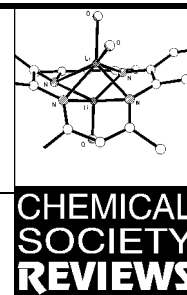# Dibenzotetraaza[14]annulenes: versatile ligands for transition and main group metal chemistry

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This article presents an overview of the chemistry of metal complexes of dibenzotetraaza[14]annulene ligands and highlights most of the recent developments. The title tetraazamacrocycles are related to the porphyrins but have a smaller N_4 coordination cavity 'hole size' and typically possess a non-planar, saddle-shaped conformation. The similarity of the dibenzotetraaza[14]annulenes to the porphyrins means that these synthetic macrocycles are of bioinorganic relevance, while their distinctive individual characteristics make them interesting ligands in their own right. In early transition metal chemistry, for example, the dibenzotetraaza[14]annulenes have been studied as potential alternatives to the ubiquitous bis(η-cyclopentadienyl) ligand set, while later transition metal derivatives can mimic certain biological systems and act as precursors to electroactive polymeric films. The dibenzotetraaza[14]annulenes have also recently allowed advances in structural and reactivity studies of main group organometallic and coordination compounds, including the stabilisation of new metal–chalcogenide multiple bonds.

1 Introduction

There is a tremendous interest in exploring new ligand environments for transition and main group metal chemistry, and for developing synthetic mimics of biological systems. One class of ligand that has stimulated continuing interest in a wide range of areas for nearly thirty years are the dibenzotetraaza[14]annulenes [Fig. 1(a)]. The chemistry of macrocyclic ligand complexes in general represents a vast area of research ranging over many areas of chemistry and biochemistry, and the reader is referred to Lindoy's excellent book for a succinct introduction to this topic.[1] In the context of this current review it suffices to point out that macrocyclic ligands are considerably attractive in the quest for new chemistry, not least because they can offer a wide variety of donor atom types, ligand charges, coordination numbers and resultant complex geometries. Macrocyclic complexes can also exhibit enhanced kinetic and thermodynamic stability in comparison with those of unidentate ligands.

The purpose of this article is to provide the reader with a general introduction to the synthesis and properties of transition and main group metal compounds of dibenzotetraaza[14]annulene ligands, and to highlight the more recent developments in their chemistry. It is not within the scope of *Chem. Soc. Rev.* to provide a full and comprehensive account of this area, but it is hoped that this article will provide a suitable springboard for further reading. A detailed review of the transition metal chemistry of the Me_4taa ligand [Fig. 1(a)] up to 1990 has been published.[2]

## 2 Typical features of dibenzotetraaza[14]annulenes and their complexes

2.1 Opening remarks

We shall begin by examining the characteristic important features of the ligands and their metal complexes. Fig. 1 illustrates the general structure of dibenzotetraaza[14]annulenes, together with that of the naturally-occurring macrocycle, porphyrin, with which they are often compared. Abbreviations used herein for some of the more common dibenzotetraaza[14]annulenes are also provided in Fig. 1 for ease of reference. Note that in some of the literature the alternative abbreviations used for the Me_4taa and Me_8taa ligands are 'tmtaa' and 'omtaa' respectively. It is instructive to compare and contrast the two types of tetraazamacrocycle. The dibenzotetraaza[14]annulene and porphyrin ligands both have

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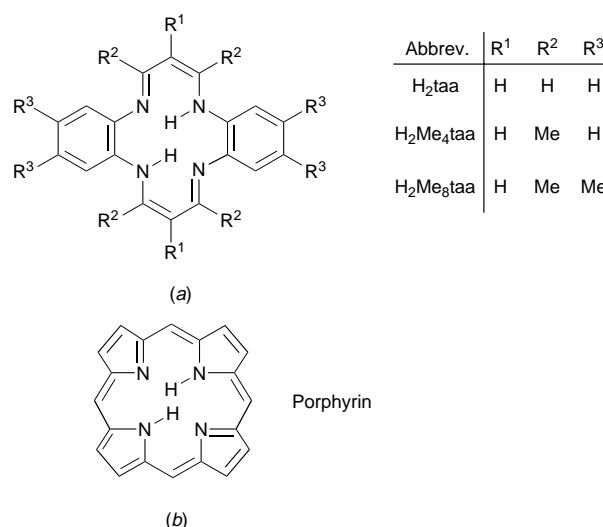
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Fig. 1 Comparison of the dibenzotetraaza[14]annulenes (showing the abbreviations used in this review) and porphyrin

Abbrev.	R^1	R^2	R^3
H_2taa	H	H	H
H_2Me_4taa	H	Me	H
H_2Me_8taa	H	Me	Me

four coplanar nitrogen donor atoms, can readily be deprotonated to form a dianion, and possess a number of double bonds in the ligand framework. However, the dibenzotetraaza[14]annulenes are Hückel anti-aromatic ($4n$) whereas the porphyrins are fully delocalised, aromatic ($4n + 2$) systems. Furthermore, structural and theoretical (see Section 2.3) studies of dibenzotetraaza[14]annulenes and their complexes have shown that there is negligible delocalisation between the two o-phenylene and the 1,3-diiminato fragments. This is apparently due to the aromatic stability of the individual benzenoid rings, and so π-delocalisation is confined within (but not between) the two types of fragment. Consequently, in the deprotonated dibenzotetraaza[14]annulene dianions, the negative charges tend to be localised on the 1,3-diiminato linkages [Fig. 2(a)], whereas in
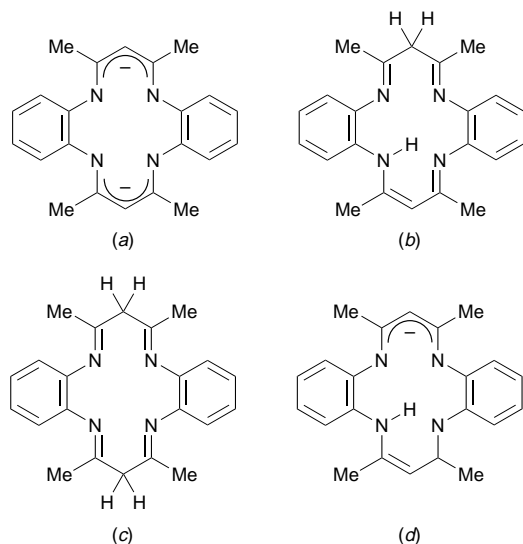

Fig. 2 (a) Dianionic, (b, c) neutral and (d) monoanionic forms of tetramethyl dibenzotetraazatraaza[14]annulenes. See the text for further details.

porphyrins the charge can be more delocalised over the entire ligand. The flexibility (i.e. ability to adopt different conformations) of the dibenzotetraaza[14]annulene ligands may be placed somewhere between the essentially rigid, delocalised porphyrins and the fully-saturated [16]aneN₄ cyclam systems.

2.2 Ligand conformations and metal coordination geometries

Further important differences between the dibenzotetraaza[14]annulene and porphyrin systems concern the 'hole size' of the macrocycle coordination cavity (defined as the average distance from N to the mid-point of the four N atoms) and the geometry of the ligand framework. As indicated by their name, the dibenzotetraaza[14]annulenes have only a fourteen-membered inner ring (as compared to the larger sixteen-atom porphyrin inner ring). This gives rise to an N_4 coordination cavity hole size of between 1.90 and 1.93 Å for H_2taa and H_2Me_ntaa, which is about 0.1 Å less than that of the porphyrins. This feature is one of the main reasons (but also see below) why many dibenzotetraaza[14]annulene complexes have the metal lying out of the N_4 plane, whereas their porphyrin analogues tend to have the metal coplanar with the N_4 donors.

The second special characteristic of the dibenzotetraaza[14]annulene ligands is their tendency to adopt a so-called 'saddle-shaped' conformation when coordinated to a metal centre. This feature is especially pronounced for Me_4taa and other homologues where R^2 = Me because of steric interactions between the R^2 methyl substituents and the hydrogen atoms of the o-phenylene rings. For Me_ntaa (n = 4 or 8) the non-planarity even persists in the free ligands as illustrated by Fig. 3(a) and (b) which show the structures of H_2taa (planar) and H_2Me_4taa
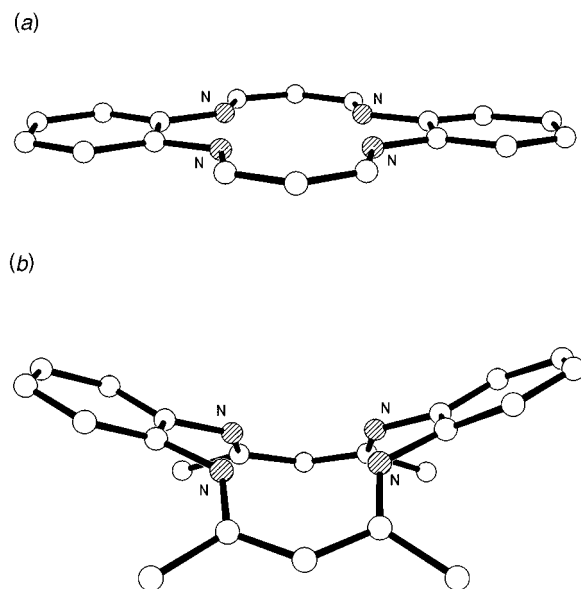
Fig. 3 The planar and saddle-shaped solid state structures of (a) H_2taa[3] and (b) H_2Me_4taa.[2] Hydrogen atoms are omitted for clarity and the remaining atoms are drawn as spheres of arbitary radius.

respectively.[2,3] The steric constraints imposed by the iminato methyl substituents are very important because they also contribute to the tendency for complexes of Me_4taa and its homologues to have the metal atom lying out of the N_4 plane (as mentioned above). This, in turn, leads the metal centres to favour five-coordination over six-coordination. Furthermore, the non-planarity of Me_4taa and other systems where $R^2 \neq$ H is believed to inhibit the types of intermolecular interactions in the solid state that give rise to the typically poor solubility of unsubstituted porphyrin and phthalocyanine complexes.

