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Transition metal complexes with polydentate amido ligands: novel structural building blocks and chemical reagents

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Dedicated to Professor Helmut Werner, a mentor and friend, in recognition of his tremendous contributions to organometallic chemistry

Abstract

Polydentate amido ligands have recently been widely employed in the coordination chemistry of the early transition metals and the heavy p-block elements. Formally, trianionic tripodal amides have provided the key to a systematic program of complex synthesis aimed at the construction of di- or trinuclear compounds through direct metal–metal bonding. These include unsupported, metal–metal bonded early–late heterodimetallic complexes as well as a wide range of transition-metal-Group 14 complexes. These developments as well as the application of C_3-chiral complexes in stereoselective alkylations of organic carbonyl compounds will be reviewed in this article. An extension of the underlying principles of ligand design to a new class of diamidopyridine ligands will also be highlighted.

Keywords: Polydentate amido ligands; Transition metal complexes; Metal-metal bonds

1. Introduction

During the past decade, amido ligands, $[NR_2]^-$, have established themselves as highly versatile tools of ligand design in transition metal and in main group coordination chemistry. The pioneering studies in the field were carried out in the 1960s and 1970s by Bradley, Lappert and others and established the principal synthetic strategies and structural motifs of such compounds [1,2]. Their increasingly dominant role in ligand design has developed more recently and is linked to their unique σ and π donor capabilities as well as the availability of two substituent positions at the amido N-donor atom. This dual substitution pattern allows the integration of amido functions into ligand systems of both podand and macrocyclic topology [3,4], which leads not only to a well-defined relative orientation of the ligating atoms but opens up manifold possibilities of steric control. In such polyfunctional ligand systems, amido functions may be combined with other donor functionalities which possess a different formal charge and chemical hardness and, more generally, a different thermodynamic and kinetic stability of their interaction with the metal centre [5,6]. In the latter case, the strong metal–amide bonds form the anchoring elements of the polydentate ligands while the remaining donor functions may either influence the electronic properties of the central atom or mask potentially reactive coordination sites by virtue of their hemilabile nature [7].

This short overview will focus on two classes of amido podands, the symmetrical tripodal amido ligands **A**–**C** [8] as well as the formally *dianionic* diamidopyridine ligand **D** which we developed alongside the *trianionic* tripods (Fig. 1) [7,9]. Whereas **A** is derived from 1,1,1-tris(aminomethyl)ethane, which is a well-established ligand in its own right in Werner-type coordination chemistry [10], the silylamides **B** and **C** are obtained by aminolysis of the respective silylhalide precursors with three molar equivalents of essentially any commercially available primary amine [11]. The diamine precursor of the diamido-donor ligand **D** is readily accessible in

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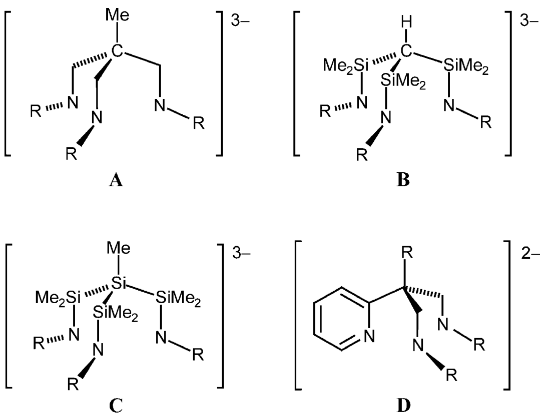
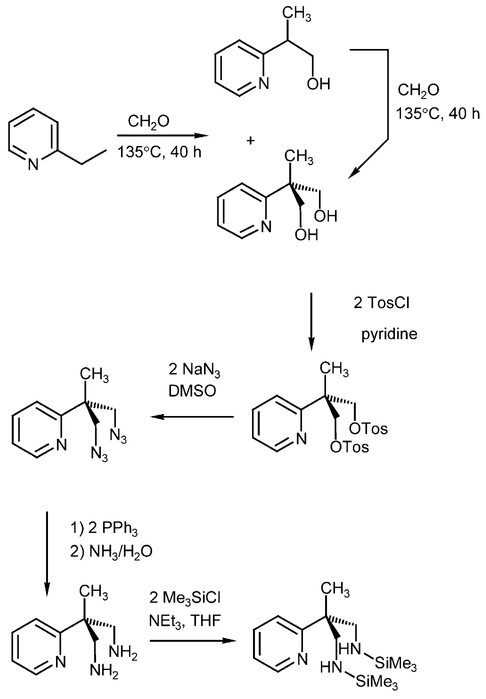


Fig. 1. The tripodal amides **A**–**D** the chemistry of which is highlighted in this review.

several reaction steps from a 2-alkylpyridine as the starting material (Scheme 1) [12].

2. Transition and main group metal complexes of the tripodal amides A–C as molecular building blocks

The tripodal amido ligands displayed in Fig. 1 have provided the key to a systematic program of complex synthesis aimed at the construction of di- or trinuclear compounds through direct metal–metal bonding. While the ligand framework of the amido tripods effectively shields a part of the coordination sphere of both metal centres engaged in metal–metal bonding, the metal bearing the tripod ligand is particularly kinetically protected by the peripheral (silyl or aryl) substituents at the nitrogen donor functions. At least as important as this kinetic stabilization of the dinuclear complexes is a significant thermodynamic contribution to their stability, which is the result of the incorporation of the early transition metal into the rigid [2,2,2]-bicyclooctane cage structure of the tripod-amide unit.



