Acc. Chem. Res. **2002,** *35,* 575−582

Tripodal Amido Complexes: Molecular “Claws” in Main Group and Transition Metal Chemistry

LUTZ H. GADE

Laboratoire de Chimie Organométallique et de Catalyse (CNRS, UMR 7513), Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France

Received October 30, 2001

ABSTRACT

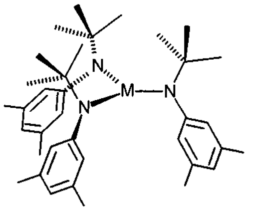
The chemistry of transition metal amides has received new impetus in recent years due to the systematic exploitation of the amido function $[NR_2]^-$ in ligand design. A class of 3-fold symmetrical tripodal amido ligands has proved to be a valuable tool in the stabilization of early transition metal and main group metal complexes and complex fragments. Moreover, promising strategies for their use as chemical reagents and homogeneous catalysts have been developed. An overwiew of the current state of this field is given and the potential for further development will be highlighted.

Introduction

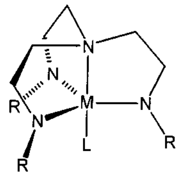
The possibility of predetermining the structure, stability, and reactivity of a coordination compound has been the main driving force in the development of increasingly complex and sophisticated ligand systems (“ligand design”). It is the relative arrangement and nature of the functional groups as well as the structure of the ligand framework (“ligand topology”) that ultimately define these characteristics. The application of these principles to the coordination chemistry of the high-valent, Lewis acidic early transition elements required charged ligand systems that meet their electronic demands. During the past decade, amido ligands, $[NR_2]^-$, have established themselves as highly versatile tools of ligand design in this field as well as in main group coordination chemistry. These recent developments are based on the pioneering studies of the 1960s and -70s, carried out by Bradley, Lappert, and others, which had established the principal synthetic strategies and structural motifs of such compounds.[1,2]

Amides are strong σ and π donors, the electronic properties of which may be varied by choice of the two N-substituents, as well as hard Lewis bases matching the hardness of the metal center. The N-bound substituents, in turn, allow the facile integration of amido functions into polydentate ligands of macrocyclic or podand topology, as well as their combination with other charged or neutral donor functions.[3,4] This combination of properties makes the amido function a versatile tool in ligand design.

The power of appropriately combining the substituent groups at a single N-atom in *monodentate* ligands in order to access novel complex structures, and the chemical reactivity which goes along with it, has been demonstrated inter alia by the spectacular results obtained in Cummins’ group. These recent developments, which are in part based on the stabilization of tricoordinate transition metal amides (**A**), have been reviewed previously.[5]



A



B

The most comprehensively studied *polydentate* amido podands are the triamidoamines derived from the tris(2-aminoethyl)amine (“tren”) ligands, which have found widespread application in main group and transition metal chemistry through the work of Verkade,[6] Schrock,[7] and others.[8] The arrangement of the amido functions around the metal centers and the participation (or non-participation) of the apical tertiary amino unit in the coordination to the central atom has led to unique molecular structures and patterns of reactivity. Alongside with these “azametallatranes” (**B**), a class of amido complexes containing tripodal tridentate ligands has been developed that display distictly different properties. As will be discussed below, this is due to the more constrained arrangement of their N-donor atoms, the rigid ligand−metal cage structure, and the more open remaining coordination sphere.

This account will focus on the chemistry of three closely related tripodal amido ligands, **C**, **D**, and **E**, which we studied in detail (Figure 1).[9−11]

Their syntheses are straightforward and feasible on a large scale from inexpensive starting materials, which allowed the rapid development of their coordination chemistry. Whereas **C** is derived from 1,1,1-tris(aminomethyl)ethane, which is a well-established ligand in its own right in Werner-type coordination chemistry,[12] the silylamides **D** and **E** are obtained by aminolysis of the respective silylhalide precursors with 3 molar equiv of essentially any commercially available primary amine.[10,11,13]

Lutz H. Gade is a professor of chemistry at the Université Louis Pasteur, Strasbourg. His research interests are in the fields of coordination chemistry, organometallic chemistry, and catalysis. After undergraduate studies at the University of Bonn and the Technical University of Munich, he he obtained his Ph.D. with Jack Lewis at Cambridge University. He then 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). In 2000, he was elected a Member of the Institut Universitaire de France.

10.1021/ar010116f CCC: $22.00

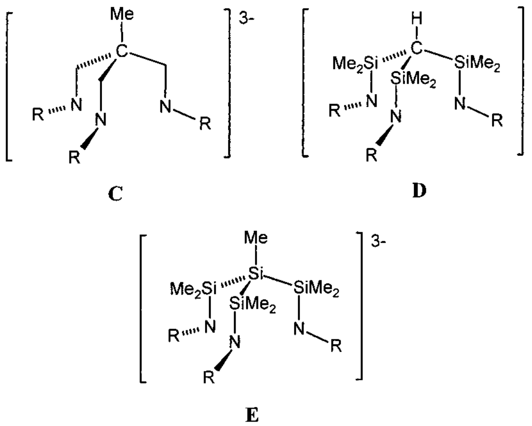
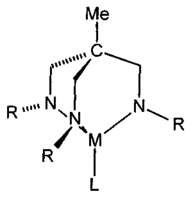
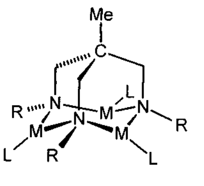


FIGURE 1. The three types of triamido podands discussed in this overview.

All three types of ligands give essentially similar complex structures; however, the possibility of varying the size of the metal binding site upon going from the wholly carbon based ligand backbone in **C** to the branched tetrasilane in **E** allowed the appropriate choice of the ligand for the metal and the control of the relative orientation of the peripheral N-substituent groups. Depending on the transition or main group metals to which these ligands are coordinated, the resulting ligand–metal unit is a relatively rigid molecular cage of bicyclo[2.2.2]octane topology (**F**) or a metalla-adamantane unit (**G**).



F



G

Ligand–Metal Cages as Molecular Building Blocks in Oligonuclear Main Group and Transition Metal Compounds and Aggregates

The thermodynamic stabilization of metal complex fragments within the amidometal cages as well as the kinetic stabilization offered by the steric shielding of the metal centers to which the tripods are coordinated has been employed in several studies of chemically very different amides that are building blocks in oligonuclear compounds (Figure 2).