Two other important factors affect the degree of non-planarity of the macrocyclic ligands in their metal complexes. These are the radius and d-electron count (for transition elements) of the metal ion itself and, to a lesser extent, the number and type of any axial ligands. Hence even complexes of the parent taa ligand [Fig. 1(a)], which itself is planar in the solid state as H_2taa, can adopt a slightly saddle-shaped conformation depending on the identity of the metal and any ancilliary ligands present.

For a given type of dibenzotetraaza[14]annulene complex, the extent to which a metal atom is displaced from the N_4 plane depends primarily on the metal radius and ligand field stabilisation effects. For example, in the M^{III} complexes [M(Me_4taa)X] (M = Co, X = I; M = Fe, X = Cl) the Co and Fe atoms lie 0.234 and 0.600 Å from the N_4 plane respectively, reflecting the larger effective radius of high-spin (S = 5/2) Fe^{III}.[2] The structure of the iron complex is shown in Fig. 4(a) by way of example and demonstrates clearly the displacement of the Fe atom from the N_4 plane. Note that in [Co(Me_4taa)I] the metal atom is apparently small enough to lie in the N_4 plane and therefore it may be the inherent non-planarity of Me_4taa and concomitant redirection of the N atom lone pairs out of the plane that causes the 0.234 Å displacement in this case.

The remaining pair of structures in Fig. 4 illustrate the geometries found for six-coordinate Me_ntaa (n = 4 or 8) complexes. The two possibilities are cis-trigonal prismatic, as exemplified by [Zr(Me_4taa)Cl₂] [Fig. 4(b)],[4] and trans-octahedral as found for [Sn(Me_4taa)Cl₂] [Fig. 4(c)].[5a] Because of the relatively small hole size and typical saddle-shape of the Me_ntaa ligands, the cis-trigonal prism is the most commonly encountered of the two six-coordinate geometries. Note that in [Sn(Me_4taa)Cl₂] the Sn–Cl bond pointing 'down' (as drawn) is 0.068(2) Å longer than the other. This relative lengthening of the 'down' metal–ligand bond is a typical feature of trans-octahedral Me_ntaa derivatives.
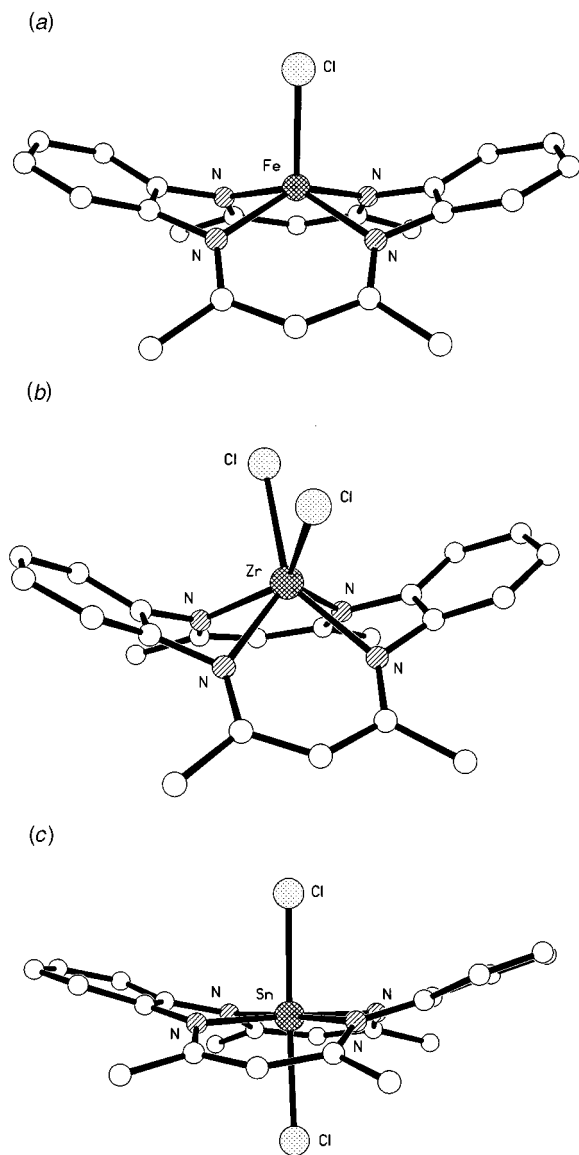
Fig. 4 Typical Me$_n$taa saddle-shaped conformations and metal coordination geometries. Solid state structures of (a) square base pyramidal [Fe-(Me$_4$taa)Cl],[2] (b) trigonal prismatic [Zr(Me$_4$taa)Cl$_2$],[4] and (c) octahedral [Sn(Me$_4$taa)Cl$_2$].[5a] Hydrogen atoms are omitted for clarity and the remaining atoms are drawn as spheres of arbitary radius.

2.3 Theoretical studies

A number of computational studies of dibenzotetraaza[14]annulene complexes have been carried out at various levels of sophistication (extended-Hückel, density functional, SCF-Xα-SW), and in some instances the results have been augmented by photoelectron spectroscopic data. The key conclusions from the various studies are summarised below and underline some of the general points made above.[2,6,7–10]

To simplify computational matters, it is possible to model the methyl and o-C$_6$H$_4$ groups of Me$_4$taa with H and cis-C$_2$H$_2$ respectively.[6,7] That o-C$_6$H$_4$ can be successfully substituted by cis-C$_2$H$_2$ emphasises the lack of conjugation between the 1,3-diiminato and o-phenylene fragments, which was confirmed by density functional calculations for the whole complex [Ni(taa)].[8] Furthermore, calculations for the free planar and non-planar dibenzotetraaza[14]annulene ligands,[9] and also for the metal complexes [Cu(taa)] (planar ligand) and [Cu(Me$_4$taa)] (saddle-shaped ligand),[8] found minimal electronic structure effects on the macrocycle donor orbitals, despite the quite different ligand conformations.

As expected, the dibenzotetraaza[14]annulene ligands carry a formal dinegative charge. This is localised mainly on the nitrogen atoms, but a significant negative charge is also found on the so-called γ-carbons [i.e. the ones bearing R^1 substituents in Fig. 1(a)].[9] In contrast, the iminato (–C=N) carbons carry a partial positive charge. This charge distribution gives rise to electrophilic (at the γ-carbons) and nucleophilic (at the iminato carbons) patterns of attack as described in Section 5 below. The ability of the iminato carbons to 'carry' some of the positive charge also, for example, contributes towards the reduced electrophilicity of the [Zr(Me$_4$taa)]$^{2+}$ fragment versus the apparently related [Zr(η-C$_5$H$_5$)$_2$]$^{2+}$.[6]

For the later transition metal complexes [M(dibenzotetraaza[14]annulene)] (M = Cu, Ni), metal–ligand π-bonding effects appear to be quite small, although it is thought that the ligands can act as modest π-acceptors. Calculations for the binuclear complex [Cr$_2$(Me$_4$taa)$_2$], however, suggest that there is sufficient π-donation from the macrocycle to disrupt the formation of a possible Cr–Cr δ bond.[10a] The dichromium complex thus possesses only a metal–metal triple bond, despite the eclipsed geometry found in the solid state. In contrast, the dimolybdenum congener [Mo$_2$(Me$_4$taa)$_2$] is proposed to have a full Mo–Mo quadruple bond because the more diffuse 4d orbitals of Mo overlap better with the orbitals of the neighbouring metal than with the π-donor orbitals of the Me$_4$taa.