Scheme 1. Synthesis of the type **D** diamido-pyridine ligands.

2.1. *Stabilization of early–late heterodinuclear complexes by use of tripodal amido ligands*

The tripodal amides **A**–**C** have allowed the synthesis of early–late heterodimetallic complexes containing highly polar metal–metal bonds [13,14]. These were sufficiently stable for a systematic study of their reactivity towards a wide range of organic substrates. Three basic examples of these heterodinuclear compounds, containing unsupported polar metal–metal bonds, are depicted in Fig. 2.

In the simplest case, heterodinuclear complexes will react as pairs of metal electrophiles and nucleophiles. Cooperative reactivity is particularly likely with polar substrates. In this case, the electropositive early transition metal centre may react with the more Lewis basic part of the substrate while the nucleophilic late transition metal complex fragment will attack the more Lewis-acidic part of the substrate molecule. For metal–metal single bonds between the two metal centres, this interaction will go along with the cleavage of the metal–metal bond. In many cases, it is difficult to establish whether the cission of the metal–metal bond precedes the transformation of the substrate or whether it occurs at a later stage.

An example of the nucleophile/electrophile reactive pattern is the insertion of an unsaturated polar organic substrate into the metal–metal bond. The first such reaction was reported by Culter and coworkers who showed that Casey's Zr–M complexes insert CO_2 into their metal–metal bond [15,16] while Bergman et al. studied the reactions of an imido-bridged Ir–Zr complex with CO_2, COS, CS_2 and MeNCS (Scheme 2) [17].

While the insertion of CO_2 occurs in the expected fashion with the CO-unit bridging the two metal centres still remaining linked by the imido ligand, the other heteroallenes undergo fragmentation.

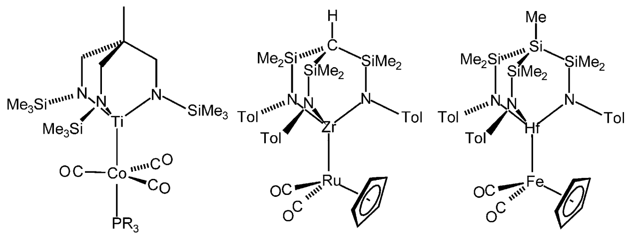
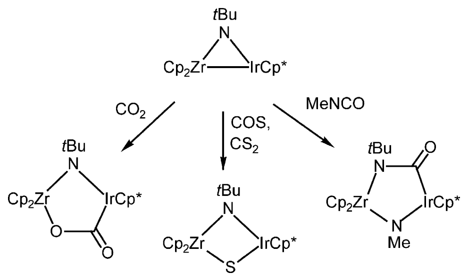


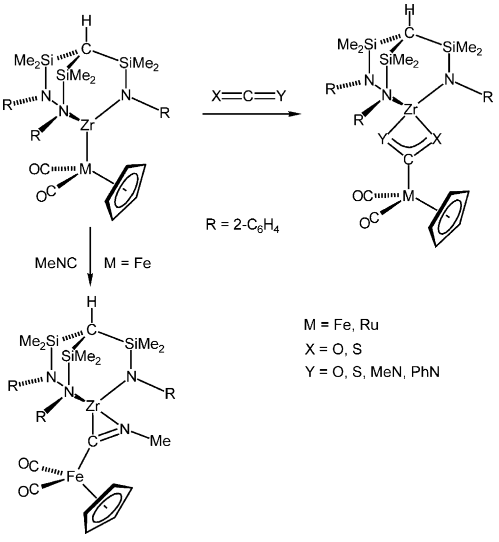
Fig. 2. Three representative examples of tripod-stabilized early–late heterodimetallic complexes containing unsupported metal–metal bonds.



Scheme 2. Insertion and fragmentation of heteroallenes upon reaction with the Zr–Ir complex.

The insertion of isocyanides provides another example of this reactive behaviour. Insertion reactions of isocyanides and heteroallenes carried out with the tripod-stabilized early–late heterodinuclear complexes which led to stable products are summarized in Scheme 3 [18].

The products of the simple insertion of an organic molecule (or a functional group in it) into the polar metal–metal bond are rarely isolable and, most often, further transformations follow this initial step. In the simplest case, these subsequent transformations closely mimic those which the organic molecules undergo with 'classical' nucleophiles and electrophiles. An example is the cleavage of esters RC(O)OR′ giving the early transition metal alkoxide and the acyl–metal derivative of the late transition metal complex fragment [19]. This reaction was extended to include lactones, in particular configurationally labile prochiral biaryllactones which were readily cleaved and subsequently decarbonylated to give the ring-opened products. The chiral biaryl axis in the reaction product is evident in the view of the molecular structure of one of the product complexes shown in Fig. 3 [20].



Scheme 3. Insertion of isonitriles and heteroallenes into the unsupported metal–metal bond of Zr–M heterodinuclear complexes.

