CH{=}CH_2)$, since substitution of the ethylene ligand with various non-chelating two-electron ligands L′ takes place smoothly to give complexes with the chelate structure retained. Furthermore, the prochiral olefin dimethyl fumarate reacts with $Co(\eta^5:\eta^2-C_5Me_4CH_2CH_2-CH{=}CH_2)(\eta^2-C_2H_4)$ to give a 67:33 mixture of two isomers (Eq. (4)). According to NMR spectroscopic data the isomers are diastereomers solely differing in the arrangement of the ester groups relative to the chelated 3-butenyl chain. Evidently, at a certain stage of the substitution reaction, the re and si faces of the incoming olefin are differentiated at the chiral cobalt fragment, a situation similar to that found for the thoroughly studied $[Re(\eta^5-C_5H_5)(NO)(PPh_3)]^+$ fragment.[24]



(4)

The ethylene complex undergoes a variety of reactions with alkynes to give some products which bear relevance to the [2 + 2 + 2] cycloaddition of alkynes mediated by organocobalt complexes. Again, the conformational rigidity of the 3-butenyl group accounts for the peculiarity of the products formed in the ligand sphere of Co(η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$), as summarized in Scheme 2. It is noteworthy that alkyne trimerization is completely suppressed, whereas [2 + 2 + 2] cycloaddition involving the 3-butenyl group takes place with activated alkynes to give a cyclohexadiene moiety linked to the cyclopentadienyl ligand.[21c,d,e]

A number of related complexes with functionalized side chains

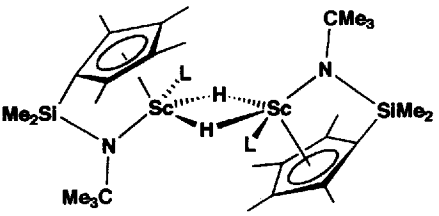


SCHEME 2 Reactivity of alkynes at the Co(η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$) fragment (Refs. 21c, 21d and 21e).

containing intramolecularly coordinated additional ligands L such as diene[25] and arene[26] have been reported.

C. LIGANDS BASED ON A NITROGEN FUNCTIONALITY

One of the problems associated with the bis(cyclopentadienyl) ligand systems is the substantial steric blocking of the metal-centered reaction site due to the characteristic electronic structure of the bent metallocene unit.[4b] Enhancement of reactivity is observed when the two ring ligands are "tied back" by a dimethylsilanediyl link as in some ansa-metallocene complexes.[6,17] However, even in such cases the "wedge" of the metallocene moiety may still be too congested to allow, for instance, the smooth polymerization of α-alkenes. In order to alleviate this steric constraint at the metal center, Bercaw and Shapiro replaced one ring ligand in the per-



L = PMe3

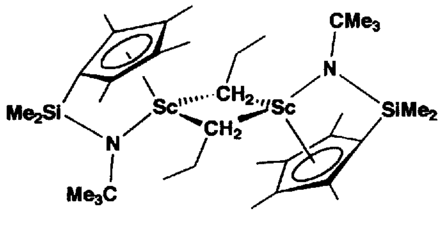
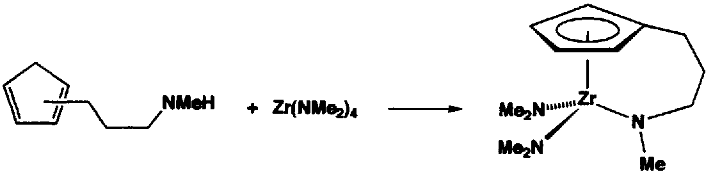


FIGURE 4 Scandium complexes containing a linked amido-cyclopentadienyl ligand that are examples of homogeneous single-component 1-olefin polymerization catalysts (Ref. 27).

methylscandocene complex Sc{(η^5-C_5Me_4)$_2$$SiMe_2$}R with a tert-butyl amido group. The new ligand system differs both electronically and sterically from the linked bis(cyclopentadienyl) ligand in Brintzinger-type ansa-metallocene derivatives, since the amido group can be regarded, at most, as a 3-electron ligand (including π-donation from the trigonal planar nitrogen atom). Whereas Sc{(η^5-C_5Me_4)$_2$$SiMe_2$}R dimerize α-olefins, the clearly more Lewis-acidic derivatives [Sc{η^5:η^1-C_5Me_4($SiMe_2NCMe_3$)}(PMe_3)(μ-H)]$_2$ and [Sc{η^5:η^1-C_5Me_4($SiMe_2NCMe_3$)}(μ-$CH_2CH_2CH_3$)]$_2$ (Fig. 4) were found to polymerize α-olefins in a quasi-living manner.[27]

