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Taming early transition metals: the use of polydentate amido-donor ligands to create well defined reactive sites in reagents and catalysts

Lutz H. Gade

Laboratoire de Chimie Organométallique et de Catalyse, UMR 7513, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France. E-mail: gade@chimie.u-strasbg.fr

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Ligand design in early transition metal chemistry has focussed recently on amide chemistry. The availability of two substituent positions at the amido N-donor atom allows its integration into ligand systems of both podand and macrocyclic topology. 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. Early transition metal complexes containing polydentate amido-donor ligands not only display unprecedented patterns of reactivity but are the focus of recent developments in olefin polymerization catalysis.

Introduction

Amido–transition metal chemistry, a field which developed with limited momentum after the pioneering work of the 1960s and early 1970s,[1,2] has grown dramatically during the past decade. These recent advances are not due to the received wisdom of the structural chemistry and reactive behaviour gained in the early studies having undergone dramatic changes. It is the realization that the amido donor function R_2N^- may be placed into a great variety of structural environments which has ultimately led to the dramatic expansion of the area. It may be readily incorporated into complex polydentate ligand structures and combined with other donor functionalities. Amido units are thus suitable tools in ligand design for early transition metal complexes.

The stabilization, *i.e.* protection, of part of the coordination sphere of a high valent, Lewis acidic early transition metal may be achieved by considering several important aspects. First, the ligands chosen for the non-reactive metal ligand interactions (frequently referred to as *spectator* or *ancillary* ligands) should adequately match the electronic demands of the metal centre.[3] In the case at hand this requires strong σ- and π-donor capabilities and, given the hard nature of the Lewis acid, matching chemically hard donor atoms. Secondly, the ancillary ligands must obviously have significantly different bonding and reactive properties in comparison to the *reactive* ligands, *i.e.* those which undergo transformations in the stoichiometric or catalytic processes of interest. Third, the distribution of donor functions over the protected sector of the coordination sphere should be well balanced. This latter situation is demonstrated particularly well by the early transition metal metallocenes and their derivatives which are at the centre of a vast area of modern organometallic chemistry.[4] During the past decade the dominating position of the cyclopentadienide complexes in the coordination chemistry of the d-electron poor metals has been challenged by the rapid development of amido complex chemistry.

Lutz H. Gade is Professor of Chemistry at the Université Louis Pasteur, Strasbourg. His research interests are in the fields of coordination chemistry, organometallic chemistry and catalysis. After completing his undergraduate studies at the University of Bonn and the Technical University of Munich, he went to Cambridge to work for his Ph.D. with Jack Lewis. Having returned to Germany after completing his thesis in 1991, he joined the Chemistry Department at the University of Würzburg where he finished his habilitation in 1996 and where he subsequently worked as a lecturer. In 1998 he moved to Strasbourg to take up his present position. His scientific work has found recognition through the award of the ADUC prize for 1994, the Heinz–Maier–Leibnitz Preis of the DFG and the Federal Ministry of Research and Education (1997), the Gerhard–Hess-Research Award of the DFG (1998) as well as the Award in Chemistry of the Academy of Sciences at Göttingen (1999).

The availability of two substituent positions at the amido N-donor atom allows its integration into ligand systems of both podand and macrocyclic topology (Fig. 1).[5] This not only leads to a well defined relative orientation of the ligating atoms but opens up manifold possibilities of steric control. Moreover, 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. In the latter case the strong metal–amide bonds form the anchoring elements of the polyfunctional 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. In catalytic applications of amido complexes, the availablity of additional weakly coordinating donor functions may crucially determine the lifetimes of certain intermediates in the catalytic cycle and thus the nature of the reaction products. It is the aim of this article to provide an overview of the present state of the area of amido complex chemistry in which the amido functions in the ligand are combined with other *neutral donors* and in which all these considerations have played a role.

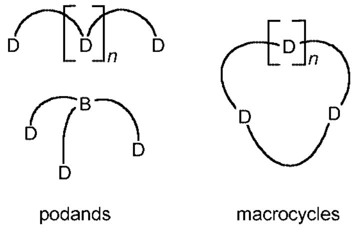

Fig. 1 Topologies of polydentate ligands (D = donor function, B = bridgehead function).

Combining anionic and neutral donor functions: amidoamine and amidopyridine ligands

The addition of a neutral tertiary amino function to a polydentate amido ligand may lead to a variety of conse-

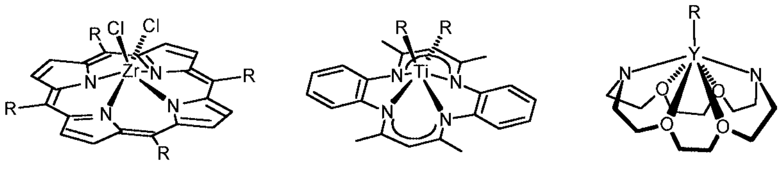

Fig. 2 N-donor macrocycles of different flexibility which have been employed in early transition metal chemistry.

quences. Incorporated within more or less rigid *macrocylic* structures they mostly remain coordinated to an early transition metal centre during transformations at the remaining coordination site(s) and thus serve the 'passive' purpose of maintaining a particular ligand environment with a given overall ligand charge thoughout the transformations. The extremes of macrocyclic rigidity and flexibility are represented by early transition metal porphyrins on the one hand[6] and metallated azacrown ethers on the other[7] as exemplified in Fig. 2. In both cases, the macrocycle–metal complex fragment does not seem to undergo significant changes in chemical reactions involving the reactive ligands. Other macrocyclic systems of intermediate flexibility include tetraazaanulenes the coordination chemistry of which has been recently reviewed.[8]

On the other hand, neutral amino groups (as well as ether or organosulfido groups, *vide infra*) are more readily displaced from early transition metal centres than anionic amido units and therefore may play a flexible role in organometallic transformations. The latter is of particular importance in the development of new early transition metal polymerization catalysts which will be discussed in detail below.

