

# Anionic triazacyclononanes: new supporting ligands in main group and transition metal organometallic chemistry

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In the course of developing new ligands to support chemistry with main-group, transition and lanthanide elements, a number of research groups have focused attention on functionalized triazacyclononanes; this article provides a summary of the more recent findings with an emphasis on the organometallic chemistry of one particular class of tacn ligands, namely those involving the anionic tacn moiety.

## Introduction

The quest for new ligands capable of supporting novel structures and reactivity in p-, d- and f-element metal complexes has attracted considerable attention over the last two decades. Research groups from around the world have explored a wide range of novel ligand frameworks and a number of important

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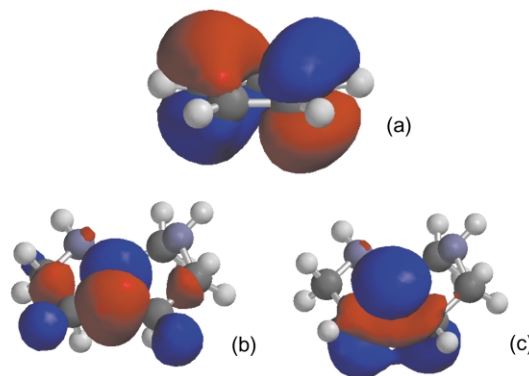
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new classes have been developed. Cyclopentadienyl ligands, and substituted derivatives thereof, dominate the literature;<sup>1</sup> nevertheless, considerable attention has been paid to alternative, non-Cp ligands over the past decade.<sup>2</sup> Most of this latter work has been conducted with anionic species that incorporate O- or N-donor ligands and a great deal of novel and useful chemistry has emerged as a result.

Despite the popularity of neutral R<sub>3</sub>tacn ligands for middle to late transition metals, there are very few related species known for the early metals or lanthanides.<sup>3–5</sup> This is surprising as, in its *fac*, tridentate binding mode, the tacn moiety is isoelectronic (6e<sup>-</sup>) with Cp<sup>-</sup>. We reasoned that changing the donor properties of the tacn fragment to make it an anionic, rather than a neutral ligand would render it much more amenable to coordination to hard, electropositive metals. Most work in this area has involved use of <sup>1</sup>Pr<sub>2</sub>tacnH, a result that is easily attributed to (a) its relative ease of synthesis (see below); (b) the favorable solubility properties of its complexes; and (c) its versatility with regard to further substitution.

In its deprotonated, anionic form, <sup>1</sup>Pr<sub>2</sub>tacn<sup>-</sup> has provided a wide range of complexes in which it acts as a stable 6e<sup>-</sup> tridentate donor. The latter behavior allows an analogy to be drawn between the coordinating ability of [<sup>1</sup>Pr<sub>2</sub>tacn]<sup>-</sup> and Cp<sup>-</sup>, although, as shown by frontier orbital considerations (see respective HOMOs in Fig. 1(a)–(c)), the relationship is tenuous.



**Fig. 1** (a) One of the two degenerate HOMOs of the Cp anion (b) and (c) the HOMO and HOMO–1 of the Me<sub>2</sub>tacn anion.

Thus, whereas Cp<sup>-</sup> is an excellent  $\pi$ -ligand, the <sup>1</sup>Pr<sub>2</sub>tacn<sup>-</sup> anion is expected to exhibit only a diminished  $\pi$ -donor capability resulting from the lone pair of electrons in a p orbital on the amido nitrogen; this is the HOMO shown in Fig. 1(b). A good deal of attention has been paid to whether or not this lone pair of electrons participates in bonding to transition metals. If it did, it may be more accurate to consider the tacn<sup>-</sup> ligand an eight-electron donor.