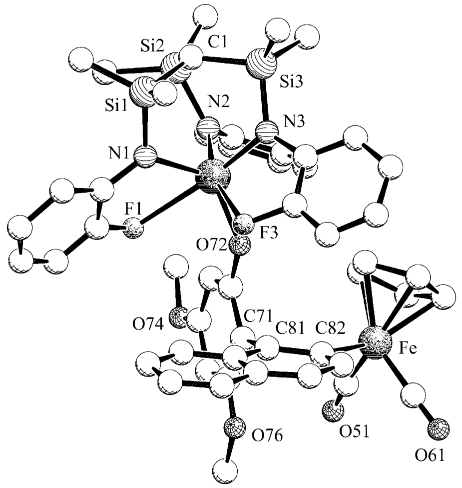
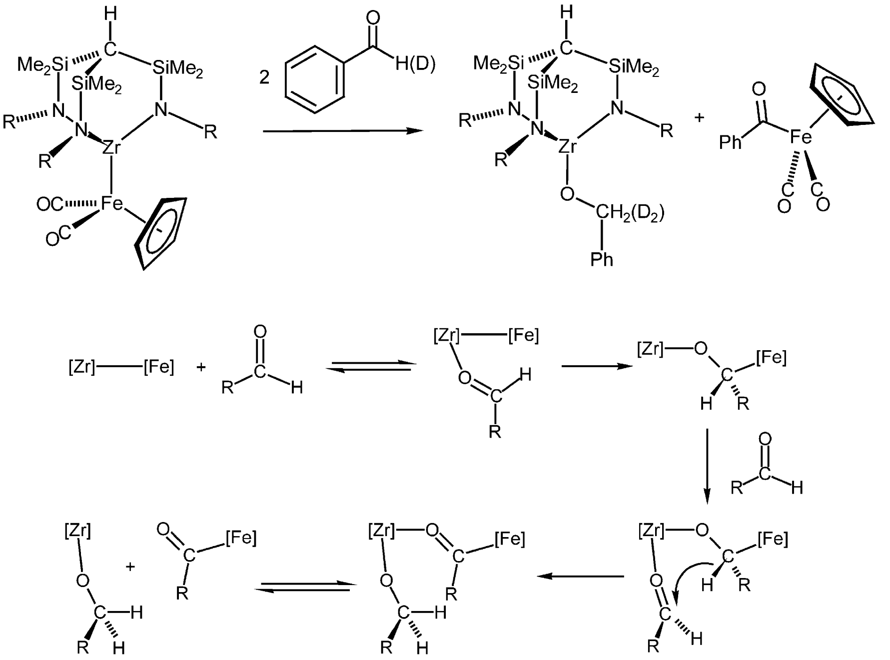


Fig. 3. Molecular structure of the ring oping product of [HC{$SiMe_2N(2\text{-}FC_6H_4)$}$_3$Zr–FeCp$(CO)_2$] with a biaryl lactone showing the chiral biaryl axis.

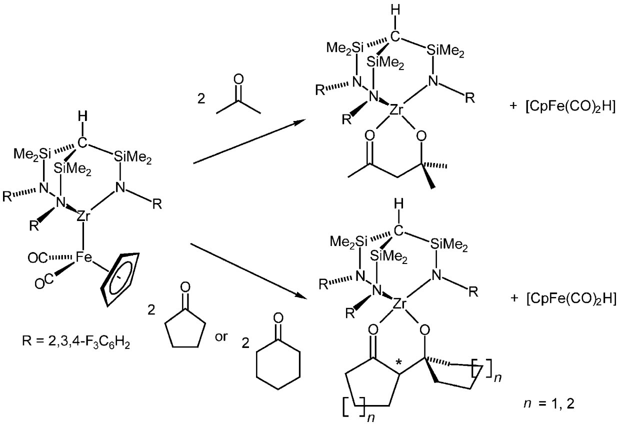
Aryl aldehydes react with Zr–M (M = Fe, Ru) heterodinuclear complexes according to the pattern of a Cannizzaro or Tishchenkov reaction yielding the aroyl–M complex and the benzoxyzirconium derivative (Scheme 4) [19]. The first step in the reaction sequence is thought to be the addition of an aldehyde molecule to the Lewis acidic early transition metal centre which is followed by its insertion into the metal–metal bond. The cleavage of the Zr–Fe (Zr–Ru) bond reduces the coordination number at zirconium which in turn facilitates the addition of the second molecule of the aldehyde. The crucial reaction step is the hydride transfer which follows and involves an analogous intermediate as proposed for the Cannizzaro disproportionation. Support for this intramolecular mechanism was obtained from the results of an isotope labeling experiment employing C_6H_5CDO.

Finally, reaction of [HC{$SiMe_2N(2,3,4\text{-}F_3C_6H_2)$}$_3$-Zr–FeCp$(CO)_2$] with ketones gave the aldol coupling products ligated to the Zr centre and equivalent amounts of the hydridoiron complex [CpFeH$(CO)_2$] (Scheme 5). The hydrido complex is thought to be formed in a first reaction step following the insertion of the carbonyl group into the metal–metal bond yielding an extremely reactive enolate which in turn rapidly undergoes aldol coupling with a second molecule of ketone [19].