2.4 Choice of dibenzotetraaza[14]annulene ligand

It is the R^2-methylated (i.e. Me$_n$taa-type) systems that have been most extensively studied. This is probably due to their unusual and interesting properties, ease of synthesis and generally better solubility. For example (at the time of writing), there are currently over 140 crystallographically characterised dibenzotetraaza[14]annulene ligands and/or their complexes on the Cambridge Crystallographic Database, but only about twenty of these have R^2 = H. The examples given throughout this article reflect the emphasis on the Me$_n$taa homologues, but refererence will be made to the taa-type systems as appropriate.

3 Preparative methods

3.1 Ligand syntheses

This section describes the general methods used to prepare dibenzotetraaza[14]annulenes. It has long been known that o-phenylene diamines and 1,3-dicarbonyl compounds (Scheme 1) undergo 1:1 condensation reactions to form 1,5-benzodiazepines. Therefore this type of direct approach is not suitable for the synthesis of macrocycles. However, reliable synthetic routes to the dibenzotetraaza[14]annulenes are now well-established and can be divided into two distinct categories depending on the kind of R^2 substituent required.[2,11–15]
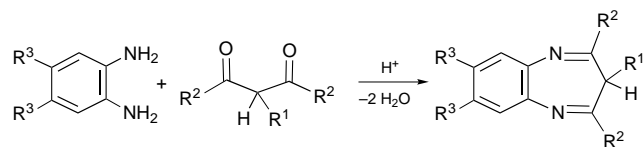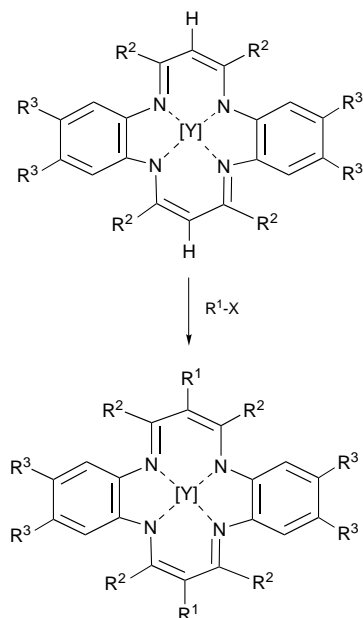

Scheme 1

For R^2 = H, non-template methods (Scheme 2) may be used, starting from o-phenylene diamines and either propynal or substituted acroleins as first reported by Hiller in 1968.[11] The acrolein method is useful for introducing R^1 = alkyl or aryl substituents into the γ-position. For dibenzotetraaza[14]annulenes where R^2 ≠ H, template methods (Scheme 3) are required. The template synthesis of tetramethyl dibenzotetraaza[14]annulene was first reported by Jäger in 1969 and subsequently developed by Goedken and others.[2,14,15] Typically Ni^{2+} (introduced as the tetrahydrate of the diacetate salt) is used as the templating ion in a reaction between an o-phenylene diamine and a 1,3-dicarbonyl species. The metal can then be stripped from the macrocycle using anhydrous hydrogen
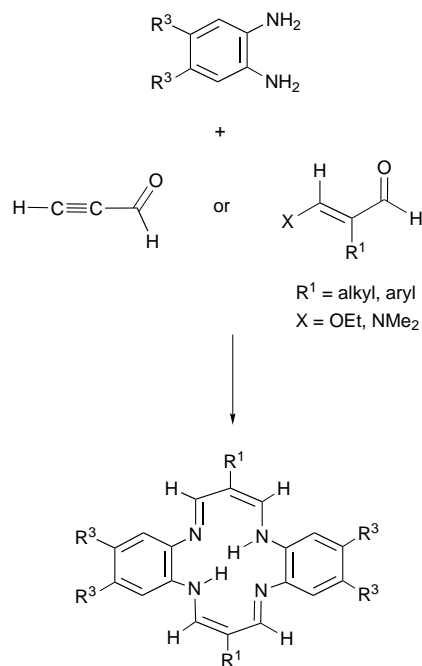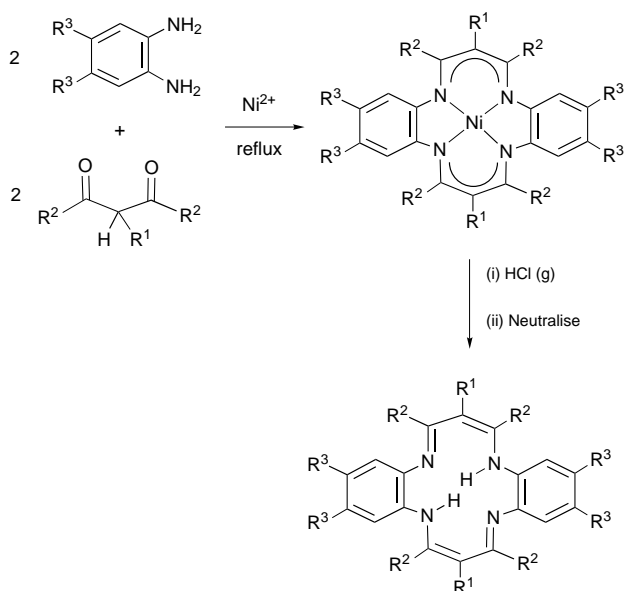
Scheme 2

$[Y]$ = Ni or $(H)_2$
R^1 = ArC(O)-, ArCH$_2$-, (NC)$_2$C=C(CO$_2$Et)-; X = Cl or Br
Scheme 4

Scheme 3

chloride to afford the desired macrocycle after a straightforward workup.

Once the macrocycle has been formed, further substitution of certain R^1 functional groups into one or (more usually) both of the γ-positions is possible, starting either from the neutral macrocycle itself or, more typically, from the metal complex (Scheme 4). The type of R^1 group that may be introduced this way appears to be restricted to benzyl and benzoyl functionalities, although these can contain quite elaborate substituents (such as crown ethers).[16]

3.2 Synthesis of metal complexes

There are two principal methods (*i.e.* template and non-template) for preparing metal complexes of dibenzotetraaza[14]annulenes. Scheme 5 shows some specific preparations by way of example. As already seen (Scheme 3), template syntheses for Ni^{2+} (in some instances also for Co^{2+} and Cu^{2+}) can be used to effect the direct cyclisation of *o*-phenylene

diamines with 1,3-dicarbonyl compounds. Furthermore, although metal ions are not essential for macrocycle formation from *o*-phenylene diamines with propynal or 3-substituted acroleins (Scheme 2), carrying out these reactions in the presence of Co^{2+}, Ni^{2+} or Cu^{2+} directly affords the corresponding M^{II} macrocyclic complexes [Scheme 5(*a*)].[12a,13]

The template syntheses described above are generally restricted to the later transition metals only. For other transition and main group metal derivatives, routes based on the reaction of the preformed neutral macrocycle itself or its dilithiated derivative are used. The dilithium species Li$_2$[Me$_n$taa] are themselves conveniently prepared by treating the neutral dibenzotetraaza[14]annulene with methyl- or *n*-butyl-lithium in a hydrocarbon solvent.[4] The dme (dme = 1,2-dimethoxy-ethane) adduct 'Li$_2$[Me$_4$taa]·1.5(dme)' has been crystallo-graphically characterised (see below) but the solid state structures of the non-solvated species are unknown.

The choice of using a neutral *versus* a dilithiated macrocycle generally depends on the metal substrate to be employed and the desired product. If, for example, metal alkyl or amide groups are to be substituted then using the neutral macrocycle will give simple alkane or amine by-products that are easily separated from the product complex [Scheme 5(*b*)]. On the other hand, if metal halide substrates are to be used then the dilithiated ligand may be the better choice [Scheme 5(*c*)] since use of a neutral macrocycle generally requires the addition of a tertiary amine base to take up the hydrogen halide that will be eliminated. Because lithium halide side products are often more easy to separate than alkylammonium halides, using the dilithiated ligand is generally more convenient. The best choice of reagent for other metal substrates (such as acetate or carbonyl complexes) is made according to similar considerations.

4 Unusual ligand conformations and coordination modes

Section 2.2 and Fig. 4 summarised the typical conformations and coordination modes found for dibenzotetraaza[14]annulene ligands. This having been established, it is appropriate now to consider some of the more interesting exceptions.