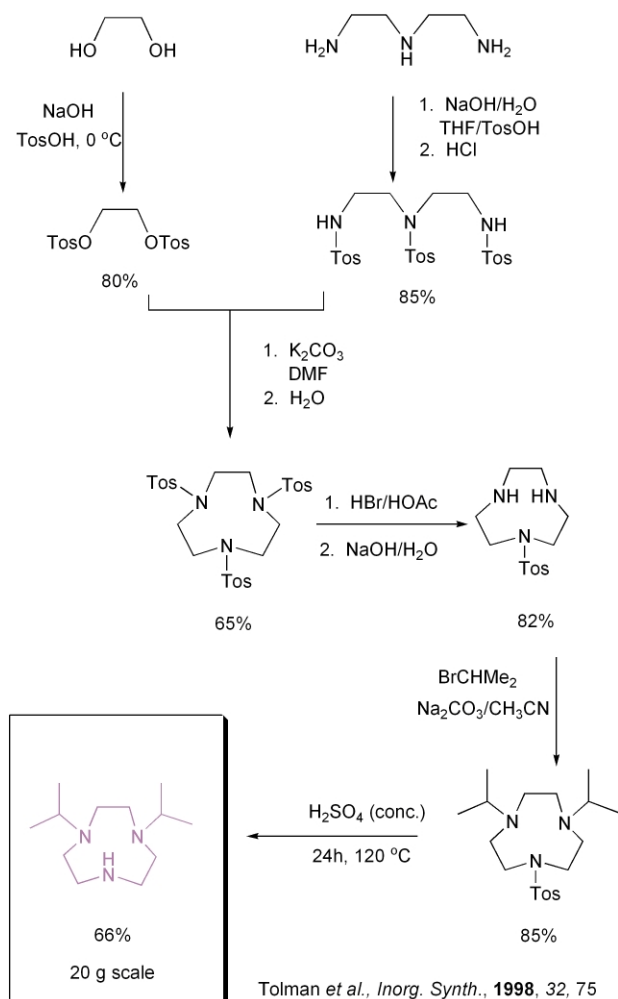
In addition, we have found that <sup>1</sup>Pr<sub>2</sub>tacn<sup>-</sup> displays hemilabile behavior in some transition metal complexes, *i.e.*, the ligand

binds in a monodentate fashion analogous to a simple four-electron amido ligand. The ability of hemilabile ligands to modulate reactivity in stoichiometric and catalytic systems is a topic of considerable interest.<sup>6</sup>

The focus of this short review is to give a brief overview of the chemistry of anionic tacn ligands, paying particular attention to the structure and reactivity of their metal complexes.

## Ligand syntheses

Fortunately, there are well-developed syntheses to the more important tacn ligands. The compounds are therefore available in useful amounts at reasonable costs. As an example, the preparation of one of the more important tacn derivatives used in much of the chemistry described in this article, <sup>i</sup>Pr<sub>2</sub>tacnH, which was developed by Tolman and coworkers,<sup>7,8</sup> is shown in Scheme 1.

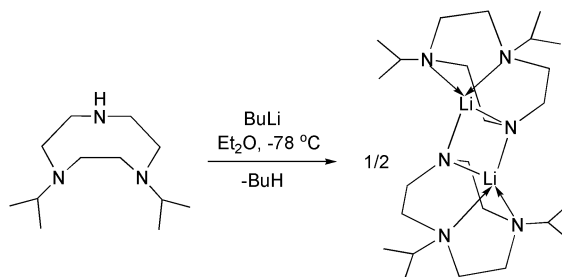


Scheme 1

We routinely prepare <sup>i</sup>Pr<sub>2</sub>tacnH on a 20 g-scale using this methodology. Using related chemistry, Me<sub>2</sub>tacnH can also be generated on useful scales.<sup>9</sup> Both are distillable liquids that can be obtained in very high purity. To date, in addition to the chemistry described here, the main synthetic uses of these compounds have been directed towards the preparation of pendant arm derivatives. A number of these have been used to form complexes with a range of metals, with the tacn moiety being employed as either a neutral or anionic ligand.<sup>10–18</sup>

## Main group chemistry

A number of main group derivatives of [R<sub>2</sub>tacn]<sup>–</sup> anions have been isolated and characterized. In 2000, three groups independently described the synthesis and characterization of the lithium salt of [<sup>i</sup>Pr<sub>2</sub>tacn]<sup>–</sup>.<sup>5,15,19</sup> The complex is obtained in high yield by a simple deprotonation with <sup>n</sup>BuLi in diethyl ether and the complex may be crystallized directly from the reaction solvent (Scheme 2).



Scheme 2

The molecule has been crystallographically characterized by two groups.<sup>15,19</sup> In the solid state, the compound exists as a dimer in which each lithium center is pseudo-tetrahedral, ligated by three nitrogens of a single triazacyclononane ligand, and the amide nitrogen of a second tacn ring (Fig. 2). The unit

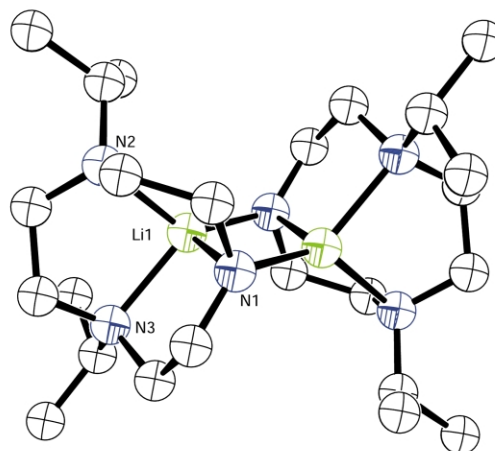


Fig. 2 ORTEP view of the structure of the dimer [(<sup>i</sup>Pr<sub>2</sub>tacn)Li]<sub>2</sub>.