In contrast to the macrocyclic structures discussed so far, neutral donors in *bridgehead* positions of *podands* with amido 'arms' may remain essentially passive within the cage structure of the metal complexes containing these ligands. The paradigm for the use of such ligand systems are the triamidoamine ligands found in the azametallatranes **1** studied by Verkade, Schrock and others.[9,10] These are essentially tripodal ligands in which the apical bridgehead atom participates in the coordination to the metal centre generating a particularly stable cage structure. The arrangement of the triamidoamine creates a reactive site at the metal centre, occupied by the remaining ligand, which may be varied in size and geometry by choice of the appropriate peripheral substituents at the amido nitrogen donor atoms. A set of frontier orbitals comprising one σ and two π orbitals is in principle available for ligand binding at the remaining coordination site (Fig. 3).[10]

This situation is thought to provide the appropriate frontier orbital set at the metal for the extremely rich metal–ligand multiple bond chemistry found for these systems to date.[11] Whereas the tertiary amino function at the apex influences the orbital energies of the frontier orbitals, it apparently adopts a 'passive' role in most of the compounds studied to date. Only in rare cases has it been posssible to establish the involvement or association/dissociation of the amino function in reactions of azametallatranes.[12] The chemistry of this class of complexes has developed rapidly during this decade and has been reviewed in detail.[9,10] It will therefore not be discussed in this overview of the field.

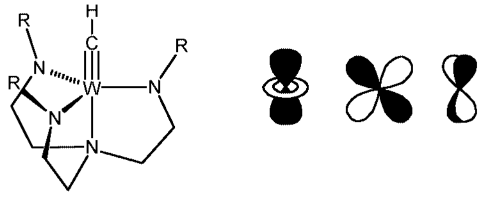

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Fig. 3 Molecular structure of an azametallatrane, **1**, along with a depiction of the metal centred frontier orbitals which may be involved in ligand binding.

Greater flexibility in the coordination geometry and more open structures are found in a number of early transition metal complexes containing new types of diamidoamine ligands (Fig. 4). In these the amino donor function is less strongly bound and its *active* participation in chemical transformations, *i.e.* the coordination and dissociation, is possible. Whereas the tridentate diamidoamine ligand **A**, first reported by Cloke *et al.* adopts a facial coordination mode in **2**,[13] a meridional arrangement was observed in the crystal structure of the analogous complex **3** studied in Schrock's group.[14] Both compounds are precursors of cationic olefin polymerization catalysts the reactivity of which is strongly influenced by the availability of a neutral (dissociable) donor function (*vide infra*).

In contrast to these catalytically active dialkyldiamido zirconium complexes, complex **3a** bearing a tridentate ligand in which the aminofunction is not positioned between the anionic amido units has been found to be inactive in attempted polymerizations.[15]

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 **D** (Fig. 5)[16] which have found application in the development of novel olefin polymerization catalysts of high activity (**4**, *vide infra*).[17] We first developed and studied the coordination chemistry of type **E** diamido pyridine ligands[18] which were found to adopt facial arrangents in early transition metal complexes such as **5**.[19]

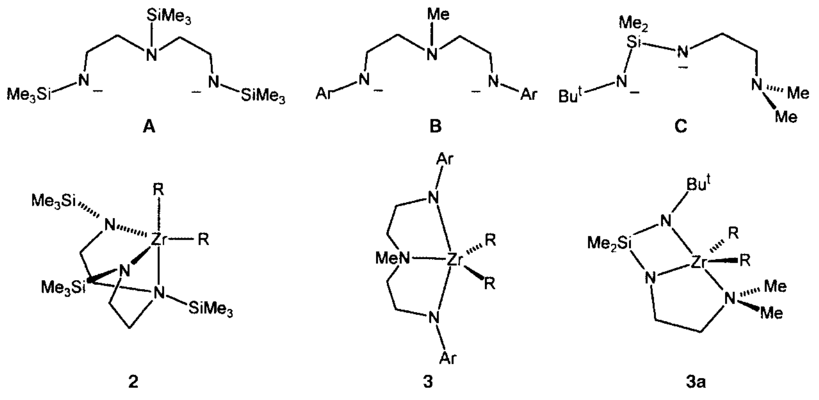


Fig. 4 Zirconium complexes containing the diamidoamine ligands **A**, **B** and **C**.

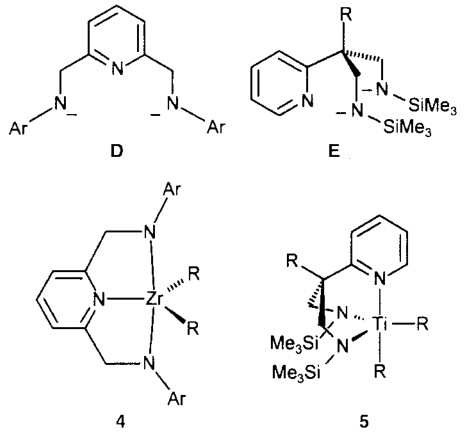
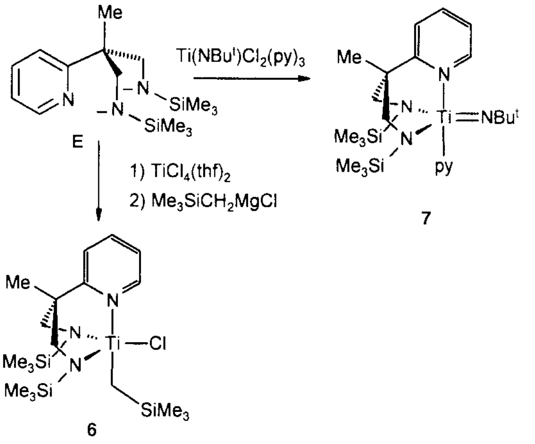


Fig. 5 The diamidopyridine ligands **D** and **E** adopting meridional and facial coordination modes, respectively.

Formally, the dianionic tripods may be derived from the threefold symmetrical tripodal ligands through the replacement of one of the anionic amido 'claws' by the neutral pyridyl function. This class of ligands has been employed in the synthesis of tetravalent titanium and pentavalent vanadium group metal complexes. 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,[19] alternatively, a formally dianionic unit as achieved in the synthesis of a series of stable imido complexes (Scheme 1).[20,21]



Scheme 1 Synthesis of pentacoordinate titanium complexes containing the diamidopyridine ligand **E**.