4.1 Ligand conformations

Dibenzotetraaza[14]annulene complexes with R^2 = H offer few surprises in this regard and are either planar or slightly saddle-shaped. The R^2 = Me derivatives, however, can show some

(b)

$\xrightarrow[-2\ RH]{0.5\ Al_2R_6}$

R = Me or Et

(c)

(Li$^+$)$_2$

$\xrightarrow[-2\ LiCl]{ZrCl_4(thf)_2}$
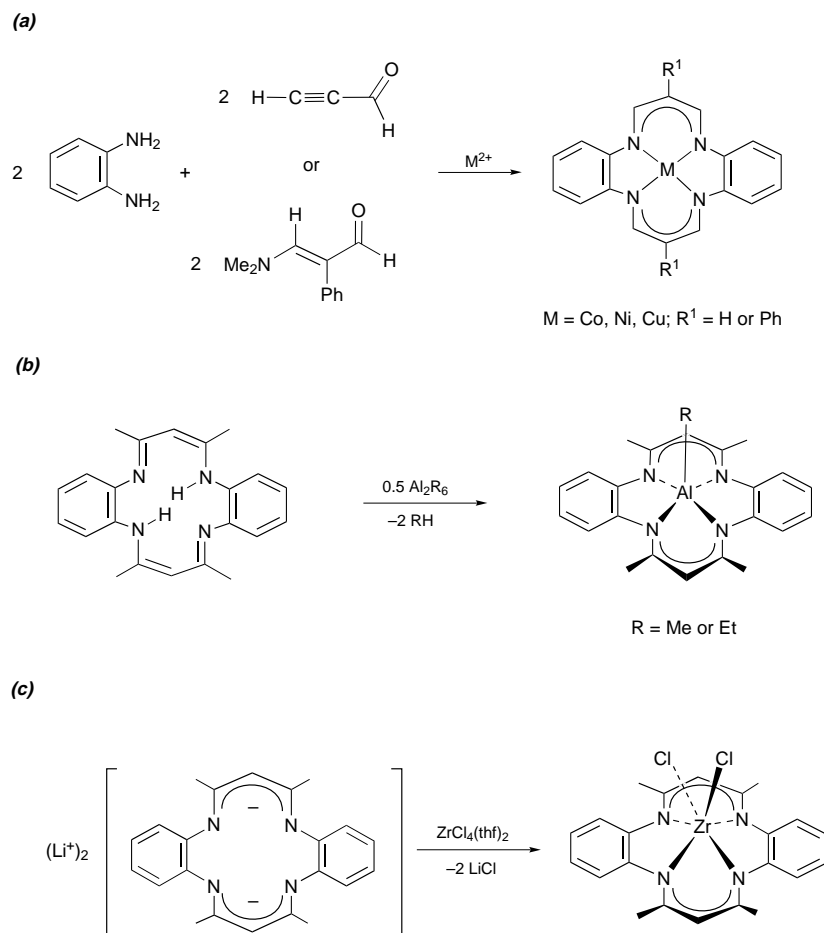
Scheme 5 Examples of the synthesis of dibenzotetraaza[14]annulene compexes using (*a*) template,[11–13] and (*b, c*) non-template methods.[4,21] See also Scheme 3.[14,15]

interesting and unusual conformations. As explained for the Me$_n$taa (n = 4 or 8) systems, the most typical conformation of the complexed ligand is analogous to that found in the solid state for the free H$_2$Me$_n$taa themselves—*i.e.* substantially non-planar with the *o*-phenylene rings tilted 'up' (*i.e.* towards the metal coordination site) and the 1,3-diiminato linkages oriented 'down' [see Figs. 3(*b*) and 4]. Fig. 5 shows three examples of Me$_n$taa ligands not adopting the conventional geometry.

In Fig. 5(*a*) the compound [Ge(Me$_8$taa)Te] has an inverted saddle-shaped ligand (*i.e.* with the *o*-phenylene rings 'down' and the 1,3-diiminato moieties 'up').[17a] Intriguingly, the homologous sulfido and selenido complexes both have Me$_8$taa ligands possessing the conventional configuration. In Fig. 5(*b*) and (*c*) the dibenzotetraaza[14]annulenes do not adopt any kind of saddle-shape at all, and in these two centrosymmetric complexes the ligands are best described as 'step-like'. In [Pd(Me$_4$taa)] [Fig. 5(*b*)] the 1,3-diiminato linkages are tilted in opposite directions.[18] The tilts are not very pronounced and therefore lead to a significant twist deformation of the *o*-phenylene rings in order to minimise steric interactions with the methyl groups. In the bis(triphenylphosphine)ruthenium example [Figs. 5(*c*)] it is the *o*-phenylene rings that are tilted in opposite directions and the 1,3-diiminato fragment now must undergo a twist deformation to avoid unfavourable steric interactions. The bis(methyldiphenylphosphine) homologue also exhibits similar features.[19] It may be the favourable ligand field stabilisation of the second row Pd^{II} (low spin d^8 favouring square planar coordination) and Ru^{II} (low spin d^6 favouring octahedral coordination) complexes that helps drive the unusual distortion of the ligands so as to obtain the most favourable metal coordination geometry.

4.2 Ligand coordination modes

So far we have encountered only mononuclear dibenzotetraaza[14]annulene metal complexes in which the macrocycle acts as a doubly deprotonated, dianionic, tetradentate ligand [Fig. 2(*a*)] to a single metal centre. Examples of this type of coordination are illustrated in Figs. 4 and 5. Although this is by far the most common situation found for the dibenzotetraaza[14]annulene complexes, other coordination modes and metal nuclearities are possible as illustrated by Fig. 6.

The complex [W(η^2-H$_2$Me$_4$taa)(CO)$_4$] [Fig. 6(*a*)], prepared from H$_2$Me$_4$taa and W(CO)$_6$, has the macrocycle acting as a neutral bidentate ligand.[2] Note that in this complex (and its Mo congener) the H$_2$Me$_4$taa exists as the unusual triimine, mono-eneamine tautomer [Fig. 2(*b*)] as opposed to the diimine, diamine form found in the free ligands [Fig. 1(*a*)]. A tetraimine H$_2$Me$_4$taa tautomer [Fig. 2(*c*)] has recently been structurally characterised for the neutral ligand in [Ni(H$_2$-Me$_4$taa)][AlCl$_4$]$_2$.[20]

The main group derivative [Ga(η^2-HMe$_4$taa)Me$_2$] [Fig. 6(*b*)] also has the macrocycle coordinated in a bidentate fashion, but in this instance it acts as a monoanionic ligand with a single N–H group remaining [Fig. 2(*d*)].[21] This coordination mode has also been found in [Mo(η^2-HMe$_4$taa)(O)$_2$(acac)],[22a] and a bridging, monoanionic bis-bidentate HMe$_4$taa was recently reported for a diruthenium complex.[22b] The third example [Fig. 6(*c*)] shows a dianionic Me$_4$taa ligand bridging a Mo–Mo quadruple bond in a bis-bidentate, coordination mode that was first reported by Goedken for the dirhodium species [Rh$_2$-(Me$_4$taa)(CO)$_4$].[2] The final example [Fig. 6(*d*)] shows the lithium ion local coordination geometry at one 'end' of the interesting tetralithium species [(dme)Li(μ-Me$_4$taa)Li(μ-dme)-

Li(μ-Me$_4$taa)Li(dme)] ('Li$_2$[Me$_4$taa]·1.5dme').[4] In this complex, each dianionic Me$_4$taa macrocycle acts as a bis-tetradentate ligand to a pair of Li$^+$ ions located either side of the N$_4$ plane. The remainder of the lithium coordination sphere is comprised of oxygen donors from the dme ligands.

5 Reactivity of the dibenzotetraaza[14]annulene ligands

The majority of the reaction chemistry of dibenzotetraaza[14]annulene complexes concerns changes at the metal centre with the macrocycle acting only as a supporting ligand (see the following Sections). As already seen in Scheme 4, however, reaction of certain complexes with benzyl or benzoyl halides can lead to facile R^1 group substitution into the macrocycle at the γ-positions. Indeed, as Scheme 6 illustrates, this is the most common site for reactions occurring at the ligand itself, and

(a)

(b)