cell contains two independent molecules in which each dimer sits on a crystallographic inversion center; thus each dimer contains a symmetric Li<sub>2</sub>N<sub>2</sub> core. The lithium centers exhibit two longer (2.097(6) and 2.101(6) Å) and two shorter (1.961(6) and 2.049(7) Å) Li–N bonds consistent with two metal–amine bonds and the two bridging metal–amide bonds of the Li<sub>2</sub>N<sub>2</sub> unit. The compound is a useful synthon for delivery of the [<sup>i</sup>Pr<sub>2</sub>tacn]<sup>–</sup> anion to other metals, as discussed below.

The synthesis of the related dimethyl species [Me<sub>2</sub>tacn]Li was reported by Mountford and coworkers.<sup>5</sup> A recent structure determination shows<sup>20</sup> that this complex crystallizes in trimeric form in the solid state, as shown in Fig. 3.

Again, each Li is bonded to two amino nitrogens and one amido nitrogen of the tacn macrocycle, although in this case, the smaller methyl substituents permit a more open, higher nuclearity structure than in the <sup>i</sup>Pr derivative. The six-membered Li<sub>3</sub>N<sub>3</sub> ring is very close to planar with N–Li–N angles in the range 135.3–137.3°. The Li–N bond distances (2.006 Å mean) are typical for lithium amides and, as expected, are shorter than the Li–N<sub>amine</sub> distances (2.163 Å mean).

Attempts to carry out a related deprotonation reaction using AlMe<sub>3</sub> led only to the stable adduct shown in Scheme 3.<sup>21</sup> This

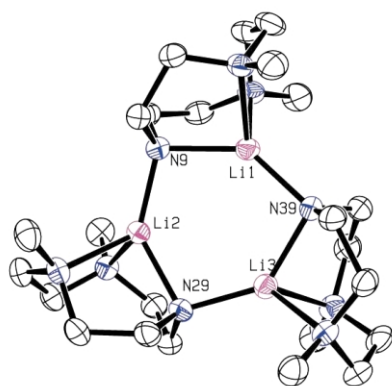
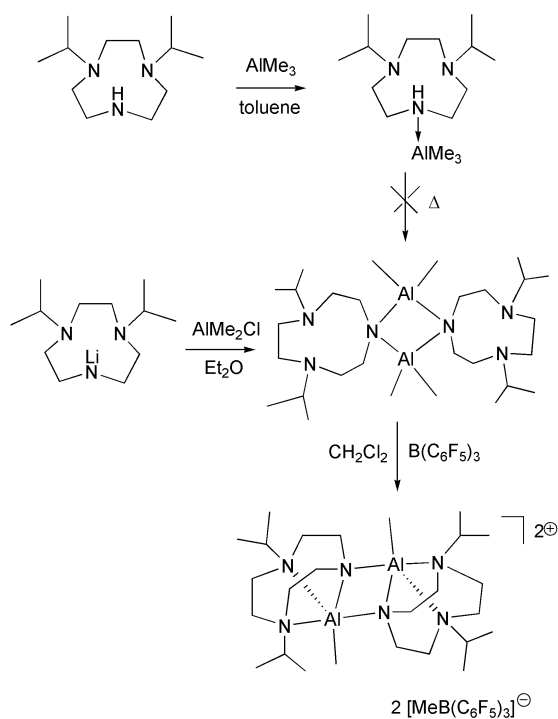


Fig. 3 ORTEP view of the structure of the trimer  $[(\text{Me}_2\text{tacn})\text{Li}]_3$ .



Scheme 3

compound is stable in refluxing toluene and no conditions were found under which it eliminates methane. The desired dimethylaluminum complex was instead isolated in moderate yield *via* metathesis between  $\text{AlMe}_2\text{Cl}$  and  $[\text{Pr}_2\text{tacn}]\text{Li}$ . The structure of the resulting dimeric product is shown in Fig. 4. As summarized

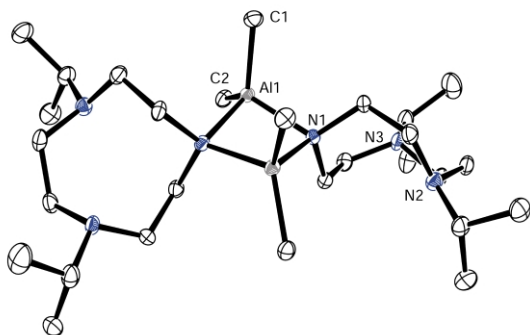


Fig. 4 ORTEP view of the structure of  $[(\text{Pr}_2\text{tacn})\text{AlMe}_2]_2$ .

in Scheme 3, reaction of the latter species with tris(pentafluorophenyl)borane leads to methide abstraction and formation of the dicationic aluminum alkyl shown in Fig. 5.