The coordination of the pyridyl unit to the metal centre and thus the formation of a pentacoordinate complex **7** (Fig. 6) 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 **8** 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 $[\mathrm{Nb\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}(NBu^t)\{CH(SiMe_3)_2\}}]$ **9**.[19,21]

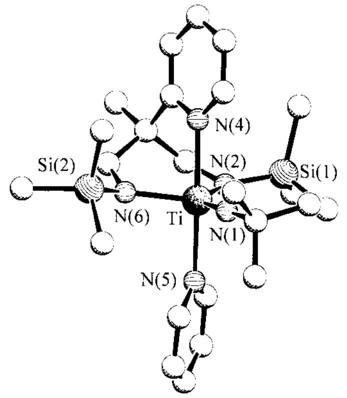
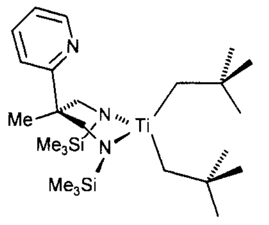


Fig. 6 Molecular structure of complex **7**.[20]



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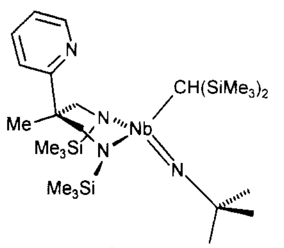

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The imidotitanium complexes such as $[\mathrm{Ti\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}(NBu^t)(py)}]$ **7** were found to have considerable thermal stability which allows their facile isolation and manipulation. However, they possess labile pyridine and pyridyl ligands that, under appropriate reaction conditions, may dissociate to yield unsaturated and highly reactive imido complexes of the type investigated by Wolczanski and coworkers *via* irreversible thermolysis of the respective precursor molecules (Fig. 7).[22] In fact, sublimation of **7** in high vacuum has yielded the four-coordinate complex **7a** which has been structurally characterized by X-ray crystallography.[21] In contrast, there has been no evidence, as yet, for the postulated highly unsaturated, three-coordinate species **7b**.

It is this flexibility of the tridentate ligand which is thought to be responsible for the remarkable reactivity of **7** towards a variety of organic substrates and represents an example of the 'taming' of a reactive structural element as implied in the title of this article. In reactions with methyl acetylenes we have found slow but selective cyclization yielding the metalla-azetidines **10**.[23]

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,[22] and subsequent cyclization. The observation that the same products were obtained from the analogous 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 **7** to alkyl isocyanides to give metal bound

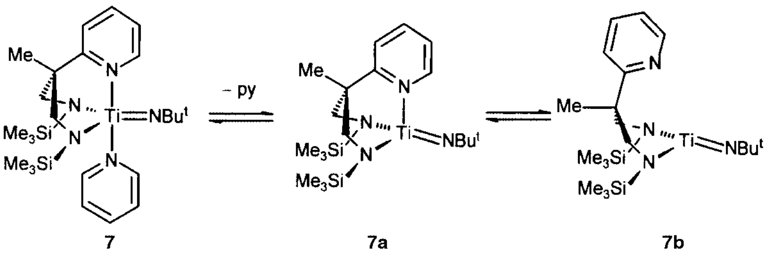
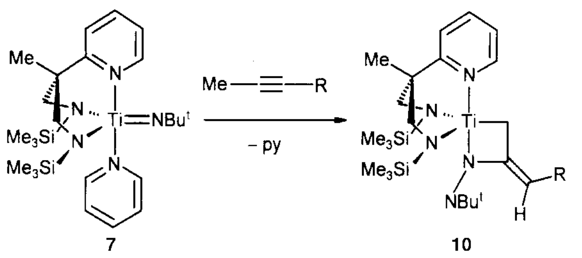
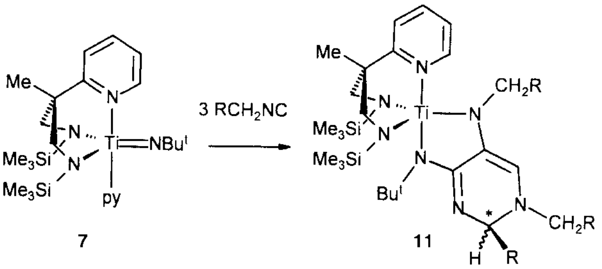


Fig. 7 Stabilization and "masking" of low-coordinate imidotitanium complexes.



5,6-diamino-2,3-dihydropyrimidines **11**.[20] The reaction sequence is thought to occur along the pathway shown in Scheme 2.[24] Remarkably, no reaction intermediate could be detected for most of the isocyanide derivatives we studied. However, it has been possible to isolate and structurally characterize a derivative of **ii** which could be converted to **iii** upon addition of another molar equivalent of an isocyanide.