These include monovalent thallium amides, such as the adamantanoid compound **1**, which aggregates in the solid state to form metal–metal connected dimers and which may be thermally converted to complex **2** containing a rare example of a covalent $\mathrm{Tl^{II}}$–$\mathrm{Tl^{II}}$ bond.[14,15] In fact, the use of the amido tripod in the previously almost untouched chemistry of thallium(I) amides has led to a great variety of novel structural motifs as well as unusual redox chemical transformations.[16]

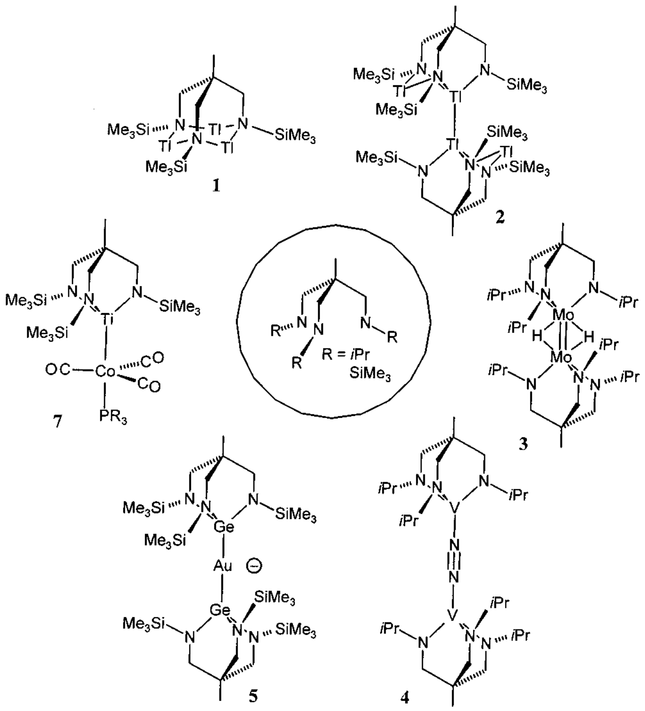


FIGURE 2. Triamido transition and main group metal complex fragments bearing type **A** tripod ligands, building blocks in oligonuclear compounds and molecular aggregates.

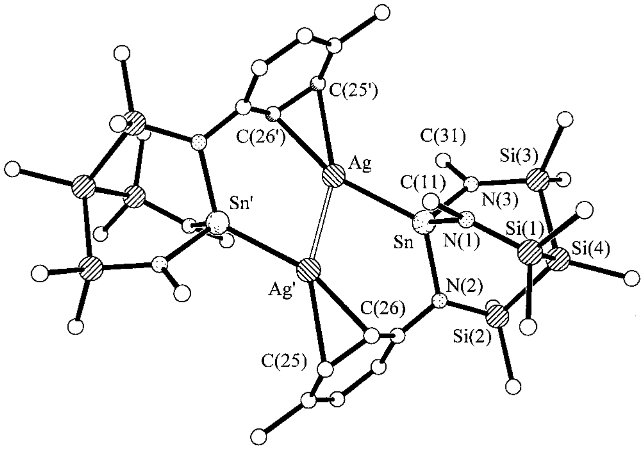


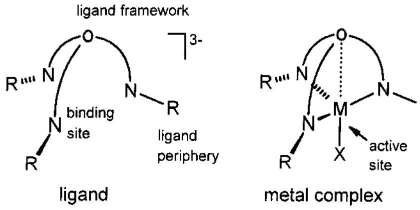
FIGURE 3. Molecular structure of $[\mathrm{MeSi\{SiMe_2N(}p\mathrm{\text{-}Tol)\}_3Sn{-}Ag}]_2$ (**7**). Two of the three peripheral tolyl groups of the tripodal ligands, which are not coordinated to Ag, have been omitted for clarity; $d(\mathrm{Ag{-}Sn}) = 2.6567(7)$ Å, $d(\mathrm{Ag{-}Ag'}) = 2.6544(11)$ Å.

Triamidometalates of the group 14 metals were found to act as versatile "ligands" such as shown for the digermanylaurate(I) (**5**),[17] along with a whole series of $\mathrm{Au^{I}}$, $\mathrm{Au^{II}}$, and $\mathrm{Au^{III}}$ complexes.[18] The triamidostannates form stable metal–metal bonds with the group 4 transition metals[19] and have given access to the first structurally characterized example of a Ag–Sn heterodimetallic complex $[\mathrm{MeSi\{SiMe_2N(}p\mathrm{\text{-}Tol)\}_3Sn{-}Ag}]_2$ (**7**) containing a direct silver–tin bond (Figure 3).[20]

Applications of the building block principle in transition metal chemistry include the homodinuclear complexes **3** [21] and **4**,[22] as well as the Ti–Co heterodinuclear compound **6** in Figure 2, which will be discussed in more detail below.[23]

Creating Well-Defined Reactive Sites in Early Transition Metal Reagents and Catalysts

As is evident from the examples cited above, the notion of the metal ligand cage has been useful in the development of the structural chemistry of these amido compounds. However, this rigid molecular cage structure of the bicyclo[2.2.2]octane type is of equal significance for the understanding of their chemical reactivity. One of the three-connected vertices of the cage is occupied by a transition or main group metal atom, while the remaining coordination sites at this metal center constitute the "reactive" site of the complex, the size and geometry of which are determined both by the dimensions in the framework of the tripod and the steric demand and nature of the peripheral substituents at the amido N atoms.



Apart from the modeling of the active space at the metal center, the integration of a transition metal into this type of molecular cage amounts to the "tying back" of the three amido functions and the enforcement of significantly reduced N—M—N angles in comparison to complex derivatives containing monodentate amido ligands. In the following two sections, we will therefore discuss two examples of the effect that the metal—ligand geometry in these complexes has upon their reactivity.

Enforced Coordination Geometry, Part I: "Tying Back" the Amido Donor Atoms To Increase the Electrophilicity in Neutral Olefin Polymerization Catalysts

As stated above, the tying back of the three amido functions by the means of their integration into the ligand framework leads to a distorted arrangement with respect to ligand sets of monodentate amides. This enforced distortion is expected to modify the reactivity of especially the early transition metal complexes. It has been argued that the reduced N—M—N angles in comparison to the known structurally characterized triamido complexes bearing monodentate ligands reduces the N→M π donation and thus renders the early transition metal center more electrophilic.[24] The situation thus created is not unlike—and may be viewed as a molecular analogue of—the surface organometallic complex fragments (Figure 4), supported by tricoordination through the silica surface they are deposited on, which Basset and co-workers have studied in detail in recent years.[25] These surface-coordinated complex fragments (bearing M—H or M—alkyl groups) have been shown to polymerize olefins or to depolymerize polyolefins as well as to induce C—H activation and C—C σ bond metathesis in alkanes.[26]