(c)
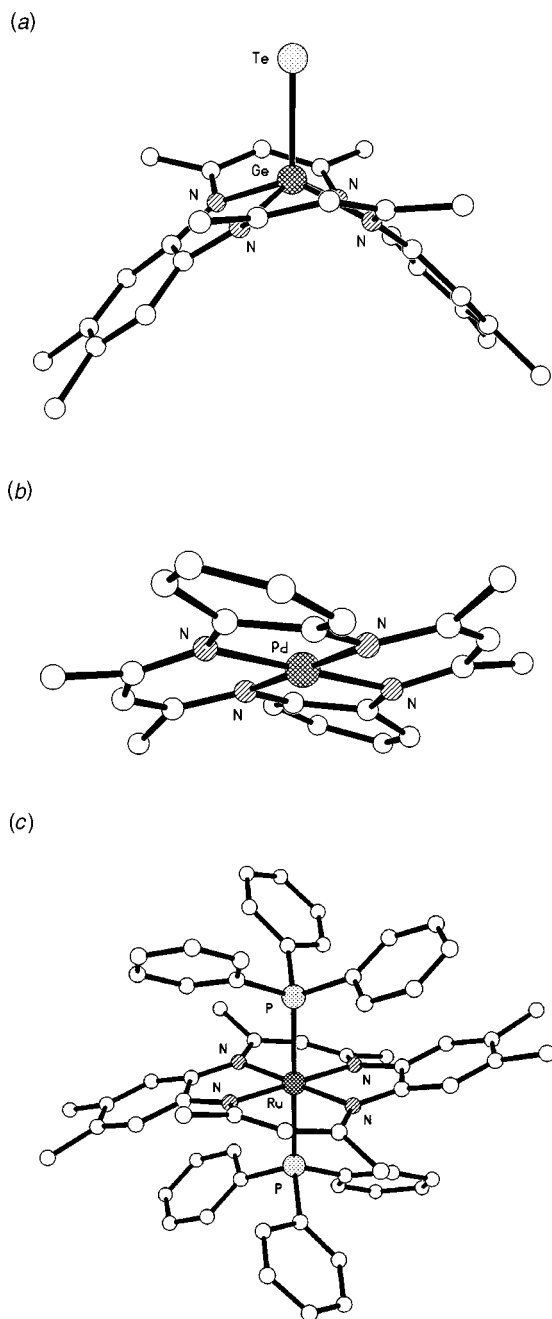
Fig. 5 Unusual dibenzotetraaza[14]annulene ligand conformations. Solid state structures of (a) [Ge(Me$_4$taa)Te],[17a] (b) [Pd(Me$_4$taa)],[18] and (c) [Ru(Me$_8$taa)(PPh$_3$)$_2$].[19] Hydrogen atoms are omitted for clarity and the remaining atoms are drawn as spheres of arbitary radius.
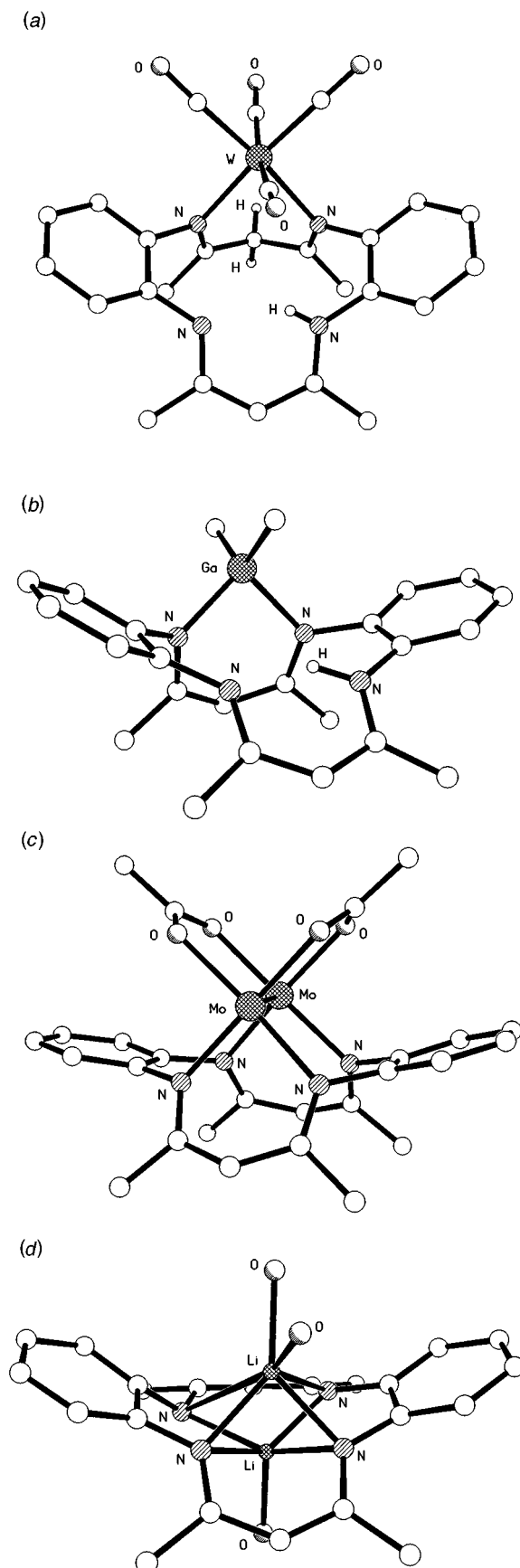
(a)

(b)

(c)

(d)

Fig. 6 Unusual dibenzotetraaza[14]annulene coordination modes. Solid state structures of (a) [W(η^2-H$_2$Me$_4$taa)(CO)$_4$],[2] (b) [Ga(η^2- HMe$_4$taa)-Me$_2$],[21] (c) [Mo$_2$(Me$_4$taa)$_2$(OAc)$_2$],[2] and (d) the lithium local coordination geometry for one 'end' of [(dme)Li(μ-Me$_4$taa)Li(μ-dme)Li(μ-Me$_4$taa)-Li(dme)].[4] Most hydrogen atoms are omitted for clarity and the remaining atoms are drawn as spheres of arbitary radius.

(a)

(b)

(c)

R = Me or CH₂Ph
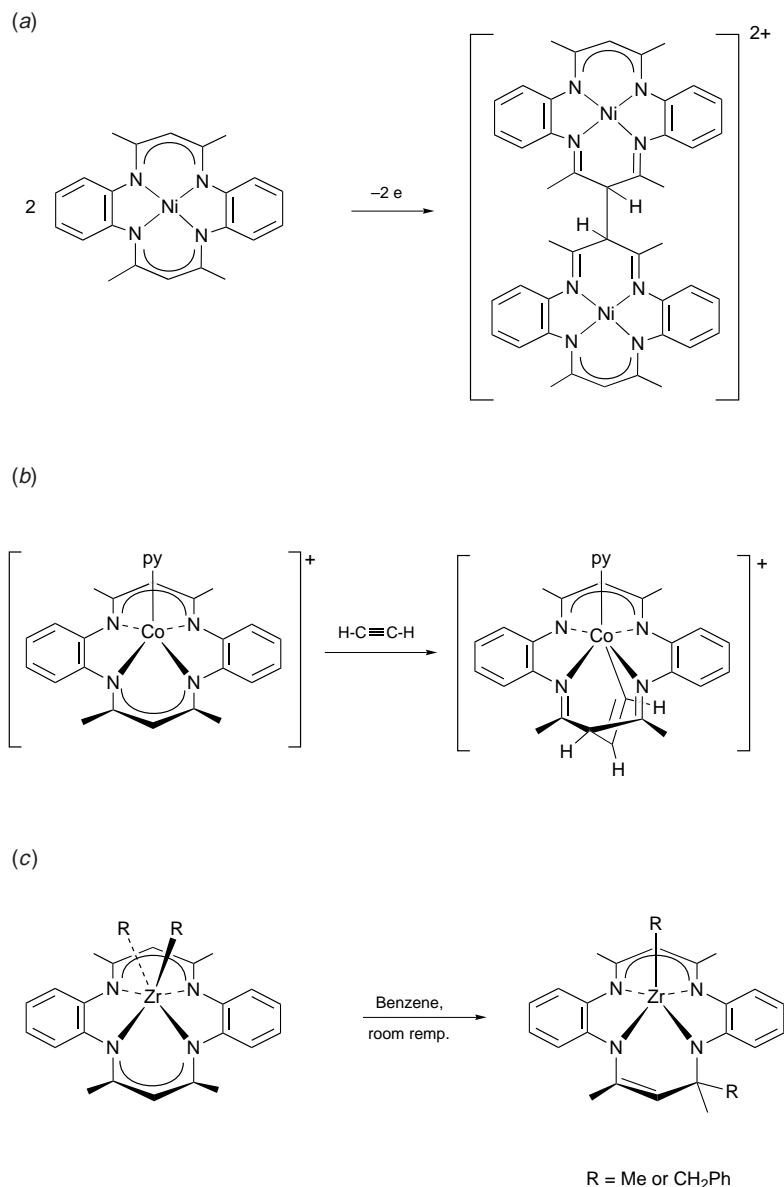
Scheme 6 Reactions involving coordinated dibenzotetraaza[14]annulene ligands.[6,23,24]

reflects the activated character of the γ-carbon in complexed dibenzotetraaza[14]annulenes.

Thus Scheme 6(a) shows that electrochemical or chemical oxidation of [Ni(Me₄taa)] does not give a stable radical cation, and instead a dimeric compound containing two macrocyclic moieties linked by a new carbon–carbon bond is formed.[23a] This dication is easily deprotonated at the bridging C–H groups to form the corresponding neutral species. Similar oxidative couplings are found for Cu and Co complexes of Me₄taa. Indeed, electroactive, surface-modified electrodes (featuring polymers of C–C linked metal macrocycles) may be prepared by the oxidative electropolymerisation of [Ni(Me₄taa)] and its *o*-phenylene ring-substituted homologues.[23b] The C–C linking process is readily inhibited, however, by the presence of R¹ ≠ H substituents in the γ-positions of the Me₄taa ligand. In this case a stable ligand-centred radical cation is formed as is typical for unsaturated nitrogen-based macrocycles.