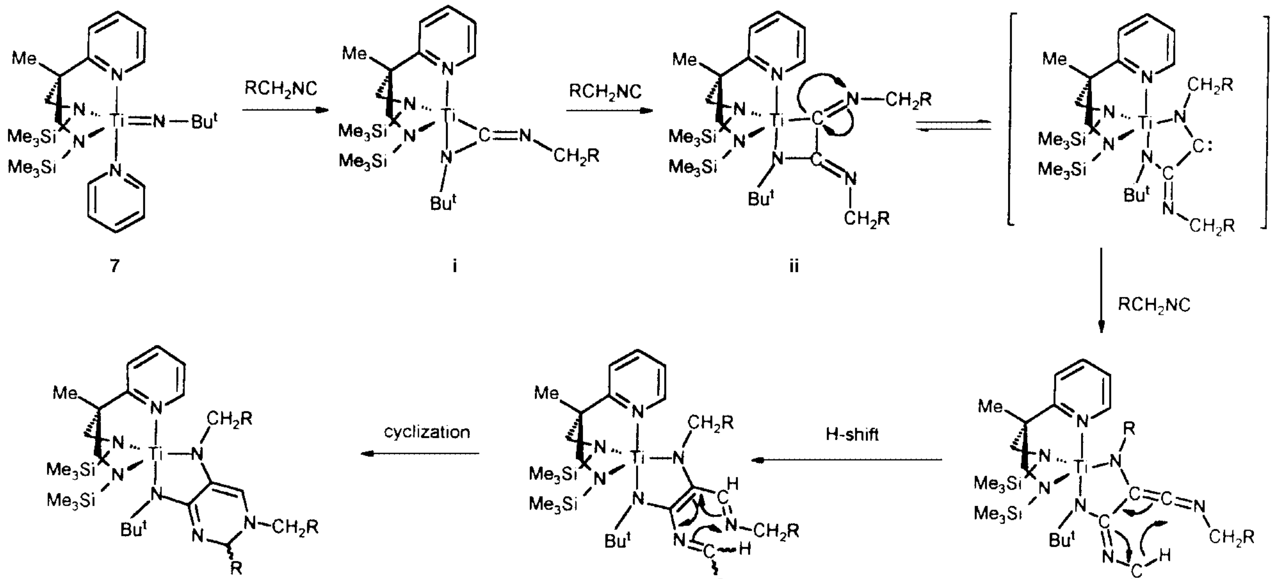


Several potentially tetra- and hexa-dentate amidopyridine ligands have been reported which contain deprotonated 2-aminopyridine units. Two of these have been connected *via* a bridging siloxane unit **F** and have been employed in the synthesis of heterodinuclear complexes in which they link neodymium and late transition metal fragments (for example **12**).[25] The combination of three aminopyridine fragments has been achieved in a trisilylmethane and trisilylsilane derived tripodal ligands for which titanium, zirconium and niobium complexes have been reported.[26,27] Although the pyridine donors in these systems are all coordinated to the respective metal centres in the crystal structures, their bonding situation in solution is not clear.

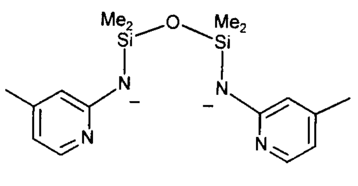
Stabilizing cationic early transition metal amido complexes: a new generation of non-metallocene polymerization catalysts

Few developments have fueled the interest in the organometallic chemistry of the early transition metals in the same way as the discovery of well defined olefin polymerization catalysts. To date, the majority of the systems, mainly based on titanium or zirconium, which have been investigated contain one or two cyclopentadienyl rings or their derivatives.[4] However, in recent years the focus has shifted to non-metallocene catalysts of which those containing chelating diamido ligands have received particular attention.[28] An ever increasing number of such complexes are currently being studied with regard to their activity as catalyst precursors for the polymerization of ethylene or longer chain α-olefins. The three complexes displayed in Fig. 8 were found to be procatalysts for highly active catalytic systems.[29]

In particular, the titanium complex **13** studied by McConville and coworkers,[29a,b] was found to behave as a living polymerization catalyst for hex-1-ene. The active species in these systems is thought to be a cationic monoalkyl complex which would be a solvated three coordinate species. In order to stabilize this



Scheme 2 Proposed mechanism of the icocyanide coupling with **7** to give Ti-bound 5,6-diamino-2,3-dihydropyrimidenes.



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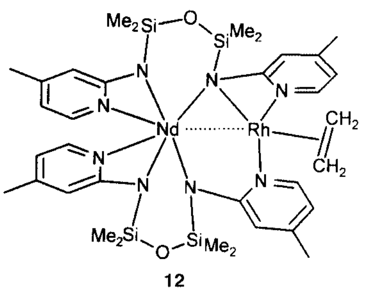

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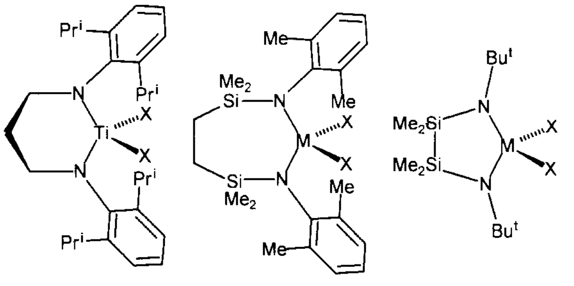


13 **14** **15**

Fig. 8 Group 4 metal complexes containing chelating diamido ligands which are active catalysts for olefin polymerization.

cationic intermediate, ligand design has very recently been extended to include chelating diamido ligands which contain a third neutral donor function. As noted above, activity in olefin polymerization has mainly been observed for those systems in which the neutral donor is placed between the two anionic amido groups. In the five coordinate procatalysts shown in Fig. 9 the tridentate ligand may adopt either meridional or facial arrangements.[13,14,17,30–33]

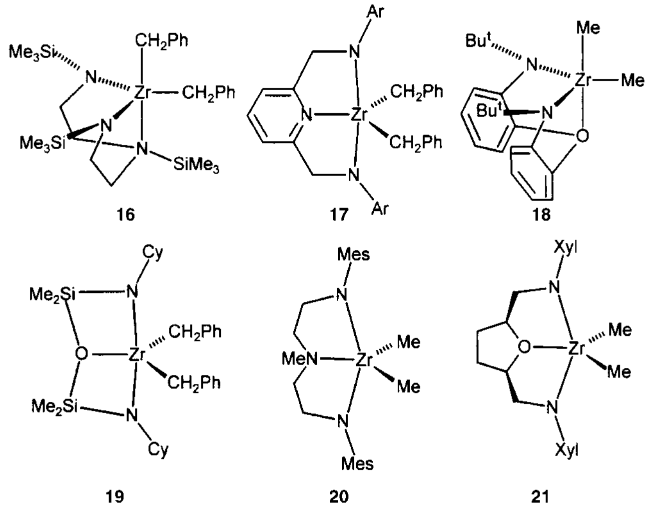
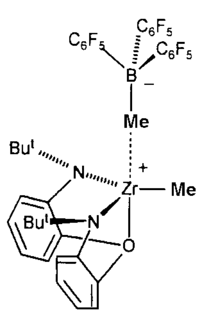


Fig. 9 Dialkylzirconium complexes, containing diamido-donor ligands, which are active olefin polymerization catalysts.