The transformations discussed so far in this section leave the ligand already present in the starting materials unchanged. The carbonyls coordinated to the late transition metal may, however, participate directly in the conversion of a substrate. The late transition metal fragment is thus not only the nucleophile in the primary reaction step with the substrate but at the same time the binding site (or source) of the second reactant. This type of cooperativity has been found in a series of oxygen



Scheme 4. Top: Cannizzaro-type disproportionation of aryl aldehydes upon reaction with a Zr–Fe heterodinuclear complex. Bottom: Proposed mechanism of the 'hydride transfer'.



Scheme 5. Aldol coupling products obtained from the reaction of $[HC\{SiMe_2N(2,3,4\text{-}F_3C_6H_2)\}_3Zr{-}FeCp(CO)_2]$ with ketones.

transfer reactions. The most remarkable of these is the reaction of a Zr–Fe complex with 1,2-diphenylcyclopropenone giving a carbeneiron complex (Fig. 4) in which the oxidized carbonyl ligand links the two metal centres as a μ-CO_2 unit (Scheme 6) [19,21]. The result is thus formally a reduction of a ketone by CO yielding a carbene and CO_2, a reaction which is thermodynamically driven by the formation of two Zr–O bonds and the stable CO_2 unit in the product.

Similar oxygen transfer reactions have been observed with sulfoxides and other element oxides yielding the late transition metal-bound thioethers or the corresponding reduced ligands [19,22]. The pattern of the oxygen transfer has been established by ^{17}O and ^{13}C labeling studies in all these cases [19,22,23]. That both

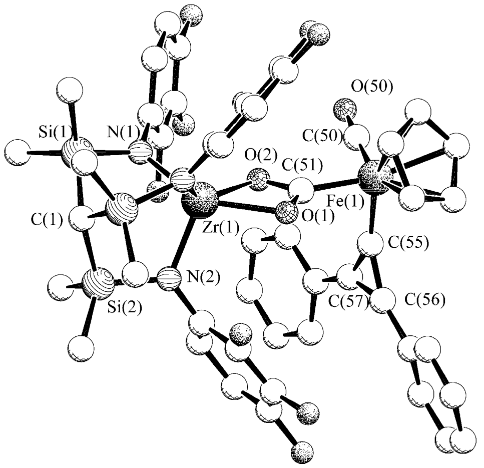
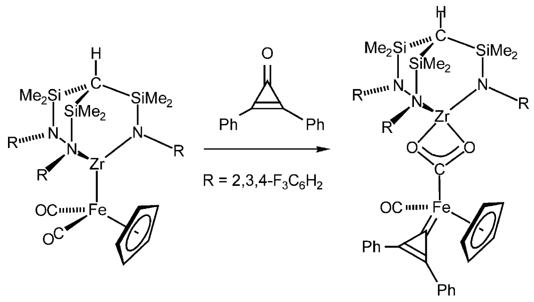
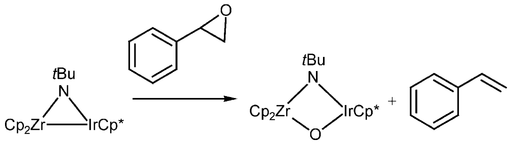


Fig. 4. Molecular structure of the Zr–Fe heterodimetallic carbene complex generated by intramolecular oxygen transfer from 2,3-diphenylcyclopropenone to a carbonyl ligand.



Scheme 6. Deoxygenation of 1,2-diphenylcyclopropenone giving a carbeneiron complex.



Scheme 7. Deoxygenation of phenyl oxirane by O-transfer to a Zr–Ir complex reported by Bergman et al.

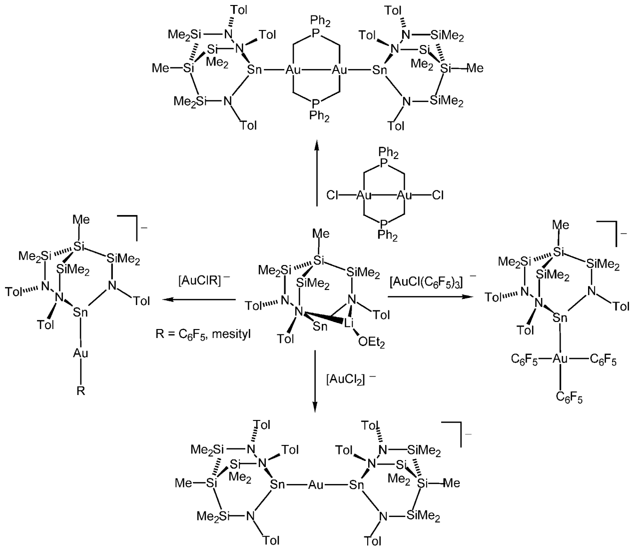
metal centres participate in the conversion of the element oxide is evident from the inability of either of the metal complex fragments linked by the Zr–M bond to effect these tranformations on their own. The interaction of these substrates with only one of the mononuclear units may, in fact, lead to quite different results, as was shown inter alia by reaction of 1,2-diphenylcyclopropenone with $[CpMCO)_2]^-$ (M = Fe, Ru) giving a metallacyclopentenedione instead of a carbene complex.

Rapid transfer of oxygen has also been observed in reactions of $[Cp_2Zr(\mu\text{-}N^tBu)Ir(C_5Me_5)]$ with pyridine N-oxide, nitrous oxide and styrene oxide (Scheme 7) [24]. However, the result of these reactions is the formation of oxo-bridged heterobimetallic complexes.