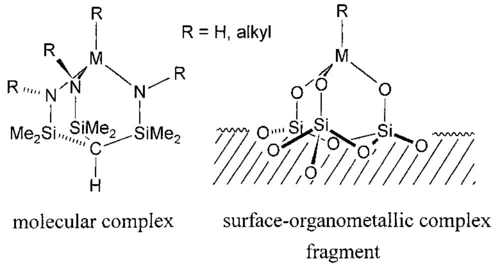


FIGURE 4. The analogy between the local molecular geometry of the tripodal amido complexes of the early transition metals and the surface organometallics studied by Basset et al.[25,26]

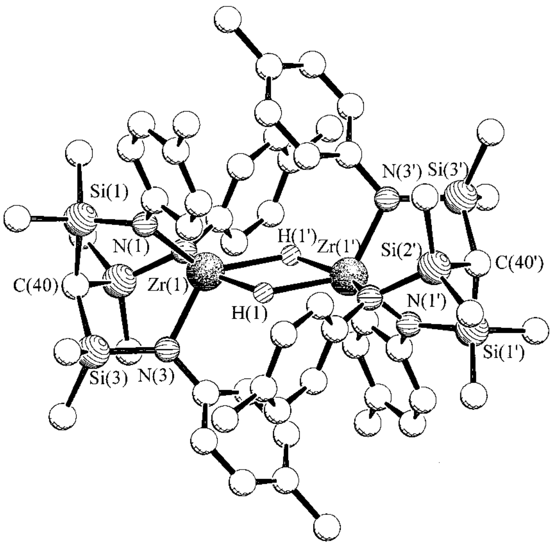
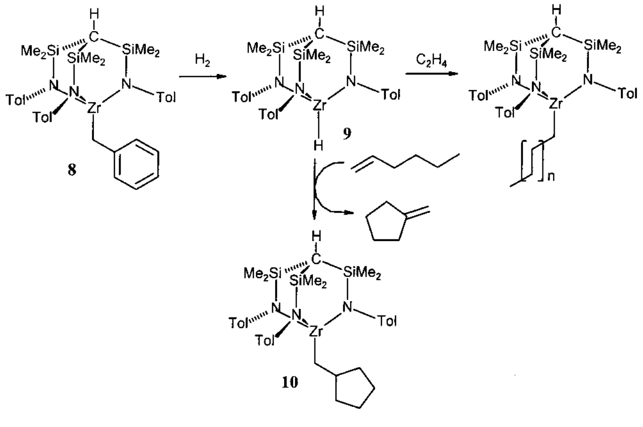
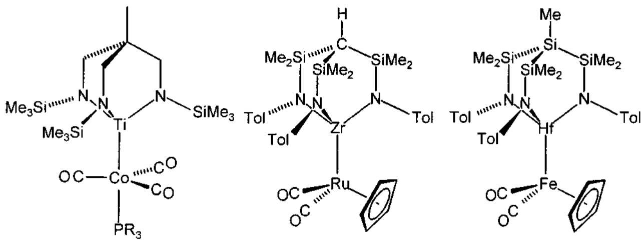


FIGURE 5. Molecular structure of the dimeric complex [(HC{$SiMe_2N(p\text{-}Tol)$}$_3Zr)_2(\mu\text{-}H)_2$].

Scheme 1. Generation of the Hydridozirconium Complex 9 and Multiple Insertions of Olefins into the Zr—H Bond



That neutral 14-electron triamidoalkylzirconium complexes bearing a trisilylmethane derived type **D** ligand are active catalysts in olefin oligomerization and polymerization has been demonstrated recently.[24] In their study of the reactivity of [HC{$SiMe_2N(p\text{-}Tol)$}$_3Zr(CH_2Ph)$] (**8**), Jia et al. obtained the corresponding hydridozirconium compound **9** by hydogenolysis (Scheme 1). While being monomeric in solution, as evidenced by the NMR spec-



11 **12** **13**

FIGURE 6. Three representative examples of tripod-stabilized early–late heterodimetallic complexes containing unsupported metal–metal bonds.

troscopic data, the hydrido complex was found to be dimeric in the solid state (Figure 5).

The hydrido complex **9** is a polymerization catalyst for ethylene at elevated temperatures to give linear polyethylene. By careful choice of the reaction conditions, it was possible to generate and identify the alkylzirconium intermediates resulting from the mono, bis, and tris insertion of ethylene into the Zr–H bond. Complex **9** also catalyzes the cyclization of 1,5-hexadiene cleanly to give, after 100 catalytic cycles, the cycloalkyl complex **10**. All alkylzirconium derivatives generated and investigated in this study were found to be stable toward β-elimination. Zirconium complexes bearing the amido tripod **D** represent by no means the extreme cases of N–M–N angle compression and the concomitant enhancement of the metal electrophilicity. It will be interesting to study the behavior of the analogous compounds bearing the neopentane-derived type **C** ligands and to compare their olefin insertion activity with the case at hand.

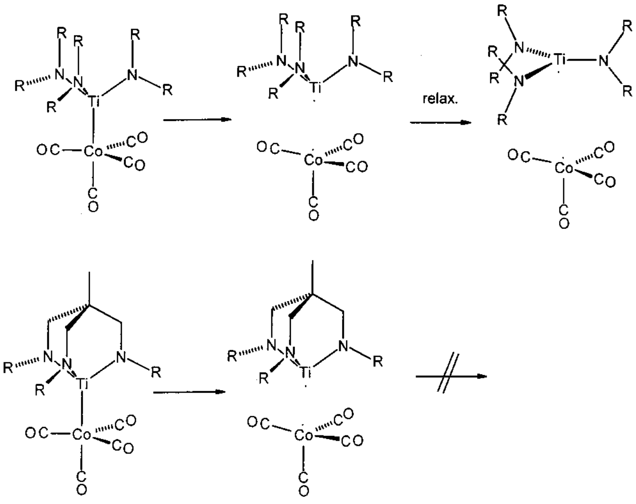
Enforced Coordination Geometry, Part II: Stabilization of Unsupported Metal–Metal Bonds in Early–Late Heterodinuclear Complexes

The tripodal amido ligands **C**–**E** have provided the key to a systematic investigation of the chemistry of early–late heterodimetallic complexes containing unsupported, highly polar metal–metal bonds.[23,27–29] Three basic examples, **11**–**13**, are depicted in Figure 6.

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 bicyclo[2.2.2]octane cage structure of the tripod-amide unit. This geometric fixation destabilizes the potential fragmentation product, the triamidometal fragment. In the analogous systems containing monodentate anionic ligands at the early transition metal center, the $\{M(NR_2)_3\}$ fragment undergoes planarization upon cleavage of the metal–metal bond, a process that stabilizes the fragment. This planarization is suppressed in the tripod–cage (Scheme 2).