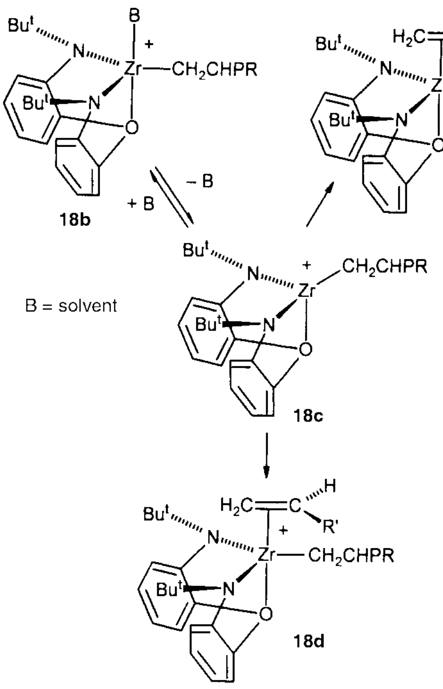
Compounds **16** and **17** have been studied by Cloke, Horton and McConville and represent the two possible arrangements of the donor functions.[13,17,30] While complex **16** was found to be moderately active in ethylene polymerization, the procatalyst **17** displays high activity. Very detailed studies into the mechanism of the polymerization and the role of the neutral donor functions have been carried out in Schrock's group. Compounds **18**, **20** and **21** are active catalysts for the polymerization of hexene.[14,31,33] An important feature in these complexes is the absence of N-bonded silyl groups which are not only easily hydrolyzed but may undergo cyclometallations. The chemically robust nature of **18**,[31] in particular, not only allows the living polymerization of hexene but has rendered the cationic intermediate suffiently stable to be characterized in solution.[34] The isolation and X-ray crystallographic characterization of the ionic adduct $[\{(Bu^tNC_6H_4)_2O\}ZrMe][MeB(C_6F_5)_3]$ **18a** upon reaction of **18** with the cocatalyst $B(C_6F_5)_3$, in which the boranate ion occupies the apical position, supports the notion that it is the apical alkyl group which is removed by the Lewis acid.[31]

Using $^{13}CH_3$-labeled **18**, it has been possible to detect the cationic solvent-stabilized catalyst by ^{13}C NMR spectroscopy in solution and to demonstrate that the 'insertion' of hex-1-ene into the Zr–CH$_3$ bond occurs in a 1,2 manner.[34]

Based on these studies, Schrock and Baumann have proposed the mechanism initiating the chain growth which is shown in Scheme 3.[34] In the first step, the dissociation of the base in the apical position in **18b** generates the four-coordinate cationic complex **18c** to which the olefin monomer may coordinate generating a five coordinate cation **18d**. The monomer occupies the apical coordination site in this intermediate. In contrast to the mechanism proposed for the cationic metallocene catalysts, which adopt a pseudo-trigonal structure and in which the olefin may approach the metal–alkyl unit from two faces,[4] the pseudo-tetrahedral nature of **18c** restricts access to the metal centre to one face.



18a



Scheme 3 Mechanism for the chain growth catalyzed by **18**.

That β-elimination which would terminate the living polymerization is a slow process is attributed to the steric congestion of the ligand sphere induced by the bulky N-bound *tert*-butyl groups. This renders the conversion of **18c** to **18c** kinetically unfavourable.

The studies discussed in this section impressively demonstrate the role played by the ancillary ligand in the control of the reactivity of a catalytic system. It is the combination of the electronic properties of the donor functions, the conformational degrees of freedom of the ligand backbone as well as the steric demand of both ligand backbone and peripheral substituents which influences their performance. This point is particularly apparent in the results of a comparative study of the catalytic properties of **21** and the simple dialkyl ether analogue $[\{O(CH_2CH_2NXyl)_2ZrMe_2]$ **22**.[33,35] Catalyst **21**, which contains a conformationally more rigid and sterically more demanding tetrahydrofuran-derived diamido-donor ligand, produced polyhexene of almost twice the molecular weight as compound **22**.

Amido ligands containing weakly coordinating donor functions: the *ortho*-fluorophenyl periphery

The neutral ligating units in the polyfunctional ligands discussed in the previous sections bind fairly strongly to the metal centres and are therefore thought to remain coordinated throughout most of the chemical conversions at the 'reactive' coordination site(s). However, the integration of very labile coordinating units into amido ligands enables the 'masking' of low coordination numbers and thus of potentially highly reactive species. The size of the reactive site in these systems is readily adjustable through coordination and decoordination of the hemilabile donors. We introduced such an *active ligand periphery* in several tripodal amido ligands in the form of *ortho*-fluorophenyl groups (Fig. 10).[36]

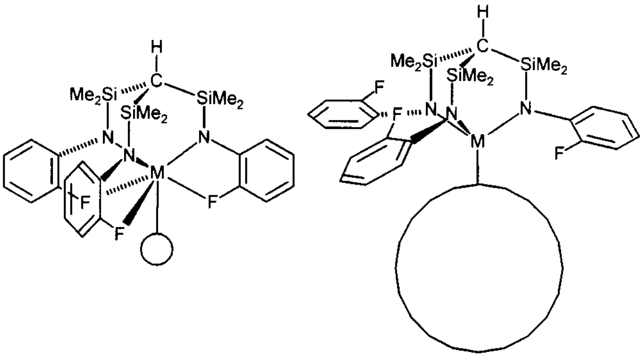


Fig. 10 Participation and non-participation of an active *ortho*-fluorophenyl ligand periphery in tripodal amido complexes.