Certain Co and Rh complexes of Me₄taa undergo C–C bond forming reactions with alkynes, nitriles and strained cyclic alkenes (see also Section 7) at the γ-position to form new penta-coordinating macrocycles.[2,24] Scheme 6(b) shows the reaction between [Co(Me₄taa)(py)]⁺ and ethyne. Hoffmann has suggested that it is the negative charge build up (see Section 2.3) at the γ-position that is responsible for the formation of this 1,4-cycloadduct.[9] The cationic, bidentate macrocycle complexes [M(η²-HMe₄taa)(CO)₃(NO)]⁺ (M = Mo or W) also undergo C–C bond formation at the γ-position.[2] Thus reaction with MeCN gives rise to a new tri-coordinate ligand which may be viewed as a monoprotonated relative of those formed in the cobalt systems above.

All the above examples involve reaction at the γ-position. However, high oxidation state, early transition metal alkyl complexes such as [Zr(Me₄taa)R₂] (R = Me, CH₂Ph) can undergo intramolecular migratory nucleophilic attack at an iminato carbon atom.[6] This reaction [Scheme 6(c)] forms a new trianionic macrocyclic ligand and is thought to be promoted by the high oxidation state metal centre generating an unfavourably large positive charge at the iminato carbon (see Section 2.3). Lower oxidation state metal [*e.g.* Tiᴵᴵᴵᴵᴵᴵᴵᴵᴵᴵᴵᴵᴵᴵ and Vᴵᴵᴵ] alkyl complexes of Me₄taa are, however, stable to this type of migration, possibly as a consequence of the reduced positive charge at the iminato carbon atom.[25]

6 Recent highlights in main group chemistry

In contrast to the wealth of transition metal chemistry of the dibenzotetraaza[14]annulenes (see also Section 7 below), there are still relatively few p-block metal compounds known, and
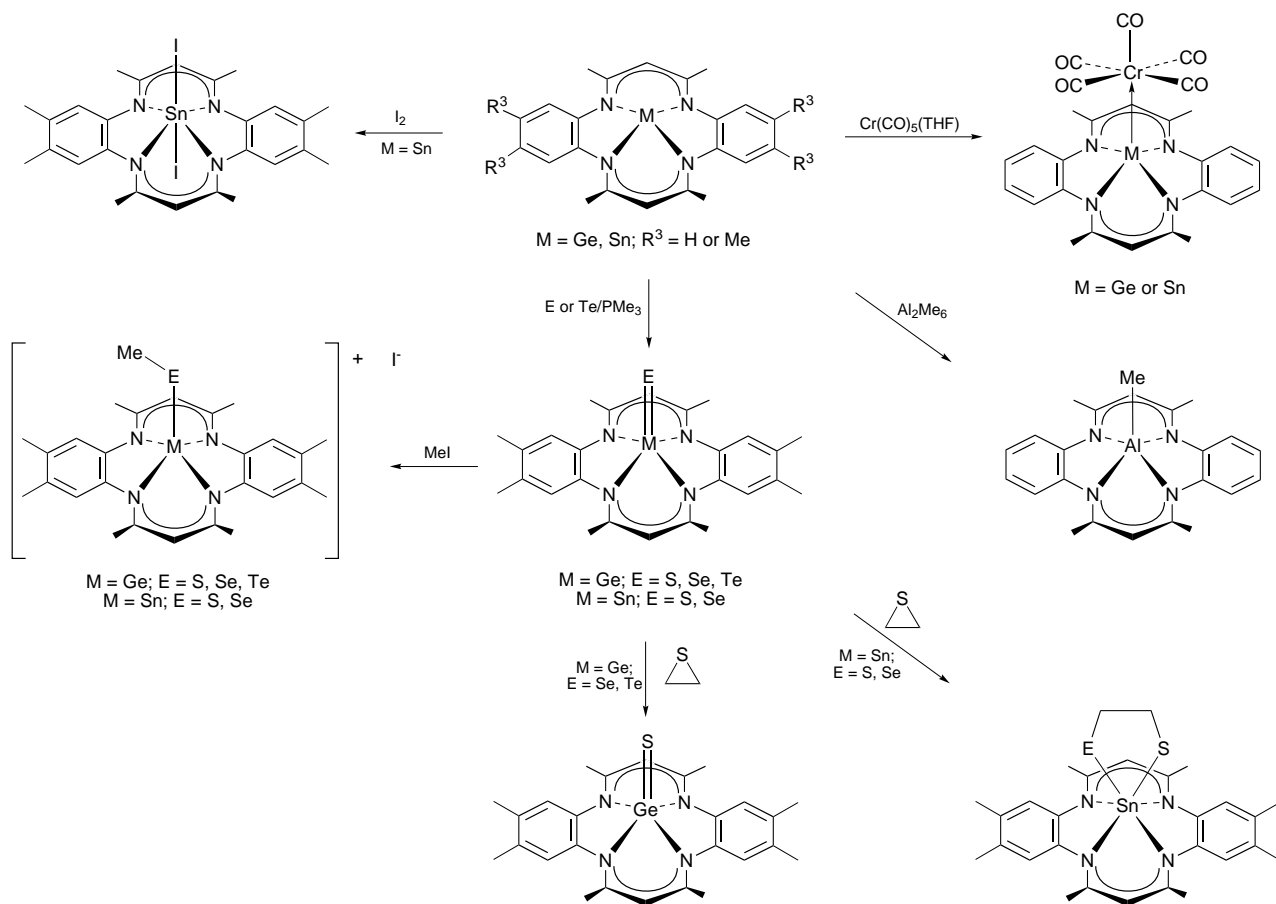
Scheme 7 Reactions of [M(Me$_n$taa)] (n = 4 or 8; M = Ge or Sn).[5,17]
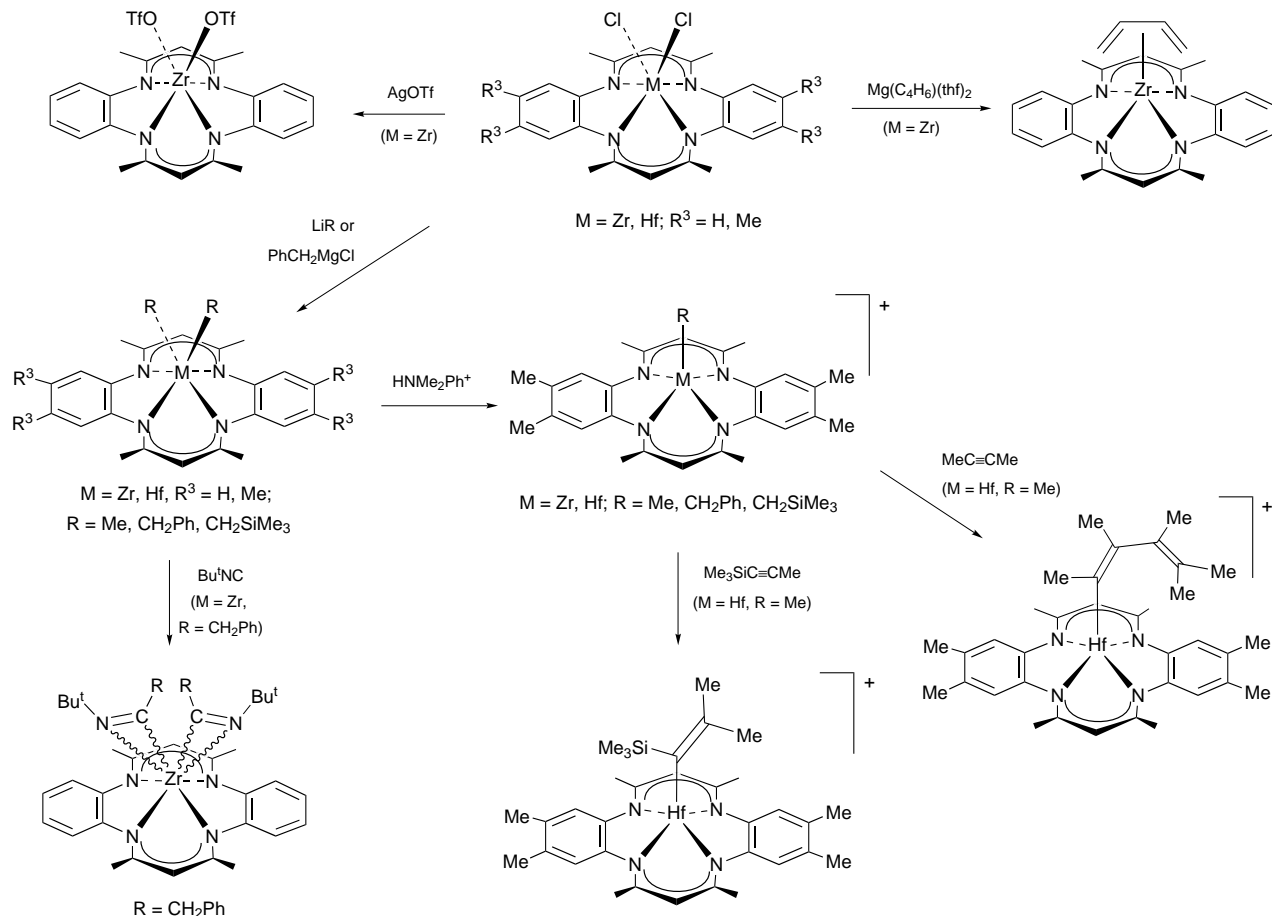
Scheme 8 Selected group 4 organometallic and related chemistry.[4,6,25,27–29] See also Scheme 6(*c*).[6]

only two well-defined examples of s-block derivatives exist. The first structurally characterised main group derivative, namely [Al(Me₄taa)Et], was reported by Goedken and coworkers in 1984.[21] The remainder of this Section gives key examples of the main group chemistry of dibenzotetraaza[14]annulenes. To date, only Me_ntaa (n = 4 or 8) systems have been reported.