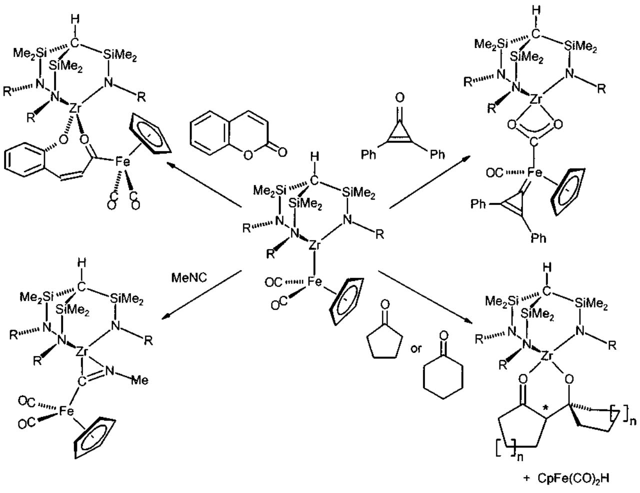
To have an estimate of the energetic contribution of this geometric relaxation of the early transition metal complex fragment, a theoretical study was carried out on the Ti–Co model complex $[(H_2N)_3Ti{-}Co(CO)_4]$. The planarization energy E_r(Ti) of the Ti fragment was found to be about 10 kcal mol^{-1}.[30] This represents an upper boundary of the hypothetical relaxation energy of the Ti fragment containing the tripod ligand, which is unable to achieve the planar geometry of the free $Ti(NH_2)_3$ fragment. Therefore, one can estimate that *the tripod ligand thermodynamically stabilizes the Co–Ti complex by about 10 kcal mol^{-1}* with respect to fragmentation of the metal–metal bond. Since the early transition metal fragment is the same in the whole range of heterodinuclear complexes coordinated by tripodal amido ligands, this figure can be regarded as a general estimate of the thermodynamic stabilization of the complexes with respect to their mononuclear fragments.

Scheme 2. Thermodynamic Stabilization of Ti–Co Dinuclear Complexes with Tripodal Amido Ligands by Suppression of the Possible Relaxation of the Ti Fragment into a Planar Structure (As Observed in Systems with Monodentate Ligands)



The successful stabilization of early–late heterodimetallic complexes containing unsupported metal–metal bonds opened up the possibility of a systematic investigation into their chemical reactivity and the establishment of a variety of examples of cooperative behavior of the

Scheme 3. Selected Cooperative Transformations of Organic Substrates by a Zr–Fe Complex Which Is Stabilized by a Type B Tripodal Amido Ligand (R = 2,3,4-$F_3C_6H_2$)



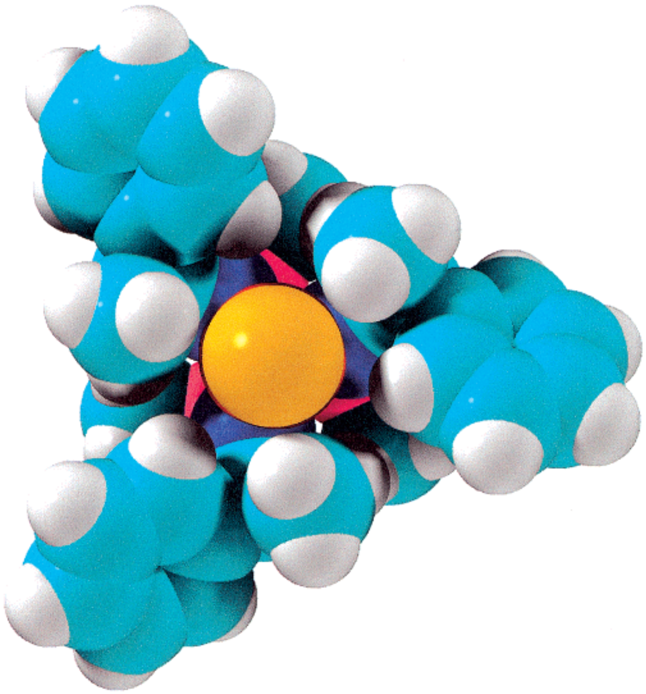
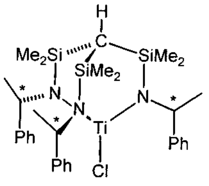


FIGURE 7. View along the 3-fold symmetry axis of a space-filling model of the C_3-chiral complex **14** illustrating the helicoidal arrangement of the peripheral *(S)*-1-phenylethyl groups.

two metal centers in reactions with organic substrates bearing polar structural units.[31−33] Several examples of this type of reactive behavior are summarized in Scheme 3. A detailed overview of this work has been published recently.[34]

C_3-Chiral Amido Complexes

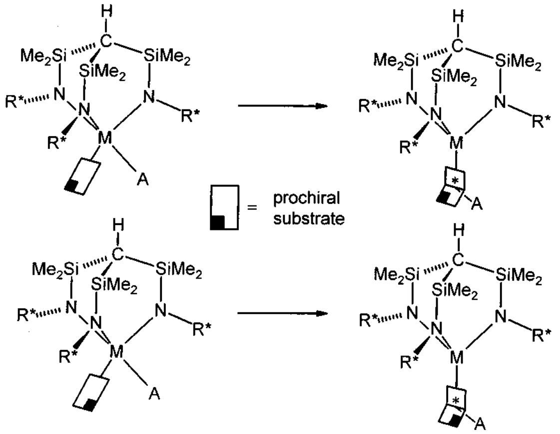
While 2-fold rotational symmetry has been successfully employed in a large number of chiral reagents and catalysts, there is still comparatively little known about the efficiency of systems of higher rotational symmetry.[35,36] There are to date two different strategies for the synthesis of C_3-chiral amido tripods. 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 my group.[37] The molecular structure of the titanium complex [TiCl{HC(SiMe$_2$N[*(S)*-1-phenylethyl])$_3$}] (**14**) is depicted in Figure 7, the view along the 3-fold molecular axis nicely demonstrating the helicoidal arrangement of the peripheral N-substituents.[38]



14

An alternative approach has been the generation of a chiral ligand tripod backbone, as pursued by Moberg and co-workers in their synthesis of chiral triamidoamine ligands.[39] In an important contribution to the field, they demonstrated that the titanium complexes containing these ligands may be used in the catalytic asymmetric alkylation, albeit with only moderate stereoselectivity.