Linked amido-cyclopentadienyl ligands were used by us in the context of stabilizing coordinatively unsaturated iron half-sandwich complexes with the aid of sterically demanding cyclopentadienyl ligands.[7] Although it proved not possible to isolate [Fe{η^5:η^1-C_5H_3(CMe_3)($SiMe_2NCMe_3$)}], we soon recognized that a number of ring-substituted ligands could be prepared and that titanium complexes such as Ti(η^5:η^1-C_5H_3(CMe_3)($SiMe_2NCMe_3$)}X_2 (X = Cl, alkyl) were easily accessible.[28c] Based on ^1H and ^{13}C NMR spectroscopic observation of inequivalent resonances for the bridging $SiMe_2$ group, the amido-cyclopentadienyl ligand was shown to generate a configurationally stable (on the NMR time scale) chiral coordination sphere. The ^1H NMR spectrum of Ti{η^5:η^1-C_5H_3(CMe_3)($SiMe_2NCMe_3$)}Me_2 is depicted in Fig. 5.

Recently, Teuben *et al.* synthesized zirconium and hafnium complexes of the type M(η^5:η^1-$C_5H_4CH_2CH_2CH_2NMe$)(NMe_2)$_2$ (M = Zr, Hf) containing a similar amido-cyclopentadienyl ligand by aminolysis of zirconium and hafnium tetrakis(dimethylamide) according to Eq. (5a). Selective cleavage of the non-linked amino groups under retention of the chelate structure led to a series of halo and alkyl derivatives (Eq. (5b)).[29]



(5a)

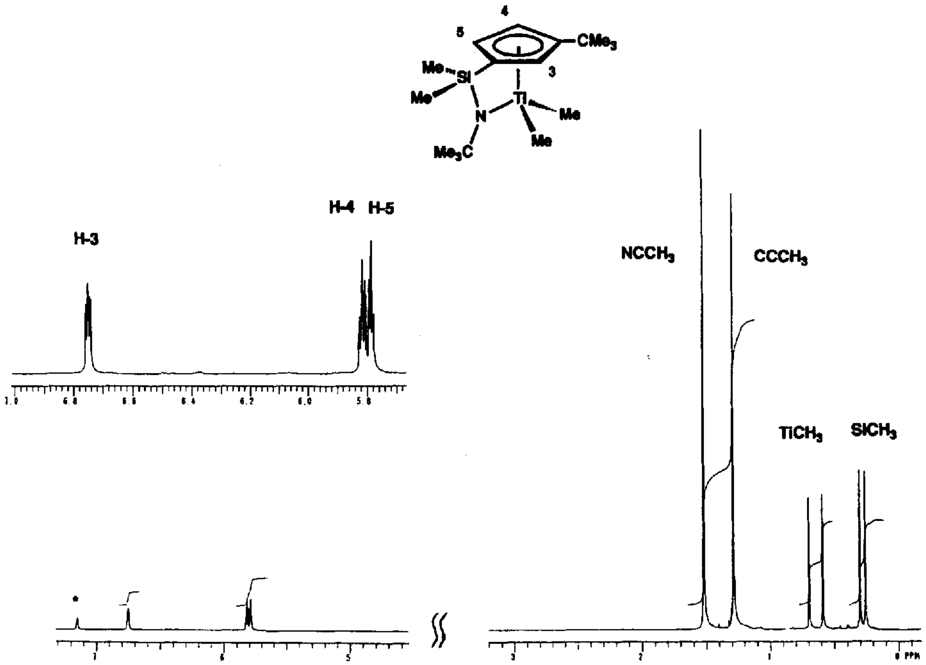
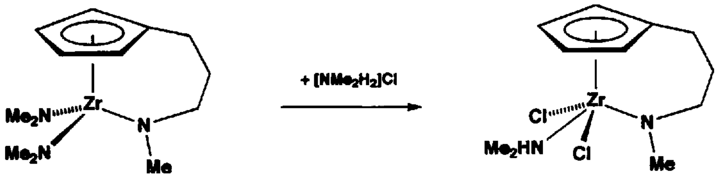


FIGURE 5 ^{1}H NMR spectrum (25°C; C_6D_6) of Ti{η^5:η^1-$C_5H_3(CMe_3)(SiMe_2NCMe_3)$}$Me_2$.