2.2. *Triamidostannates as 'ligands' in transition metal chemistry*

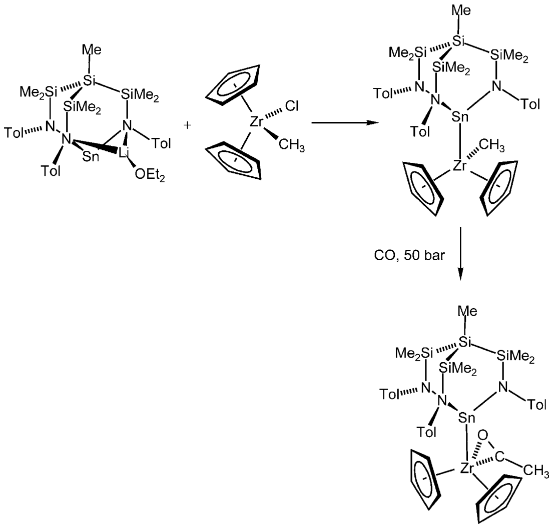
We have recently begun to explore the coordination chemistry of triamidometallates(II) of the heavy Group 14 elements, which are stabilized by a tripodal triamide (**A**–**C**) [25]. The combination of the thermodynamic stabilization by their integration into a rigid molecular cage structure along with the well-defined orientation and high variability of the peripheral N-substituents has established the tripodal triamidometallates as a versatile new class of 'ligands' in the coordination chemistry of the transition metals. The electronegative N-substituents at the divalent metal atoms render these less oxidizable than would be expected for alkyl or aryl substituted derivatives. The latter not only allowed the synthesis of stable Ag(I)–Sn or Au(I–III)–Sn compounds shown in Scheme 8 [26,27] but provided the access to stannate(II) complexes of the early transition metals, in particular the tetravalent Group 4 elements, without degradative single electron transfer [28].

A potential redoxchemical degradation pathway was completely suppressed in the reaction of the triamido stannate complex $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3SnLi(OEt_2)]$ with the metallocene dichlorides $[Cp_2MCl_2]$ of all three titanium group metals to give the corresponding Sn–M complexes $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn\text{–}M(\eta^5\text{-}C_5H_5)_2(Cl)]$ (M = Ti, Zr, Hf) [29]. These new complexes were found to be thermally highly stable and the M–Sn bonds particularly inert towards displacement of the stannate from the Group 4 metal. In order to assess the possibility of using the tin(II) ligand as an ancillary ligand in organometallic transformations we investigated the reactivity of mixed alkyl(stannyl)zirconium complexes towards CO insertion [30]. Upon pressurizing a solution of the Zr–Sn complex $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn\text{–}M(\eta^5\text{-}C_5H_5)_2(CH_3)]$ with CO (50 bar) in an autoclave at 50 °C for 1 h, it is completely converted to the product of CO insertion into the Zr–CH_3 bond while the Sn–Zr bond remains intact. The formation of the acylzirconium complex $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn\text{–}Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}OCCH_3)]$ (Scheme 9) was first evidenced by ^{13}C-NMR and infrared spectroscopy and confirmed by a single crystal X-ray structure analysis [30]. The molecular structure is depicted in Fig. 5.



Scheme 8. Synthesis of Au(I)–Sn, Au(II)–Sn and Au(III)–Sn complexes.

The Zr–Sn bond proved to be completely inert towards CO insertion under pressure which implies



Scheme 9. Synthesis of a methyl–Zr–Sn complex and its conversion to its acylzirconium derivative by CO insertion into the Zr–CH_3 bond.

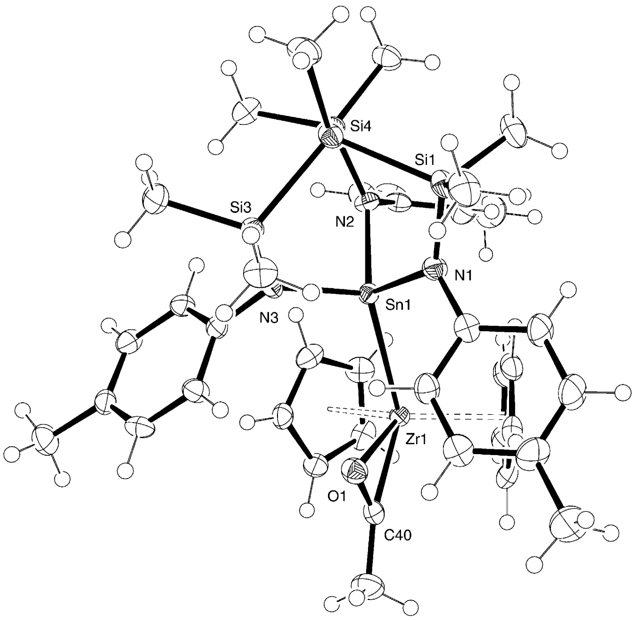
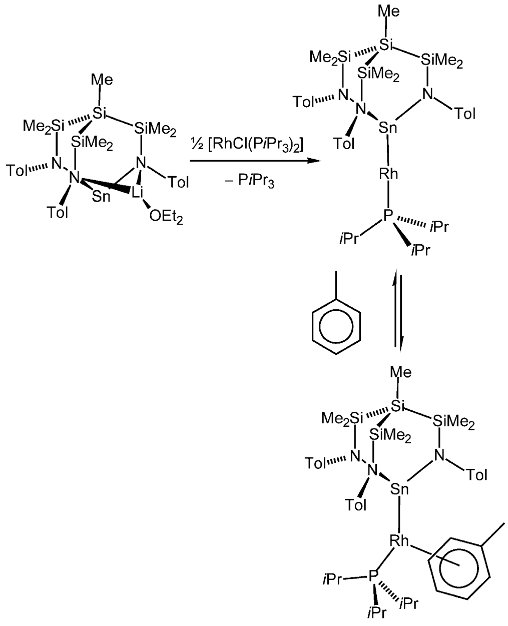