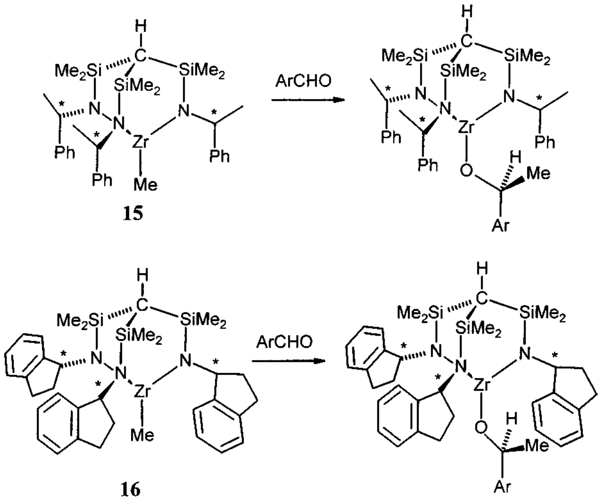
The possible reduction in selectivity-determining alternatives in stoichiometric or catalytic conversions involving 3-fold symmetrical chiral ligands has been discussed in detail for octahedral intermediates that are involved in the selectivity-determining step. However, a similar situation is expected to arise in five-coordinate complexes or reaction intermediates bearing such a chiral tripod and in which the two remaining ligands are arranged symmetrically on either side of the molecular axis. Such a coordination geometry has been postulated by Ugi et al. for the transition state in the turnstile rearrangement of five-coordinate molecules.[40] We found an arrangement such as the ground-state geometry of several five-coordinate zirconium complexes bearing tripodal amido ligands.[41] If one of these two monodentate ligands were a planar prochiral molecule and the other ligand a molecular fragment to be coupled with the prochiral unit to give a new stereoelement, the C_3-symmetrical tripod renders all possible arrangements essentially identical. Therefore, the stereochemical alternatives would be reduced to the two possible orientations of the prochiral faces with respect to the attacking ligand.



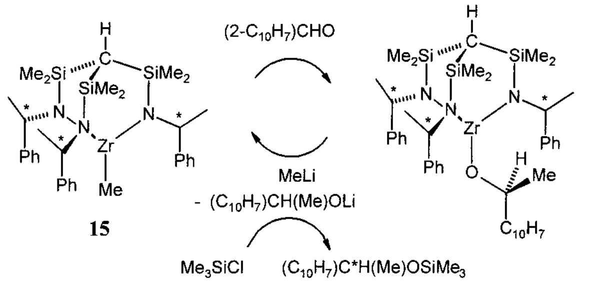
A reaction that represents exactly this situation and thus permits the practical evaluation of this conceptual approach is the stoichiometric insertion of an *O*-coordinated prochiral carbonyl compound into a metal−alkyl bond. If the three stereocenters in the ligand periphery of the tripodal ligand adopt a similar orientation, thus generating real 3-fold symmetry, this in turn defines a helicoidal environment for the remaining ligands and therefore favors one of the two possible orientations of the carbonyl compound vis-à-vis the alkyl ligand.[38]

While the reaction of [Zr(CH$_3$){HC(SiMe$_2$N[*(S)*-1-phenylethyl])$_3$}] (**15**) with the aryl ketones PhC(O)R (R = CH=CHPh, *i*Pr, Et) gave the corresponding C−O insertion products, which contain an additional chiral center in the alkoxy group, with low stereoselectivity (0−40% de), the corresponding conversions of **15** and the corresponding *(R)*-1-indanyl-substituted complex [Zr(CH$_3$){HC(SiMe$_2$N)-[*(R)*-1-indanyl])$_3$}] (**16**) with several aryl aldehydes yielded the alkoxo complexes with high stereoselectivity (Scheme

Scheme 4. Stereoselective Insertion of Aryl Aldehydes into the Zr−CH$_3$ Bonds of Complexes 15 and 16



Scheme 5. Cycle of Naphthaldehyde Insertion into 15 and Methylation of the Product Complex with Methyl Lithium to Regenerate 15[a]



[a] The alcoholate is trapped as the silyl ether with Me$_3$SiCl.

4). 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 butylzirconium analogues of **15** 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 center.[38]

The high chemoselectivity of the reaction with arylaldehydes and the observation that the alkoxo product complex reacts cleanly with methyllithium to regenerate **15** allowed us to perform repeated cycles of insertions and alkylations with benzaldehyde. 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 5).

In the meantime, it has been possible to develop a catalytic system of comparable stereoselectivity using the alkyltitanium complexes, such as those derived from **14**, and alkylzinc reagents.

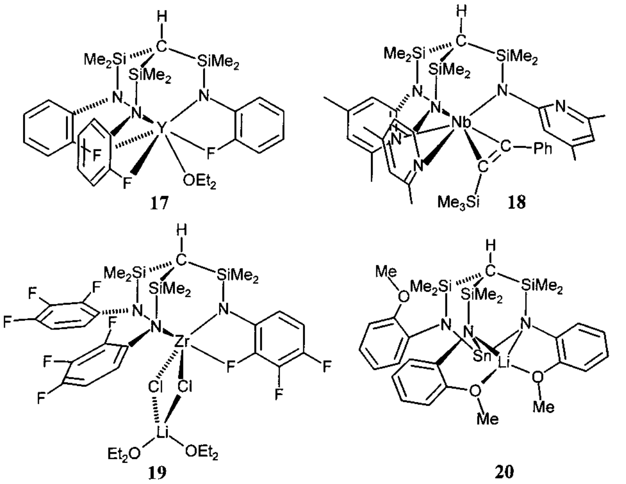


FIGURE 8. Additional donor-metal interactions in amido complexes bearing tripod ligands with an "active" ligand periphery.

An "Active" Ligand Periphery: Tripodal Amido Ligands Containing Weakly Coordinating Donor Functions

We discussed the implications of metal−ligand cage formed by the tripods **C**−**E** for the structural chemistry and the reactivity of the complexes bearing these ligands. The metal centers in these compounds are significantly more exposed than in the azatranes studied by Schrock and Verkade.[6,7] This increased accessibility of the transition metals in some compounds increased their reactivity to the point of extreme lability. In these and related cases it has proved useful to introduce additional weakly coordinating donor functions within the ligand peripheries. These weakly coordinating ligating functions, which are referred to as the "active ligand periphery",[42] offer the possibility of adjusting the size of the "reactive site" at the metal center according to the requirements of the remaining coordinated ligands and molecular fragments.