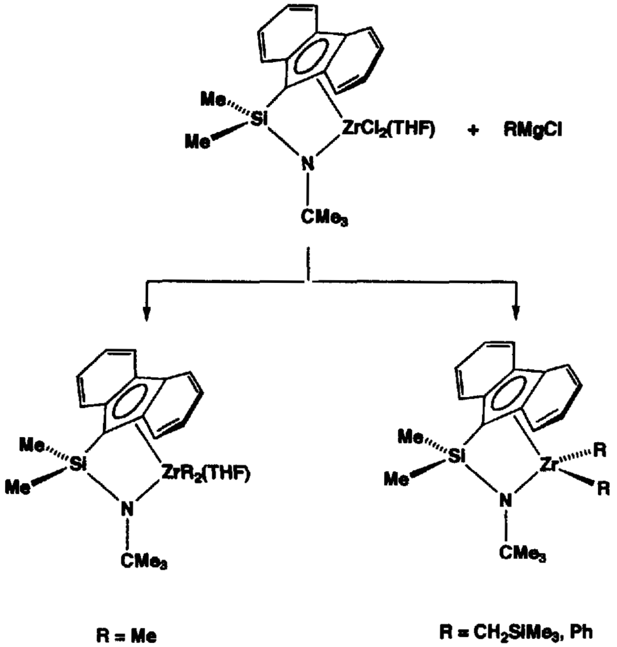


(5b)

Group 4 metal complexes containing an amido-cyclopentadienyl ligand C_5R_4-Z-NR′ have gained considerable importance as homogeneous polymerization catalysts in the presence of methyl alumoxane.[6] Copolymers of ethylene and 1-alkene with improved comonomer incorporation and distribution have been claimed by Exxon and Dow using such types of cyclopentadienyl complexes. According to patent literature,[30] practically all possible parameters, viz. the metal (Ti, Zr, Hf), substitution pattern of the ring (C_5R_4), nature of the bridge ($SiMe_2$, $SiMe_2SiMe_2$, CH_2CH_2), and the nitrogen substituent R′ appear to have been varied. However, consistent structure-activity/selectivity relationships for the polymerization reaction of ethylene and 1-alkene cannot be recognized yet.

We became interested in zirconium complexes of the fluorenyl-amido ligand, since mono(fluorenyl)zirconium chemistry was virtually unknown. Also, it was reported by Canich that $Zr\{\eta^5{:}\eta^1\text{-}(C_{13}H_8)(SiMe_2NCMe_3)\}Cl_2$/methylalumoxane produces isotactic polypropylene,[30a] whereas a cyclopentadienyl analogue, $Zr\{\eta^5{:}\eta^5\text{-}(C_{13}H_8)CMe_2(C_5H_4)\}Cl_2$, represents a syndiospecific catalyst.[31a] The modified coordination sphere generates a fairly Lewis-acidic zirconium center (Scheme 3),[28b] reminiscent of mono(cyclopentadienyl)zirconium rather than zirconocene complexes.[31b]

Green *et al.* developed a bridged cyclopentadienyl-imido ligand containing a 3-carbon link between the cyclopentadienyl ligand and the imido moiety (Fig. 6). An interesting isolobal analogy between an organoimido ligand RN^{2-} and a cyclopentadienyl ligand $C_5R_5^-$, both $2\pi,1\sigma$ 6-electron ligands, was proposed by Schrock[32] based on a series of organoimido complexes that can be classified as structural analogues of group 4 metallocene complexes according to the relation $Mo(NR)_2Cl_2 \leftrightarrow Nb(\eta^5\text{-}C_5H_5)(NR)Cl_2 \leftrightarrow Zr(\eta^5\text{-}C_5H_5)_2Cl_2$. The molecular structure of the niobium derivative $Nb(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2CH_2N)Cl_2(PMe_3)$ exhibits a strain-free



SCHEME 3 Four- and five-coordinate zirconium complexes containing an amido-fluorenyl ligand (Ref. 28b).