Fig. 5. Molecular structure $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn{-}Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}OCCH_3)]$.

that the stannate(II) cages highlighted in this section may serve as ancillary ligands in reactions requiring relatively forced conditions.

The triamidostannate cages discussed in this review may be readily coupled with carbonyl halide complexes of the late transition elements using the same approach as described above for the Group 4 derivatives [31]. The most characteristic structural consequence of the rigid amido cages is the well-defined orientation of the peripheral N-substituents which leads to very large cone angles of the monodentate ligands in their transition metal complex derivatives. These considerably excede those of 'ordinary' metallate groups or of the isolobal neutral Group 15 ligands and are thus expected to favour low coordination numbers in transition metal complexes. An illustrative example is the reaction product of $[Me\{SiMe_2N(p\text{-Tol})\}_3SnLi(thf)_3]$ with the rhodium complex $[Rh_2Cl_2(P^iPr_3)_4]$ (Scheme 10) [32].

A low temperature, ^{31}P-, ^{13}C- and ^1H-NMR study in d_8-toluene indicated the existence of a free 12-electron dicoordinate species which appears to be in rapid equilibrium with the 18-electron complex bearing an η^6 toluene ligand. The molecular structure of the isolated, crystalline solid of the latter was determined by an X-ray diffraction study (Fig. 6) [32]



Scheme 10. The effect of a large cone angle: synthesis of a Sn–Rh complex which is in equilibrium in solution with a highly unsaturated 12 electron complex.

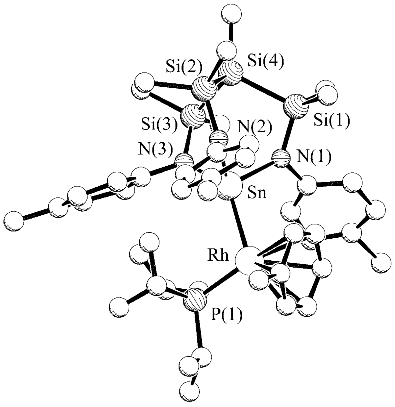


Fig. 6. Molecular structure of $[Me\{SiMe_2N(p\text{-Tol})\}_3Sn{-}Rh(P^iPr_3)(\eta^6\text{-toluene})]$.

3. C_3-chiral amido complexes

While twofold rotational symmetry has been successfully employed in a large number of chiral reagents and catalysts, there is still comparatively little known about the efficiency of systems of higher rotational symmetry [33]. There are to date two different types of C_3-chiral amido tripods reported in the literature. The first involves the introduction of chirality in the peripheral groups of the amido ligand at close proximity to the donor functions as first shown by us [34]. The molecular structure of the titanium complex $[TiCl\{HC(SiMe_2N[(S)\text{-1-phenylethyl}])_3\}]$ is depicted in Fig. 7 [35].

An alternative approach has been the generation of a chiral ligand tripod-backbone as pursued by Moberg and coworkers in their synthesis of chiral triamidoamine ligands [36]. In an important contribution to the field, they demonstrated that the titanium complexes containing these ligands may be used in a catalytic asymmetric alkylation, albeit with only moderate stereoselectivity.

While the reaction of $[Zr(CH_3)\{HC(SiMe_2N[(S)\text{-1-phenylethyl}])_3\}]$ with the aryl ketones PhC(O)R (R =