This approach was initially pursued by introducing *o*-fluorophenyl substituents at the amido N-functions which were particularly suitable for the stabilization of yttrium and zirconium complexes bearing the tripodal ligands, such as **17** and **19** (Figure 8).[33a,42] While fluoroaryl groups are useful for the stabilization of group 3−5 d^0 metal centers, they appear to be prone to C−F activation if employed in the amides of the group 6 elements. More recently, 2-pyridylamido and *o*-anisylamido have have also been employed in both early transition metal complexes (for example, **18**)[43] and group-14 amides (**20**).[44] Apart from the temporary shielding of an otherwise exposed metal center, ortho-functionalized arylamides appear to interfere with the chemical transformations at the remaining coordination site(s). In our study into the reactivity of metal−metal bonded early−late heterodimetallic compounds, this aspect has be manifested in an enhanced reactivity of the highly polar metal−metal bonds, possibly due to the stabilization of the early transition metal fragment complexes.[33a]

Perspectives

The tripodal amido ligands discussed in this short overview have provided the basis for several lines of research in early transition metal and main group chemistry. The combination of the steric shielding of a large sector in the coordination sphere of a metal and its integration into a relatively rigid metallocage have made these systems molecular building blocks in more complex molecular structures, as was shown for a new class of early−late heterodimetallics. More importantly, the tying back of the amido functions with the concomitant distortion of the ligand polyhedron and thus activation of the metal center in group 4 transion metal complexes holds promise for the development of a molecular chemistry that might emulate some aspects of the fascinating surface organometallic chemistry of the early transition elements that has emerged in recent years. It is in this area that novel reactivity patterns of M−C, M−H, and M−E bonds (E = p-block element) are to be expected, which complement the well-established chemistry of the metallocene derivatives.

The facile synthetic accessibility and the possibility of preparing large quantities of the triamines which serve as ligand precursors for the tripodal amido "claws" make them suitable "tools" for the early transition metal and p-block element coordination chemist and will aid the further development of the field.

I would like to thank my students and postdocs who worked in the area described in this Account, in particular, Stefan Friedrich, Harald Memmler, Martin Schubart, Bernd Findeis, Sylvie Fabre, Patrick Renner, and Matthias Lutz, for their enthusiasm and dedication. I also acknowledge the fruitful collaborations with the research groups of Mary McPartlin (London), Tapani Pakkanen (Joensuu), Mariano Laguna (Zaragoza), and Joe Lauher (Stony Brook). Our research was generously supported by the Deutsche Forschungsgemeinschaft, the European Union (TMR Program and COST D12), and the CNRS (France).

References

(1) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. Metal and Metalloid Amides, Ellis Horwood-Wiley: Chichester, **1980**.

(2) Chisholm, M. H.; Rothwell I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, p 161.

(3) Gade, L. H. Taming Early Transition Metals: The Use of Polydentate Amido-Donor Ligands to Create Well-Defined Reactive Sites in Reagents and Catalysts. *Chem. Commun.* **2000**, 173−181.

(4) For podands and macrocycles containing anionic N-donor functions, see: (a) Fryzuk, M. D.; Haddad, T. S.; Berg, D. J.; Rettig, S. J. Phosphine Complexes of the Early Transition Metals and the Lanthanoids. *Pure Appl. Chem.* **1991**, *63*, 845−850. (b) Fryzuk, M. D. Excursions around the Periodic Table: Ligand Design in Inorganic Chemistry. *Can. J. Chem.* **1992**, *70*, 2839−2845. (c) Brand, H.; Arnold, J. Recent Developments in the Chemistry of Early Transition Metal Phorphyrin Compounds. *Coord. Chem. Rev.* **1995**, *140*, 137−168. (d) Floriani, C. The Porphinogen-Porphyrin Relationship: The Discovery of Artificial Porphyrins. *Chem. Commun.* **1996**, 1257−1263. (e) Floriani, C. Transition Metal Complexes as Bifunctional Carriers of Polar Organometallics: Their Application to Large Molecule Modifications and to Hydrocarbon Activation. *Pure Appl. Chem.* **1996**, *68*, 1−8. For an overview of some recent developments in transition metal amide chemistry, see: (f) Kempe, R. Highlights in the Renaissance of Amidometal Chemistry *Angew. Chem., Int. Ed.* **2000**, *39*, 468−493.

(5) Reviews: (a) Cummins, C. C. Reductive Cleavage and Related Reactions Leading to Molybdenum-Element Multiple Bonds: New Pathways offered by Three-Coordinate Molybdenym(III). *Chem. Commun.* **1998**, 1777−1786. (b) Cummins, C. C. Three-Coordinate Complexes of "Hard" Ligands: Advances in Synthesis, Structure and Reactivity. *Prog. Inorg. Chem.* **1998**, *47*, 685−836.

(6) Verkade, J. G. Atranes: New examples with Unexpected Properties. *Acc. Chem. Res.* **1993**, *26*, 483−489.

(7) (a) Schrock, R. R. Transition Metal Triamidoamine Ligand Complexes. *Acc. Chem. Res.* **1997**, *30*, 9−16. (b) Schrock, R. R. High Oxidation State Coordination Chemistry with Triamidoamine Tungsten and Molybdenum Complexes. *Pure Appl. Chem.* **1997**, *69*, 2197−2203.

(8) Selected examples: (a) Cristou, V.; Arnold, J. Formation of Monomeric Terminal Chalcogenides by Template-Induced Disilylchalcogenide Elimination−The Crystal Structures of $[\mathrm{ETa}\{(\mathrm{Me_3SiNCH_2CH_2})_3\mathrm{N}\}]$ (E = Se, Te). *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450−1452. (b) Schubart, M.; O'Dwyer, L.; Gade, L. H. Synthesis and structures of N−Alkylated Azatranes. *Inorg. Chem.* **1994**, *33*, 3893−3898. (c) Roussel, P.; Hitchcock, P. B.; Tinker, N.; Scott, P. A Mixed Valence Uranium(III/IV) Bimetallic-Structure, Magnetism and Reactivity. *Chem. Commun.* **1996**, 2053−2054. (d) Roussel, P.; Allcock, N. W.; Scott, P. Triamidoamine Complexes of Scandium, Yttrium and the Lanthanides. *Chem. Commun.* **1998**, 801−802.

(9) (a) Gade, L. H.; Mahr, N. The Metalation of Multifunctional Secondary Amines: The Structural Characterization of the Tripodal Lithium Amides $[\mathrm{H_3CC}\{\mathrm{CH_2N(Li)R}\}_3]_2$. *J. Chem. Soc., Dalton Trans.* **1993**, 489−494. A triaminophosphine bearing a type **C** ligand fragment had been previously reported by Verkade: (b) Laube, B. L.; Bertrand, R. D.; Casedy, G. A.; Compton, R. D.; Verkade, J. G. Polycyclic Group V Ligands. III. 2,6,7-Trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2,2,2]octane. A bidentate donor. *Inorg. Chem.* **1967**, *6*, 173.