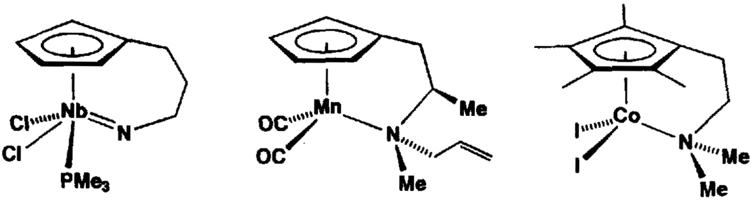


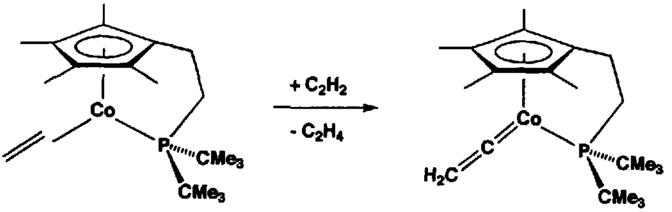
FIGURE 6 Examples of complexes with imido and amine functionalities.

chelate ring, indicating a close analogy to Brintzinger-type ansa-zirconocene complexes.[33] It will be interesting to see whether the polymerization properties of this niobium imido complex towards olefins will be comparable with those of zirconocene derivatives.[34]

As typically hard ligands, amines have been used much less frequently in organotransition metal chemistry than phosphine ligands. It is therefore striking that alkylamino groups can be coordinated to a soft organotransition metal fragment once it is tethered to the cyclopentadienyl ligand (Fig. 6).[35] Structurally characterized examples containing the ligand of the general type $\eta^5{:}\eta^1\text{-}C_5R_4CH_2CH_2NR'_2$ include $Mn\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CHMeNMe(CH_2CH{=}CH_2)\}(CO)_2$,[35a] cis-$Mo(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2NMe_2)(CO)_2I$,[35b] $Co(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)I_2$,[35d] and $\{Ti(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_5H_4N)Cl(\mu\text{-}O)\}_2$.[35e] Photolysis of $\{Mo(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)(CO)_3\}_2$ proceeded via completely different pathways compared to those of $Mo\{(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2$, even in the presence of $CH_2CH_2NH_3^+$. This finding was ascribed to the "supramolecular" reaction of the pendent group with unstable intermediates.[36]

D. LIGANDS BASED ON A PHOSPHORUS FUNCTIONALITY

Cyclopentadienyl ligands functionalized with a tethered phosphine group $-PR'_2$ are the oldest examples of the ligand types under consideration here.[37a] In view of the general importance of phosphine ligands in organometallic chemistry and homogeneous catalysis, it is somewhat surprising that only limited attention has been given to this type of ligand system.[37] Available data clearly suggest that the cyclopentadienyl-phosphino ligand, as a 5 + 2 electron ligand, forms a fairly rigid chelate ring with late transition metal centers. The optimum bridge length seems to be a 2 or 3 carbon chain corresponding to a five- or six-membered metallacycle, although a certain conformational mobility was reported for $Ru[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2](PPh_3)Cl$[37b] as well as for $Co[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PR_2](L)$ ($L = CO, C_2H_4$).[37c] The cobalt ethylene complex $Co[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PR_2](\eta^2\text{-}C_2H_4)$ undergoes an unexpected alkyne-vinylidene rearrangement within the $Co[\eta^5{:}\eta^2\text{-}C_5H_4CH_2CH_2PR_2]$ fragment, in contrast to the behavior of conventional half-sandwich complexes containing non-linked phosphine ligands (Eq. (6)).[37d,e]



(6)

By using a cyclopentadienyl ligand with two pendent diisopropyl phosphino groups, 1,3-$C_5H_3(SiMe_2CH_2P^iPr_2)_2$, the first isolable zirconium alkylidene complex Zr{η^5:η^1:η^1-1,3-$C_5H_3(SiMe_2CH_2P^iPr_2)_2$(=CHPh)Cl} was reported (Fig. 7). Obviously a highly rigid ligand sphere around the zirconium center allows a benzylidene complex to form by α-hydrogen elimination.[38]

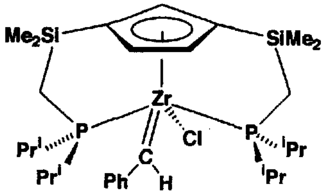


FIGURE 7 A zirconium complex containing a 1,3-difunctionalized cyclopentadienyl ligand which represents the first isolable zirconium alkylidene complex (Ref. 38).