The stabilization of Lewis acidic metal centres by weak C–F···M coordination has also been used in complexes containing appropriately functionalized monodentate amido ligands as well as in several metallocene derivatives.[37] The use of partially fluorinated aryl groups reduces the basicity at the amido N-atoms and thus increases their stability towards protolytic cleavage. Depending on the ionic radius of the metal centre and steric demand of the remaining anionic ligand(s), the coordination of one or more of the fluorine atoms both sterically shields and partially saturates the Lewis acidic metal centre. We have extended this approach to include N-bonded 2,3,4-trifluorophenyl groups which were found to stabilize complexes of the titanium triad even more efficiently.[36b]

The involvement of one, two or three *ortho*-F atoms in the coordination to the metal has been established by a systematic structural study. Coordination of all three C–F units has been observed for the yttrium complex **23** which together with an additional diethyl ether ligand leads to a sevenfold coordination geometry (Fig. 11).[36] This system was studied at the beginning of our work in view of its NMR-active metal nucleus ^{83}Y and indeed, ^{19}F NMR studies of the complex established the metal–fluorine interaction in solution by observation of ^{83}Y–^{19}F coupling.

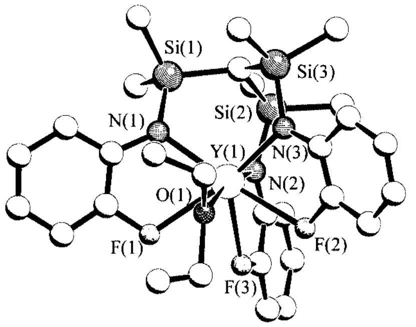
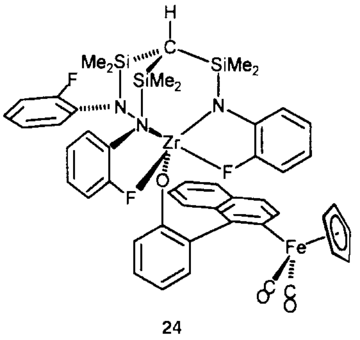


Fig. 11 Molecular structure of the yttrium complex $[\mathrm{Y}\{\mathrm{HC}[\mathrm{SiMe_2N(2\text{-}FC_6H_4)}]_3\}(\mathrm{OEt_2})]$ (**23**).

The structures of compounds **24**–**26** nicely demonstrate the relationship between the size of the anionic monodentate ligand(s) and the number of coordinated C–F groups.[37–39] While the coordination of the ligand periphery in **24** and **25** leads to sixfold coordination in the zirconium complexes, the large metal complex fragment $\{\mathrm{FeCp(CO)_2}\}$ which essentially acts as an anionic ligand in **26** enforces the dissociation of the hemilabile units (Fig. 12).

The role which the fluorine atoms adopt in the structures discussed above may be rationalized by assuming that the highly Lewis-acidic metal centre accepts as many additional donors as may be accommodated in their coordination sphere. The question of their importance in the chemical reactions of such species is more difficult to answer since intermediates are generally not detectable. However, we have carried out a comparative study of the kinetics of insertion reactions of unsaturated polar organic substrates into the polar metal–metal bonds in compounds such as **26**. These were related to the results obtained for complexes in which the fluorophenyl substituents were replaced by 'innocent' *para*-tolyl groups. In this study we found that the second order reaction rates of the fluorinated species are greater by a factor of *ca.* 10–50.[36b,39–41]



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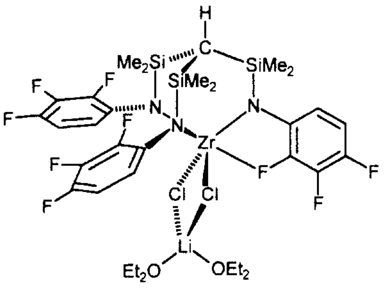

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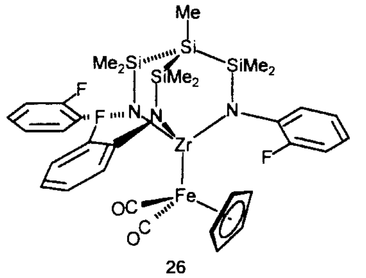

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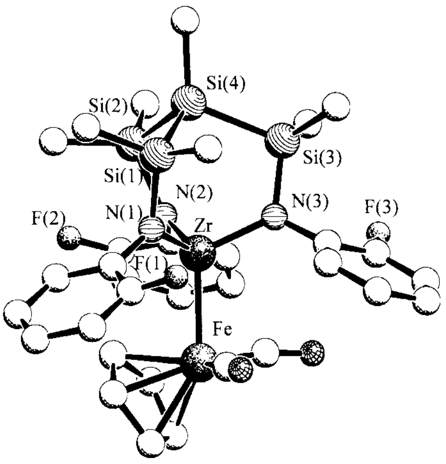


Fig. 12 Molecular structure of the Zr–Fe complex **26** showing the 'dangling' *ortho*-fluorophenyl groups.

The active periphery thus enhances the reactivity of the early–late heterobimetallics, an observation which may be understood in both possible mechanistic scenarios: an early or a late involvement of the F-donors in the process of metal–metal bond cleavage. Experimental evidence suggests that the attack of a Lewis-base at the early transition metal centre is the first step in the insertion reactions of polar substrates. The re-adjustment of electron density in the metal–metal bond destabilizes it and induces its subsequent scission. This process may be aided by the coordination of the CF groups before the cleavage of the Zr–M bond. On the other hand, the coordination of the fluorine atoms also stabilizes the fragments obtained after metal–metal bond breaking has occurred, a situation which will be reflected in the kinetics in the case of a late transition state. It has not been possible to differentiate between these two possibilities and it is quite likely that both play a role.

Labile coordination of *ortho*-fluorine atoms in N-bonded fluorinated aryl substituents has recently been observed in several other polydentate amides. X-Ray crystallographic studies carried out for $[\{(C_6F_5NCH_2CH_2)_3N\}V]$ (V–F 2.65 Å)[42] and $[\{(C_6F_5NCH_2CH_2)_2N\}TaMe_2]$ (Ta–F *ca.* 2.4 Å)[43] have also established metal–fluorine distances which are significantly longer than those found in binary fluorides or related compounds. This fact is to be seen in connection with the fluxionality of the orthofluorophenylamido complexes in solution which suggests that the strength of the interaction between the metal centres and the labile donor functions amounts to less than *ca.* 10 kcal mol^{-1}.