For the electropositive metals Li, Mg, Al and Ga, macrocyclic complexes are easily formed from the neutral H_2Me_ntaa and the appropriate metal alkyl species as discussed in Section 3.2 for $Li_2[Me_4taa]$, and illustrated in Scheme 5(b) for the synthesis of [Al(Me₄taa)R] (R = Me, Et). Similarly, reaction of [Mg(CH₂Ph)₂] with H_2Me_4taa in thf affords the crystallographically characterised [Mg(Me₄taa)(thf)] which has the usual saddle-shaped macrocycle with the Mg displaced from the N_4 plane.[26]

The synthesis of [M(Me$_n$taa)R] (M = Al, Ga; R = Me or Et) proceeds via a surprisingly stable bis(alkyl) complex [M(HMe$_n$-taa)R₂] which has been structurally characterised for M = Ga, n = 4, R = Me [Fig. 6(b)].[21] Certain complexes [M(HMe₄-taa)R₂] only eliminate alkane on heating to above 100 °C (M = Al, R = Et) or 200 °C (M = Ga, R = Me) in the solid state. However, reaction of H_2Me_4taa with Al_2Me_6 at −78 °C gives [Al(Me₄taa)Me] directly in 95% yield. Dialkyl derivatives [M(Me₄taa)Me₂] (M = Si or Sn) are also known but are prepared from $Li_2[Me_4taa]$ and the corresponding MCl_2Me_2.[5b] Crystal structures for these complexes have not been reported but they are proposed to possess cis-dimethyl geometries.

Metal halide and nitrate derivatives [M(Me$_n$taa)(X)$_m$] (for M = Ga or In, m = 1; for M = Si, Ge or Sn, m = 2, n = 4 or 8; X = F, Cl, Br, I or NO₃) have been prepared and structurally

(a)

(b)

characterised.[5] The syntheses are generally via reaction of the appropriate metal halide with $Li_2[Me_4taa]$ or H_2Me_4taa in the presence of NEt₃ (but see also Scheme 7). The X-ray structures of [Sn(Me₄taa)Cl₂] [Fig. 4(c)] and [Sn(Me₈taa)I₂] reveal octahedrally coordinated Sn atoms with halide ligands in mutually trans positions.[5a]

Main group derivatives with no additional ancilliary ligands exhibit interesting chemistry (Scheme 7). Thus reaction of $Li_2[Me_n$taa] with GeCl₂·dioxane affords the crystallographically characterised [Ge(Me$_n$taa)] {n = 4 [Fig. 7(a)] or 8 [Scheme 7]}. Similar procedures gave the Sn and Pb congeners.[17] The complexes [M(Me$_n$taa)] (M = Ge, Sn, Pb) are very reactive towards electrophiles but, as would be expected, show different behaviour depending on the identity of M. Thus reaction with [Cr(CO)₅(thf)] gave the unusual bimetallic complexes [(Me₄-taa)MCr(CO₅)] for M = Sn or Ge [X-ray structure shown in Fig. 7(b)]. However, with [Pb(Me₄taa)] a facile transmetallation reaction occurred to give [Cr(Me₄taa)(CO)₃] and 'PbO'. All three [M(Me₄taa)] (M = Ge, Sn, Pb) complexes undergo transmetallation reactions with Al_2Me_6 to form [Al(Me₄-taa)Me] and unknown group 14 alkyl side products.

The divalent complexes [M(Me$_n$taa)] (M = Ge, Sn) undergo oxidative addition reactions with certain alkyl halides, halogens and elemental chalcogens (Scheme 7).[17a] Of particular interest are the metal–ligand multiply-bonded derivatives [Ge(Me₈taa)-E] (E = Se, Te) which were the first such terminal mono-selenido or -tellurido complexes of Ge. Comparative reactivity studies of the [M(Me₈taa)E] (M = Ge, E = S, Se, Te; M = Sn, E = S, Se) systems have highlighted interesting similarities and differences in the reactivities of the terminal chalcogenido linkages as a function of the group 14 element. X-Ray diffraction analysis of the Ge and Sn complexes revealed significant metal–chalcogen multiple bond character described as a combination of $M^+–E^-$, $M^-=E^+$ and $M^-≡E^+$ resonance structures.
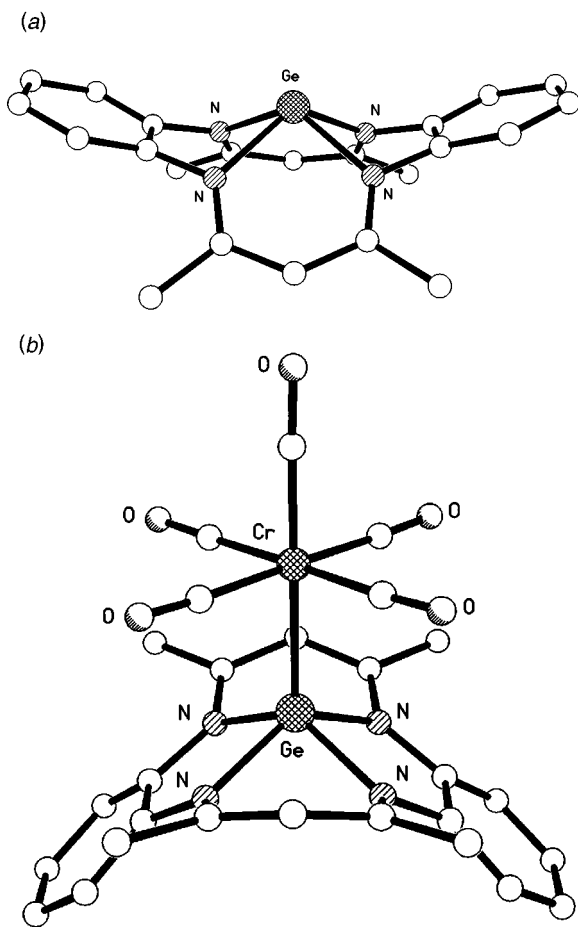
7 Recent highlights in transition metal chemistry

The chemistry of transition metal complexes of dibenzotetraaza[14]annulenes spans nearly thirty years and comprises the majority of research activity for these ligands. It is not possible to give a detailed account of this chemistry here. Cotton and Czuchajowska's general overview of transition metal–Me₄taa complexes appeared in 1990 and is currently the principal cited reference for this area. Readers should consult this review for a more detailed account of mono- and bi-nuclear transition metal Me₄taa complexes up to that time.[2] Sections 2 to 5 of this *Chem. Soc. Rev.* provided a general overview of the types of transition metal complex that may be formed and also described some recent examples. This current section will highlight current developments in the chemistry and new directions of research being pursued using dibenzotetraaza[14]annulene ligands.

The Me_ntaa dianionic tetraazamacrocycles have received much recent attention as potential alternatives to the ubiquitous bis(η-cyclopentadienyl) ligand set. The attraction of the Me_ntaa ligands in this regard is derived in part from the typical cis-disposition of the ancilliary X-ligands in complexes of the type [M(Me$_n$taa)(X)₂] (X = halide, hydrocarbyl or related; M = group 4 or 5 metal). This is also the situation found for [M(η-C₅R₅)₂(X)₂] and is known to be an essential characteristic of alkene polymerisation catalysts.