E. LIGANDS BASED ON AN OXYGEN OR A SULFUR FUNCTIONALITY

In the context of studying the intramolecular attack of a nucleophile on a carbonyl ligand, a cyclopentadienyl ligand with a hy-

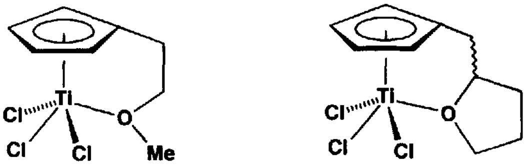
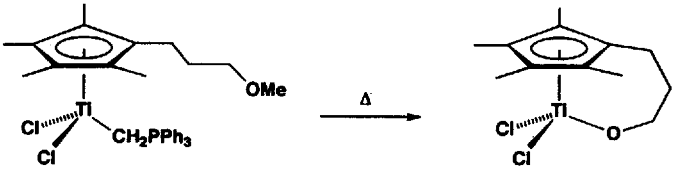
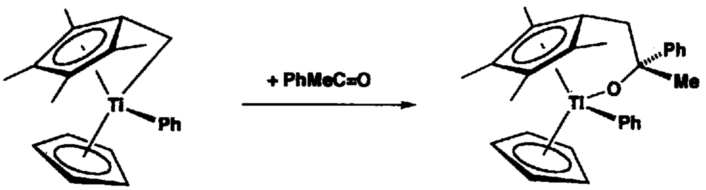


FIGURE 8 Titanium complexes of ether-functionalized cyclopentadienyl ligands (Ref. 41).

droxyalkyl function, $C_5H_4CH_2CH_2OH$, was synthesized which formed an alkoxycarbonyl ligand.[39a,b] The number of transition metal complexes containing bridged cyclopentadienyl-alkoxo ligands remains small, although appropriate ligand precursors are fairly readily available, e.g., by reaction of cyclopentadienyl anions with epoxides.[39c] One reason for the scarcity of such complexes, at least in the case of the early transition metals, might be the tendency of alkoxo complexes to di- and oligomerize with formation of bridging alkoxo groups. However, linked cyclopentadienyl-alkoxo ligand systems may be generated through other synthetic pathways, e.g., according to Eq. (7).[40]



(7a)

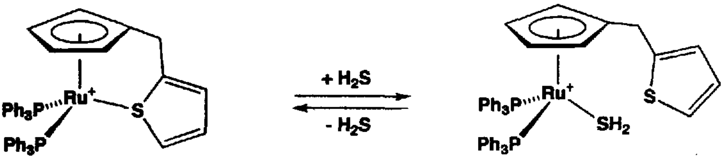


(7b)

A large number of cyclopentadienyl ligands containing a pendent ether functionality such as 2-methoxyethyl[41a] and α-tetrahydrofurylmethyl[41b] have been described in the literature (Fig. 8). These chelating ligands have drawn some attention in the context of synthesizing lipophilic and volatile mononuclear earth alkaline and lanthanide complexes.[41c] On the other hand, transition metal derivatives of these chelating ligands should be promising candidates for designing semi-labile ligands,[41d] although available data so far do not allow a conclusive judgment on how strongly the oxygen atom is bonded, e.g., in $Ti(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2OMe)Cl_3$.[41] A series of titanocene derivatives of functionalized cyclopentadienyl ligands has been studied as homogeneous catalysts for the isomerization of 1,5-hexadiene.[41d]

A cationic ruthenium half-sandwich complex, containing a 2-

thienylmethyl group, forming a chelate ring with a ruthenium-sulfur interaction was shown to react reversibly with hydrogen and hydrogen sulfide according to Eq. (8).[42]



(8)

F. CONCLUSION

Ligand design is a crucial step during the development of an efficient homogeneous catalyst, especially when high activity and selectivity are pursued. We believe that the use of the chelate effect[43] of bi- and polydentate cyclopentadienyl ligands offers a new method to control a reactive metal center more rationally and to generate a more stereochemically defined coordination sphere. It should be noted that in the area of macrocyclic ligand design a similar concept, using an intramolecular pendent group, has been successfully realized for quite some time.[44]

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