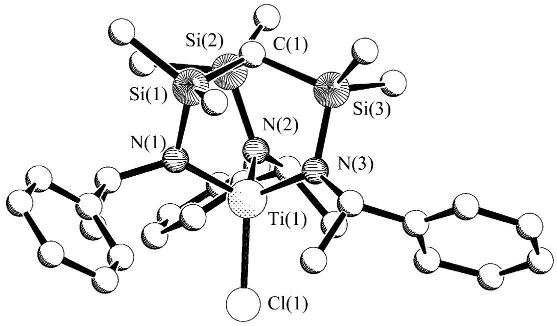
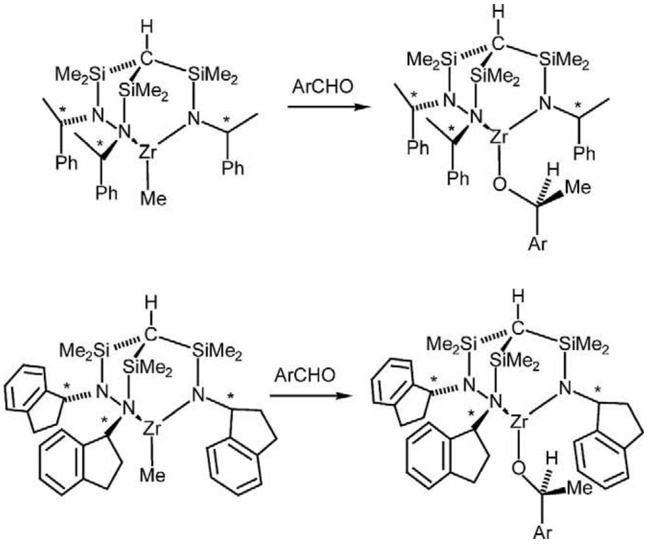
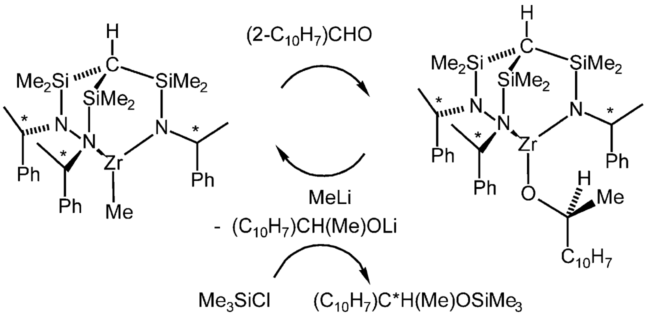


Fig. 7. Molecular structure of [HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$TiCl].

CH=CHPh, ^{i}Pr, Et) gave the corresponding C–O insertion products, which contain an additional chiral centre in the alkoxy group, with low stereoselectivity (0–40% de), the corresponding conversions of these compounds and the corresponding (*R*)-1-indanyl-substituted complex [Zr(CH$_3$){HC(SiMe$_2$N)[(*R*)-1-indanyl])$_3$}] with several aryl aldehydes yielded the alkoxo complexes with high stereoselectivity (Scheme 11). Upon hydrolysis, the chiral alcohols were isolated and shown to have enantiomeric excesses between 68 and 80%. High stereodiscrimination was also observed in the insertion reactions of several chiral ketones and aldehydes, however, this was shown to originate primarily from the chirality of the substrate. In analogous experiments with carbonyl compounds, the ethyl- and butyl-zirconium analogues did not undergo CO-insertion into the metal–alkyl bond but β-elimination and formal insertion into the metal–hydride bond. It was found that the elimination of the alkene was induced by coordination of the carbonyl substrate to the metal centre.



Scheme 11. Stereoselective insertion of aryl aldehydes into the Zr–CH$_3$ bonds of C_3-chiral amidozirconium complexes.



Scheme 12. Cycle of naphthaldehyde insertion into into the Zr–CH$_3$ bond of a C_3-chiral amidozirconium complex and methylation of the product complex with methyl lithium to regenerate the starting material. The alcoholate is trapped as the silylether with Me$_3$SiCl.

The high chemoselectivity of the reaction with arylaldehydes and the observation that the alkoxo product complex reacts cleanly with methyllithium to regenerate the methylzirconium complex allowed us to perform repeated cycles of insertions and alkylations with benzaldehyde. In order to avoid side reactions of the lithium alkoxide generated in this process, a silylation step with Me$_3$SiCl was introduced to remove the product from the reactive cycle as the silyl ether (Scheme 12) [35a].

In the meantime, it has been possible to develop a catalytic system of comparable stereoselectivity using the alkyltitanium complexes and alkylzinc reagents.

4. Combining anionic and neutral donor functions: the amido-pyridine ligand D

The combination of a pyridyl unit with two amido functions leads to tridentate ligands which, depending upon their topology, may adopt meridional or facial coordination modes. Meridional coordination is achieved using ligands of type **E** (Fig. 8) [37] which have found application in the development of novel olefin polymerization catalysts of high activity [38]. We first developed and studied the coordination chemistry of type **D** diamido-pyridine ligands which were found to adopt facial arrangements in early transition metal complexes [9,12].

Formally, the dianionic tripods may be derived from the threefold symmetrical tripodal ligands by replacement of one of the anionic amido 'claws' by the neutral pyridyl function. This class of ligands has been em-

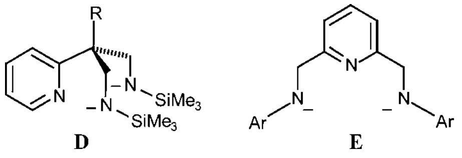
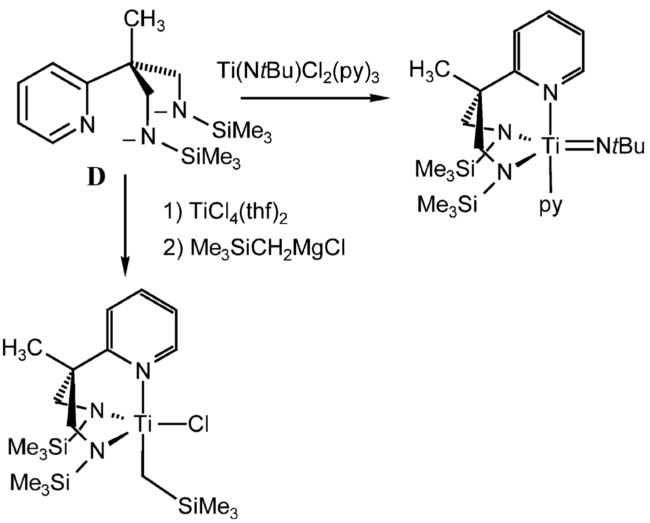


Fig. 8. Diamido-pyridine ligands for facial and meridional coordina-



Scheme 13. Synthesis of pentacoordinate titanium complexes containing the diamidopyridine ligand D.