(10) Gade, L. H.; Becker, C.; Lauher, J. W. Trisilylmethane as a Structural Backbone in Multifunctional Lithium Amides: The Syntheses and Structures of $\mathrm{HC}\{(\mathrm{CH_3})_2\mathrm{SiN(Li)}t\mathrm{Bu}\}_3$ and Its Solvate $\mathrm{HC}\{(\mathrm{CH_3})_2\mathrm{SiN(Li)}t\mathrm{Bu}\}_3$.2 THF. *Inorg. Chem.* **1993**, *32*, 2308−2314.

(11) Schubart, M.; Findeis, B.; Gade, L. H.; Li, W.-S.; McPartlin, M. Tripodal Amides Containing a Totally Silicon-Based Ligand Framework.*Chem. Ber.* **1995**, *128*, 329−334.

(12) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2.

(13) Findeis, B.; Schubart, M.; Gade, L. H. Tris[(*tert*-butylamino)-dimethylsilyl]methylsilane and its Precursors. *Inorg. Synth.* **1998**, *32*, 136−140.

(14) (a) Hellmann, K. W.; Gade, L. H.; Scowen, I. J.; McPartlin, M. Aggregation of Tripodal Thallium(I) Amides Through Weak Tl(I)···Tl(I) Interactions. *Chem. Commun.* **1996**, 2515−2516. (b) Hellmann, K. W.; Gade, L. H.; Steiner, A.; Stalke, D.; Möller, D. Redox-Disproportionation in Tripodal Indium and Thallium Amides: First Characterization of Mixed-Valence M(I)/M(II)-Compounds (M = In, Tl). *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 160−163.

(15) Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Kottke, T. Aggregation, Re-aggregation and Degradation of a Trifunctional Thallium(I) Amide Induced by Weak $\mathrm{Tl^I}\cdots\mathrm{Tl^I}$-Attraction. *Chem. Eur. J.* **1997**, *3*, 1801−1806.

(16) Hellmann, K. W.; Galka, C. H.; Rüdenauer, I.; Gade, L. H.; Scowen, I. J.; McPartlin, M. Metal−Ligand vs Metal−Metal Redox Chemistry: Thallium(I)-induced Synthesis of 1,3,8,10-Tetraaminoperylen Derivatives. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1948−1952. (b) Galka, C. H.; Gade, L. H. A Mixed Valent Thallium Amide Bearing a Butylthallium(III) Unit Stabilized by a Tripodal Amido Ligand. *Chem. Commun.* **2001**, 899−900.

(17) Contel, M.; Hellmann, K. W.; Gade, L. H.; Scowen, I. J.; McPartlin, M.; Laguna, M. Triamidogerma- and Stanna-aurates(I): First Structural Characterization of an Ge−Au−Ge Unit. *Inorg. Chem.* **1996**, *35*, 3713−3715.

(18) Findeis, B.; Contel, M.; Gade, L. H.; Laguna, M.; Gimeno, M. C.; Scowen, I. J.; McPartlin, M. Triamidostannagold Complexes in Different Oxidation States. First Structural Characterization of a Sn−Au−Au−Sn Linear Chain. *Inorg. Chem.* **1997**, *36*, 2386−2390.

(19) Lutz, M.; Findeis, B.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. Ti−Sn, Zr−Sn and Hf−Sn Heterodimetallic Complexes Containing Unsupported Metal−Metal Bonds.*Organometallics*, **2001**, *20*, 2505−2509.

(20) Findeis, B.; Gade, L. H.; Scowen, I. J.; McPartlin, M. Ligand Exchange and Molecular Aggregation of an Ag−Sn Heterobimetallic Complex: First Structural Characterization of an Ag−Sn Bond. *Inorg. Chem.* **1997**, *36*, 960−961.

(21) Garcia-Yuste, S.; Gade, L. H.; Scowen, I. J.; McPartlin, M. $[\mathrm{Mo_2}(\mu\text{-H})_2\,\{\mathrm{MeC(CH_2N}i\mathrm{Pr})_3\}]$, a Dihydrido Bridged Di-Molybdenum-(IV) Complex. To be submitted.

(22) Desmangles, N.; Jenkins, H.; Ruppa, K. B.; Gambarotta, S. Preparation and Characterization of a Vanadium(III) Dinitrogen Complex Supported by a Tripodal Anionic Amide Ligand. *Inorg. Chim Acta* **1996**, *250*, 1–4.

(23) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; McPartlin, M. Titanium Complexes with Tripodal Amidoligands: Building Blocks of Stable Bimetallic Coordination Compounds Containing Highly Polar Metal–Metal Bonds. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 676–678.

(24) Jia, L.; Ding, E.; Rheingold, A. L.; Rhatigan, B. Neutral Tripodal Amidozirconium Alkyls and Hydride. Synthesis, Structures, and Catalytic Olefin Insertions. *Organometallics* **2000**, *19*, 963–965.

(25) Lefebvre, F.; De Mallmann, A.; Basset, J.-M. Modification of the Adsorption and Catalytic Properties of Molecular Sieves by Reaction with Organometallic Complexes *Eur. J. Inorg. Chem.* **1999**, *3*, 361–372.

(26) (a) Corker, J.; Levebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J. M. Catalytic Cleavage of the C–H and C–C Bonds of Alkanes by Surface Organometallic Chemistry: An EXAFS and IR Characterization of a Zr–H Catalyst. *Science* **1996**, *271*, 966–969. (b) Dufaud, V.; Basset, J.-M. Catalytic Hydrogenolysis at Low Temperature and Pressure of Polyethylene and Polypropylene to Diesels or Lower Alkanes by a Zirconium Hydride Supported on Silica–Alumina: A Step Toward Polyolefin Degradation by the Microscopic Reverse of Ziegler–Natta Polymerization. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 806–810.

(27) Findeis, B.; Schubart, M.; Platzek, C.; Gade, L. H.; Scowen, I.; McPartlin, M. A "Passe-Partout" for the Stabilization of Highly Polar Unsupported M–M′ Bonds (M = Ti, Zr, Hf; M′ = Fe, Ru) and α-Addition of the Metal Nucleophile–Electrophile-Pairs to an Isocyanide. *Chem. Commun.* **1996**, 219–220.

(28) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; Scowen, I. J.; McPartlin, M.; Housecroft, C. E. Stabilizing Heterobimetallic Complexes Containing Unsupported Ti-M Bonds (M = Fe, Ru, Co): The Nature of Ti-M Donor–Acceptor Bonds. *Inorg. Chem.* **1996**, *35*, 2433–2441.