Combining hard and soft donor functions: chelating and macrocyclic amidophosphines

The stability of the metal–nitrogen bonds in amido complexes of the early transition metals enables their use as 'anchors' for polydentate ligands which also contain donor functions with less well matched electronic properties. This was part of the rationale behind the ligand design discussed in the previous sections. However, a particularly interesting variant of this concept has been developed and very successfully employed by Fryzuk *et al.* by combining the hard amido ligand with soft phosphine units in polydentate ligand systems.[3,44,45] The open chain PNP and NPN ligands **G** and **H** as well as the macrocyclic P_2N_2 ligand **I** displayed in Fig. 13 have been applied in the synthesis of organometallic complexes of the group 3–5 metals. Early work using **G**, which has been reviewed elsewhere, revealed that these systems may in fact be employed in the synthesis of stable late transition metal complexes with reversed roles of the two donor functions.[3,44] In d-electron rich complexes the soft phosphine ligands with their π-acceptor properties are to be viewed as the anchoring units which ensure the stabiliy of the molecules.

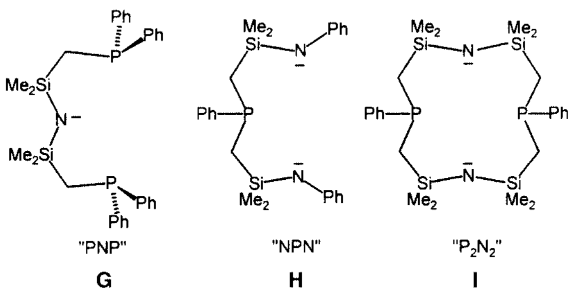
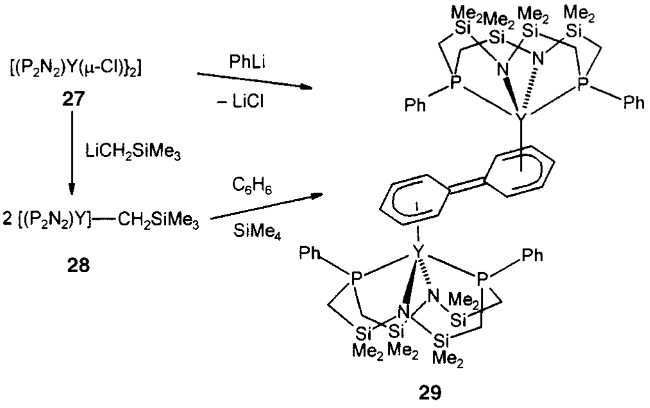


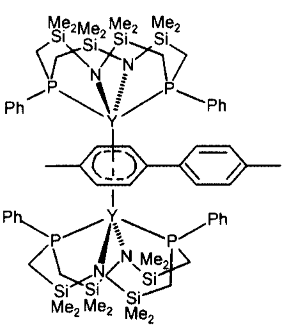
Fig. 13 Three polydentate amido-phosphine ligands introduced by Fryzuk and coworkers.

A series of early transition metal complexes containing the macrocyclic ligand **I** has been reported recently.[46,47] Particularly noteworthy is the coupling of two aryl rings in an yttrium(III) complex (Scheme 4).[47] This dinuclear species was first discovered as the thermal decomposition product of the Me_3SiCH_2 complex **28** in benzene which yielded $SiMe_4$ and the dinuclear species **29** in which the bridging diphenyl ligand may be understood as being formally dianionic and thus leaving the oxidation state of the yttrium unchanged. The mechanism of this conversion which involved C–H bond activation is not yet fully understood. However, the same product was obtained upon reaction of the chloroyttrium(III) complex **27** with phenyllithium. This reaction of an aryllithium compound with a transition metal halide to give a product with a π-bonded arene unit is reminiscent of the chromium species which were first investigated in 1919 by Hein and coworkers but were only structurally understood after Fischer's synthesis of bis(benzene)chromium in 1955.[48]



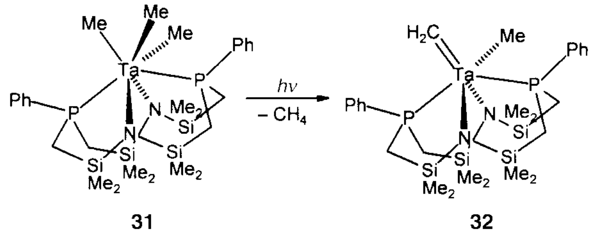
Scheme 4 Phenyl coupling induced by an yttrium complex stabilized by the macrocyclic P_2N_2 ligand **I**.

It is remarkable that this coupling reaction may be extended to other aryl fragments as was shown in the generation of the ditolyl ligand on reaction of **27** with *para*-tolyllithium.[47] The structure of complex **30** which contains this bridging ditolyl dianion shows that the arrangement of the two metal complex fragments coordinated to the organic unit appears to depend upon the substitution pattern of the latter. NMR studies carried out at variable temperature suggest a rapid migration of the complex fragments between the two ring positions in solution at room temperature.