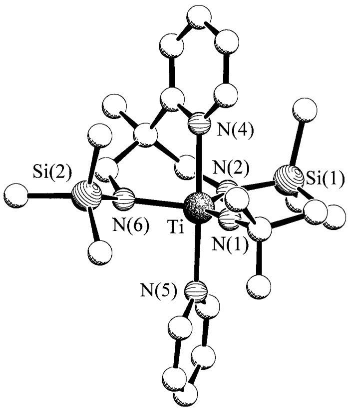


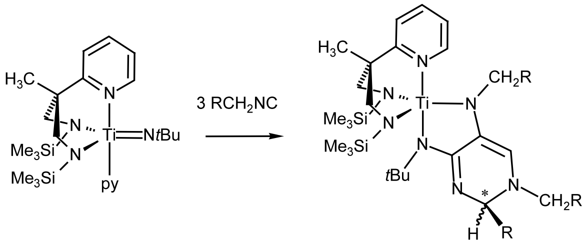
Fig. 9. Molecular structure of the imidotitanium complex [Ti{Me-C(py)(CH$_2$NSiMe$_3$)$_2$}(N^{t}Bu)(py)].

ployed in the synthesis of Group 4–6 metal complexes. A notable contribution to the field, by Schrock et al., has been the development of cationic Zr and Hf alkyl complexes which are active olefine polymerization catalysts [39]. For the complexes of the Ti triad, the ancillary ligand system has allowed the coordination of either two additional anionic (e.g. alkyl) ligands or, alternatively, a formally dianionic unit as achieved in the synthesis of a series of stable imido complexes (Scheme 13) [40].

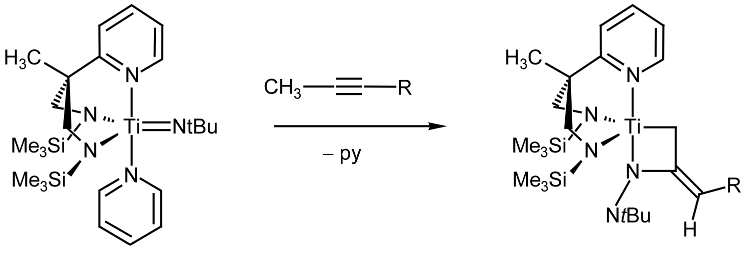
The coordination of the pyridyl unit to the metal centre and thus the formation of a pentacoordinate complex (Fig. 9) of distorted trigonal bipyramidal coordination geometry depends upon the steric requirements of the additional ligands in axial and equatorial position. Decoordination of the pyridyl function has been observed in solution for a dialkyltitanium complex bearing bulky neopentyl groups for which the fourfold coordination mode with a dangling py-unit has been established by NMR spectroscopy, or in the solid state, as demonstrated by the X-ray crystal structure analysis of [Nb{MeC(py)(CH$_2$NSiMe$_3$)$_2$}(N^{t}Bu){CH(SiMe$_3$)$_2$}] [41].

The imidotitanium complexes such as [Ti{MeC(py)(CH$_2$NSiMe$_3$)$_2$}(N^{t}Bu)(py)] were found to have considerable thermal stability which allows their facile isolation and manipulation. On the other hand, the flexibility of the tridentate ligand is thought to be responsible for the remarkable reactivity of the imidotitanium complex towards a variety of organic substrates. In reactions with methyl acetylenes, we found slow but selective cyclization yielding the metallaazetidines shown in Scheme 14 [42].

This conversion is thought to occur via a C–H bond activation step of the methyl group to the Ti=N unit, as has been established for transiently generated imido compounds by Wolczanski and others [43], and subsequent cyclization. The observation that the same products were obtained from the corresponding substituted allenes may imply that an allenetitanium intermediate is involved in this conversion. A cascade of C–N and C–C coupling reactions is the result of exposing



Scheme 15.



Scheme 14.

the imidotitanium complex to alkyl isocyanides to give metal bound 5,6-diamino-2,3-dihydropyrimidines (Scheme 15) [44].

Very recently, it has been possible to extend the imido complex chemistry of the diamidopyridine ligand discussed in this section to the Group 5 and 6 metals [40].

5. Conclusion and outlook

The exploitation of simple principles of coordination chemistry and ligand design has led to a variety of novel types of complexes of the early transition metal and the heavy main group elements, some of which have displayed unprecedented patterns of reactivity. They act both as molecular building blocks in more complex structures and as chemical reagents and thus combine molecular stability with a broad reactive potential. Future studies will be directed at the extention of this field of amide chemistry to the late transition metals with the aim of stabilizing the higher oxidation states of these elements.

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