(29) Gade, L. H.; Schubart, M.; Findeis, B.; Fabre, S.; Bezougli, I.; Lutz, M.; Scowen, I. J.; McPartlin, M. Synthesis and Reactivity of Early-Late Heterodinuclear Complexes Stabilized by a Trisilylsilane-Based Tripodal Ligand. *Inorg. Chem.* **1999**, *38*, 5282–5294.

(30) Jansen, G.; Schubart, M.; Findeis, B.; Gade, L.; H.; Scowen, I. J.; McPartlin, M. Unsupported Ti–Co and Zr–Co Bonds in Heterobimetallic Complexes: A Theoretical Description of Metal–Metal Bond Polarity. *J. Am. Chem. Soc.* **1998**, *120*, 7239–7251.

(31) (a) Memmler, H.; Kauper, U.; Gade, L. H.; Scowen, I. J.; McPartlin, M. Insertion of X=C=Y Heteroallenes into Zr-M Bonds (M = Fe, Ru). *Chem. Commun.* **1996**, 1751–1552. (b) Schneider, A.; Gade, L. H.; Breuning, M.; Bringmann, G.; Scowen, I. J.; McPartlin, M. Cooperative Reactivity of Unsupported Early-Late Heterobimetallics: Ring Opening and Subsequent Decarbonylation of Biaryllactones. *Organometallics*, **1998**, *17*, 1643–1645. (c) Gade, L. H.; Friedrich, S.; Memmler, H.; Kauper, U.; Schubart, M.; Findeis, B.; Schneider, A.; Fabre, S.; Trösch D. J. M. Organic Transformations with Early-Late Heterobimetallics: Synergism and Selectivity. In *Selective Reactions of Metal-Activated Molecules;* Werner, H., Schreier, P., Eds.; Vieweg: Braunschweig, 1998; p 229–234.

(32) (a) Schubart, M.; Mitchell, G.; Gade, L. H.; Kottke, T.; Scowen, I. J.; McPartlin, M. Ionic Cleavage of Ti–Co and Zr–Co Bonds: The Role of the Nucleophilicity of the Late Transition Metal in the Reactive Behaviour of Early-Late Heterobimetallics.*Chem. Commun.* **1999**, 233–234. (b) Fabre, S.; Findeis, B.; Trösch, D. J. M.; Gade, L. H..; Scowen, I. J.; McPartlin, M. Atom-Transfer within the Coordination Sphere of Early-Late Heterobimetallic Complexes: Rapid Deoxygenation of Sulfoxides at Low Temperatures. *Chem. Commun.* **1999**, 577–578.

(33) (a) Gade, L. H.; Memmler, H.; Kauper, U.; Schneider, A.; Fabre, S.; Bezougli, I.; Lutz, M.; Galka, C. H.; Scowen, I. J.; McPartlin, M. Cooperative Reactivity of Early-Late Heterodinuclear Complexes Towards Polar Organic Substrates. *Chem. Eur. J.* **2000**, *6*, 692–708. (b) Lutz, M.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. Structural Characterization of the Product of Intramolecular Oxygen-Transfer from a Ketone to CO within the Coordination Sphere of a Zr–Fe Heterodimetallic Complex. *Organometallics* **2001**, *20*, 2631–3634.

(34) Gade, L. H. Highly Polar Metal–Metal Bonds in "Early–Late" Heterobimetallic Complexes. *Angew. Chem., Int. Ed.* **2000**, *37*, 2658–2678.

(35) Keyes, M. C.; Tolman, W. B. *Adv. Catal. Proc.* **1997**, *2*, 189–219.

(36) Moberg, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 248–268.

(37) (a) Memmler, H.; Gade, L. H.; Lauher, J. W. Amino-functionalized Trisilylmethanes: Precursors for a New Class of Tripodal Amido Ligands in Transition Metal Complexes.*Inorg. Chem.* **1994**, *33*, 3064–3071. (b) Renner, P.; Galka, C. H.; Gade, L. H.; Radojevic, S.; McPartlin, M. Synthesis and Structural Characterization of a Novel C_3–Chiral Triamine and its Trilithium Triamide. *J. Chem. Soc., Dalton Trans* **2001**, 964–965. (c) Renner, P.; Galka, C. H.; Gade, L. H.; Radojevic, S.; McPartlin, M. Generating a New Chiral Ligand System for High-Valent Early Transition Metals: Synthesis and Structural Characterization of C_3-symmetrical Tripodal Alkyl/Silyl Amido Complexes. *Eur. J. Inorg. Chem.* **2001**, 1425–1430.

(38) Gade, L. H.; Renner, P.; Memmler, H.; Fecher, F.; Galka, C. H.; Laubender, M.; Radojevic, S.; McPartlin, M.; Lauher, J. W. C_3-Chiral Tripodal Amido Complexes. *Chem. Eur. J.* **2001**, *7*, 2563–2580.

(39) Cernerud, M.; Adolfsson, H.; Moberg, C. C_3–Symmetric Tripodal Tetra-amines–Preparation from Chiral Amino Alcohols via Aziridines. *Tetrahedron: Asymmetry* **1997**, *8*, 2655–2662.

(40) (a) Ugi, I.; Marquarding, D.; Klusacek, H.; Gokel, G.; Gillespie, P. Chemie und Logische Strukturen. *Angew. Chem.* **1970**, *82*, 741–771. (b) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P.; Ramirez, F. Berry Pseudorotation and Turnstile Rotation. *Acc. Chem. Res.* **1971**, *4*, 288–296. See also: (c) Wang, P.; Agrafiotis, D. K.; Streitwieser, A.; v. R. Schleyer, P. Berry and Turnstile Processes in the Pseudorotation of Three Phosphoranes. *J. Chem. Soc., Chem. Commun.* **1990**, 201–203 and refs cited therein.

(41) Findeis, B.; Schubart, M.; Gade, L. H.; Scowen, I. J.; McPartlin, M. Tripod-Amido Titanium and Zirconium Complexes Containing a Trisilylsilane-derived Ligand Framework. *J. Chem. Soc., Dalton Trans.* **1996**, 125–132.

(42) Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. Tripodal Amidoligands Containing an "Active" Ligand Periphery. *Inorg. Chem.* **1995**, *34*, 4062–4068.

(43) Hillebrand, G.; Spannenberg, A.; Arndt, P.; Kempe, R. Titanium and Niobium Complexes Stabilized by Tris(aminopyridinato) Ligands: Evidence of Variable Denticity in Trianionic Polydentate Ligands. *Organometallics* **1997**, *16*, 5585–5588.

(44) Lutz, M., Galka C. H.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. Cation Solvation by the Ligand Periphery in a Lithium Triamido Stannate Bearing a Tripodal Amido Ligand. *Eur. J. Inorg. Chem.* **2002**, in press.

AR010116F