The organometallic and coordination chemistry of early transition metal Me_ntaa complexes has been extensively developed by the groups of Floriani and Jordan in particular.[4,6,25,27–29] Scheme 8 shows examples of the synthesis and reactivity of group 4 Me_ntaa-supported group inorganic and organometallic complexes. As shown in [Scheme 6(c)] [Zr-(Me₄taa)(R)₂] (R = Me or CH₂Ph) are unstable to thermally-induced intramolecular migration of an R-group to one of the iminato carbon atoms. Cationic, d^0 complexes of the type [M(Me₈taa)(R)]⁺ (prepared using routes previously developed
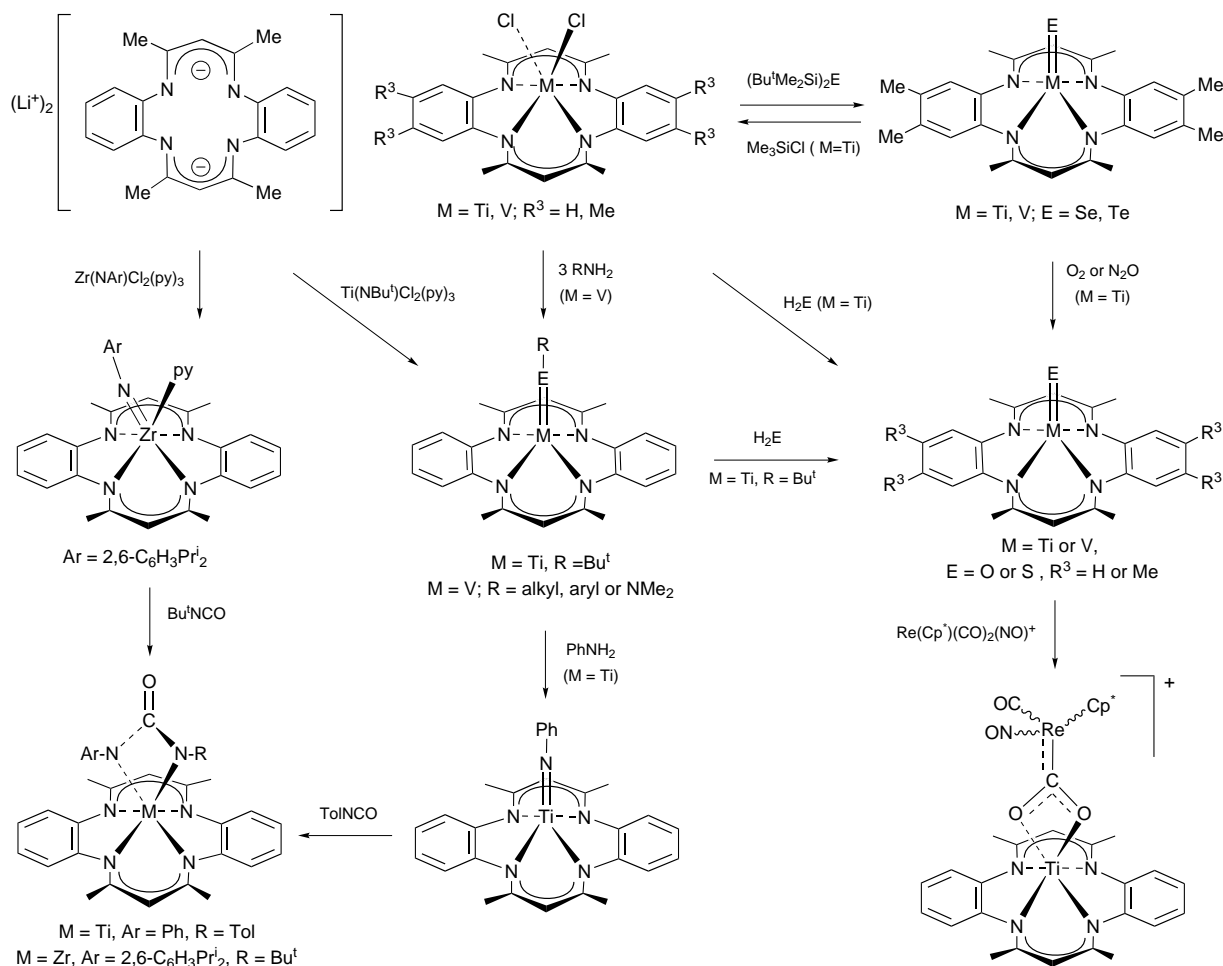
Scheme 9 Synthesis and selected reactions of early transition metal–ligand multiply-bonded complexes.[2,22a,30–33]

for metallocene systems) and these undergo C–H bond activation and insertion reactions.[27] However, the [Zr(Me8-taa)(η^2-CH2Ph)][B(C6F5)4] system (either with or without added Al(Bu$^i_3$) cocatalyst) exhibits only low ethene polymerisation activity compared to that of the corresponding [Zr(η-C5H5)2Me2]/[HNMe2Ph][B(C6F5)4] system which is about 100 times more active under identical conditions. In a similar vein, the [M(Me8taa)(R)]$^+$ systems are less reactive for alkyne insertion than are [M(η-C5H5)2R2]$^+$ species.

The M–R and M–NMe2 bonds in the complexes [M(Me8-taa)(X)2] (X = alkyl or NMe2) are highly polarised as indicated by their reaction with CH2Cl2 to yield [M(Me8taa)Cl2] and RH or CH2(NMe2)2 respectively, and by the reaction of [Zr(Me8taa)(NMe2)2] with Al2Me6 to yield the interesting Zr/Al binuclear complex [Zr(Me8taa)(μ-NMe2)2AlMe2][AlMe4].[27] This enhanced nucleophilicity of the Me8taa-supported systems (with respect to that of the metallocene analogues) apparently reflects the harder character of the macrocyclic ligands.

In accordance with the above, Floriani and coworkers have shown that the bis(triflate) complexes [Zr(Me4taa)(OTf)2] (Tf = CF3SO2) act as homogenous Lewis acid catalysts, and the best results were obtained for the Mukaiyama aldol reaction and metal-assisted allylations.[28] It was proposed that the bis(triflate) complexes mask the active mono- or di-cationic forms [Zr-(Me4taa)(OTf)]$^+$ or [Zr(Me4taa)]$^{2+}$ respectively which are thought to be generated in solution because of the typically labile nature of the triflate ligand.

Dibenzotetraaza[14]annulenes have also provided a suitable environment for the study of early transition metal–chalcogenido and –imido multiple bonds (Scheme 9).[2,22a30–33] The oxo and sulfido complexes [M(Me4taa)(E)] (M = Ti or V; E = O or

S) were first reported in the early 1980s by Goedken and Ladd.[2] However, the chemistry of these complexes was not developed until ten years later. Furthermore, the first group 4 and 5 terminal imido, hydrazido, selenido and tellurido Me$_n$taa derivatives have only very recently been described. As with the metal–ligand multiply-bonded main group complexes [M(Me8-taa)(E)] discussed in Section 6, these macrocyclic ligands allow the isolation and study of comparatively reactive unsaturated linkages. In particular, the metal–ligand multiple bond in the oxo and imido complexes [Ti(Me4taa)(E)] (E = O, NBu^t or NAr) have a well-established reaction chemistry at the Ti = E functional group including cycloaddition reactions.

In the area of bioinorganic chemistry, dibenzotetraaza[14]annulene complexes of the middle to late transition metals have continued to be studied as models for the active sites of certain naturally-occurring enzymes. The complex [Co(Me4taa)] has been studied by Moore and coworkers because of the resemblance of the macrocyclic ligand to the corrin ring of vitamin B12 coenzyme.[24] In a reaction reminiscent of that shown in Scheme 6(b), addition of the strained alkene, norbornene, to [Co(Me4taa)] followed by air oxidation afforded a cationic complex in which the C=C bond of norbornene had added across the Co and one of the Me4taa γ-carbon atoms. The crystallographically characterised product contains a pendant alkyl–cobalt bond and may be viewed as a new model compound for vitamin B12 coenzyme. An analogous reaction occurs between [Rh2(Me4taa)2] and norbornene.

Other biomimetic systems have also been reported recently. The reductive dehalogenation of alkyl halides by Na[BH4] or Na[BH(OMe)3] to yield alkane is efficiently catalysed by [Ni(Me4taa)].[34] This system is considered to be a mimic of

factor F$_{430}$, the active centre of methyl coenzyme M reductase. Manganese(III) complexes of peripherally-substituted dibenzo-tetraaza[14]annulenes are effective catalysts for the oxidation of certain nitroso compounds to the nitro derivatives, and in this respect may be considered mimics of the function of the cytochrome P-450 enzymes.[16a]

In another area of activity, electrochemical studies of middle to late transition metal dibenzotetraaza[14]annulene complexes can lead to the synthesis of new materials.[23,35] Modification of the ring substituents can affect the redox properties of the complexes and influence their tendency to form dimeric or polymeric systems *via* ring-coupling reactions (see Section 5). Further electrochemical studies of mono- and bi-nuclear dibenzotetraaza[14]annulene complexes have recently been reported. Electrochemically-generated copolymers of [Ni-(Me$_4$taa)] and pyrrole have been prepared from solutions containing carefully-controlled amounts of the two mono-mers.

8 Concluding remarks

In this brief overview it has been shown that dibenzotetra-aza[14]annulenes are the organometallic and coordination chemist's flexible friends. These ligands are tunable, easily prepared and readily introduced. They provide a reliable and generally robust framework that continues to allow new main group and transition metal chemistry to flourish.

9 Acknowledgements

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