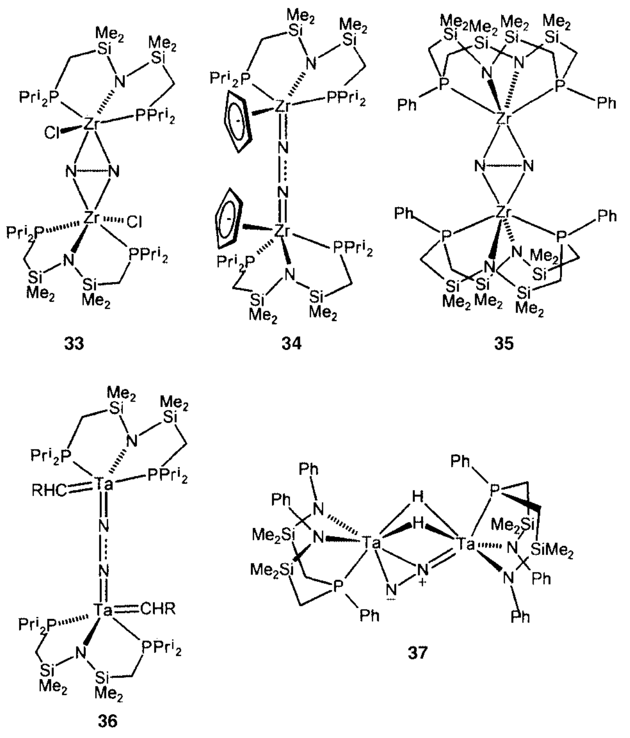
30

The macrocyclic diamidodiphosphine ligand **I** has been used in the synthesis of the trimethyltantalum complex **31** in which all ligand donor atoms are bonded to the metal centre and which consequently adopts a sevenfold coordination geometry best described as capped trigonal prismatic.[49] This compound undergoes a photochemically induced methane abstraction to give the methylmethylidene complex **32**. The latter displays an interesting dynamic behaviour in solution which amounts to a libration and/or rotation of the Ta(=CH_2)Me unit relative to the macrocycle–Ta fragment.



31 **32**

The most spectacular application of the amidophosphine ligands **G** – **I** has been in the synthesis of the dinitrogen-zirconium and -tantalum complexes **33**–**37** (Fig. 14) which not only display different N_2 bonding modes but remarkable chemical reactivity.[50–53] The different coordination modes in the zirconium complexes have been explained by the way the monodentate ancillary ligands, Cl^- or Cp^-, influence the set of frontier orbitals available for N_2 binding at the metal centre. In the chloro complex **33** the unavailability of one of the d-orbitals at the zirconium which would normally be involved in an end-on coordination mode favours the side-on coordination observed in the molecular structure of the compound.

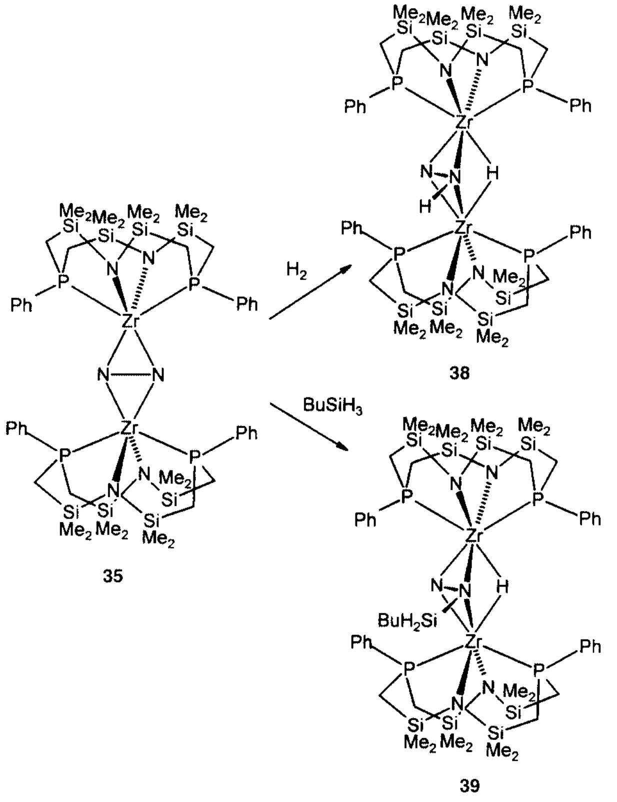


33 **34** **35** **36** **37**

Fig. 14 Different structural types in dinuclear zirconium and tantalum complexes containing bridging N_2 ligands.

The coordination mode of the dinitrogen ligand in the tantalum complex **37** is unprecedented in transition metal chemistry.[53] The compound was obtained by displacement of dihydrogen from the dinuclear tetrahydridotantalum complex [{($PhNSiMe_2CH_2)_2PPh$}Ta(μ-H$)_2]_2$ which is the first time that N_2-binding is observed by substitution of hydrido ligands. This observation may be relevant to a potential catalytic cycle for the reduction of N_2 to NH_3. The second step would then entail N–H formation and addition of further H_2 to regenerate the hydride.

That N–H coupling is indeed feasible in such hydrido N_2-complexes has been shown for compound **35**.[52] Stirring of the dinitrogen complex in hexane under an H_2 atmosphere slowly produced the remarkable dinuclear μ-η^2-N_2H complex **38** (Scheme 5).



35 **38** **39**

Scheme 5 Hydrogenation of the (μ-N_2)Zr_2 complex **35** giving the (HN_2)Zr complex **38** and addition of Bu^nSiH_3 to **35** to give the {($BuH_2Si)N_2$}Zr complex **39**.

The molecular structure of **38** was established by NMR spectroscopy in solution and by a single crystal neutron diffraction study for the solid state. An X-ray diffraction study of a closely related complex **39** has been carried out which was obtained by reaction of **35** with Bu_3SiH. This result confirms the previously noted close analogy between H–H and H–Si bonds in metal induced bond activation reactions.[54]

Conclusions and outlook

The amido function offers many possibilities of inclusion within a complex polydentate ligand system and the combination with other types of donor functionalities. This combination of hard, anionic amido functions with a range of neutral donor functions within the same ligand systems has led to the stabilization and isolation of new types of early transition metal complexes. Moreover, this concept has found its way into the systematic design of new olefin polymerization catalysts. Stabilization of the reactive site by additional ligating functions within a polydentate amide may play a role both in the isolated complexes themselves and in reactive intermediates in catalytic cycles.

The development of this area is still at an early stage, and the potential of creating novel types of reactive sites in the complexes of early transition metals is largely untapped. In particular, the combination of hard and soft donor functions appears to lead the way to novel patterns of structure and reactivity. The use of weakly coordination units, such as the CF fragments discussed above may offer an alternative strategy not only to stabilize otherwise highly reactive compounds but also to control the catalytic activity of molecular catalysts. Moreover, it is the combination of both the renewed academic interest in amide chemistry and the prospect of the commercial application of its results which provides the driving force for current and future progress.

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