The two aluminium atoms are bridged by the amide N atom of the tacn ligand while the other N atoms are all coordinated to

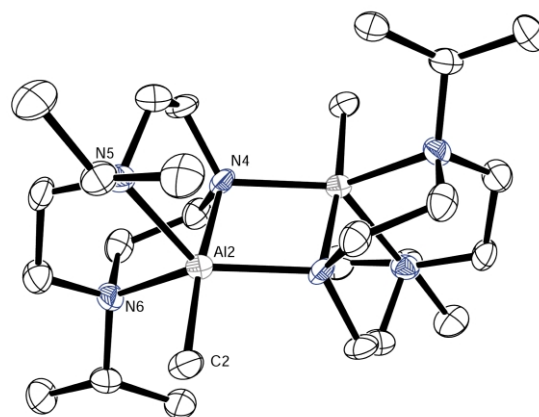
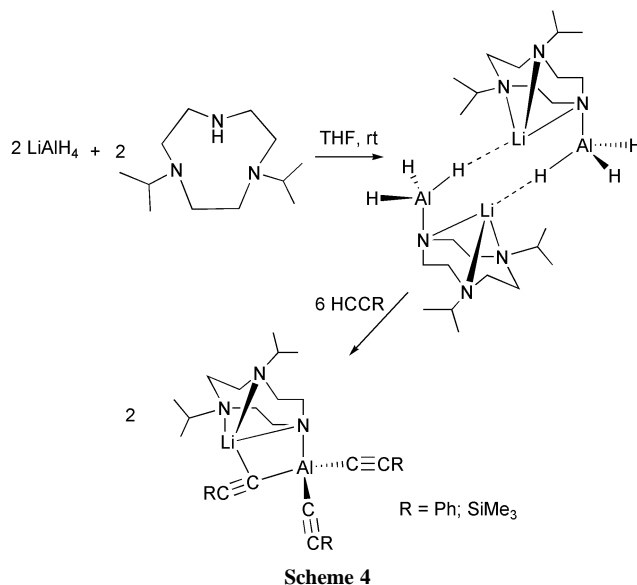


Fig. 5 ORTEP view of the structure of the dication  $[(\text{Pr}_2\text{tacn})\text{AlMe}]_2^{2+}$ .

the aluminium atoms forming a five-coordinate aluminium center. Despite its dicationic nature, the Al–C (2.00(1) and 1.978(8) Å) and Al–N (amide) (1.978(6) and 1.992(7) Å) bond lengths in the complex are slightly longer than those found in the neutral precursor; the higher coordination number at aluminium in the dicationic complex is presumably responsible for this effect.

The  $\text{Pr}_2\text{tacn}$  ligand also serves to stabilize aluminohydride and alkynyl species as shown in Scheme 4.<sup>22</sup> The aluminium



Scheme 4

atom in the aluminohydride is coordinated to the amido nitrogen atom of the tacn-ligand, and three hydride ligands, one of which bridges to a lithium atom (Fig. 6). Addition of terminal

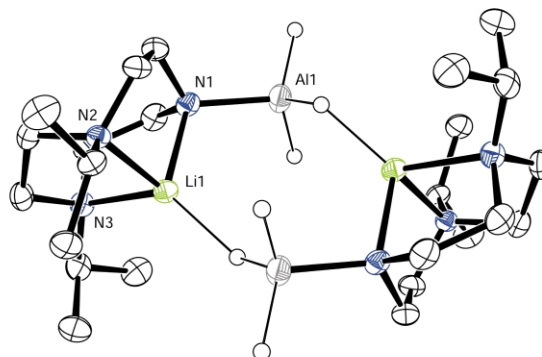


Fig. 6 ORTEP view of the structure of  $[\text{Li}(\text{Pr}_2\text{tacn})\text{AlH}_3]_2$ .

acetylenes ( $\text{HCCPh}$  or  $\text{HCCSiMe}_3$ ) at room temperature leads to the elimination of  $\text{H}_2$  and the formation of trialkynylalumi-

nates. The compounds are monomeric in the solid state, with a four-coordinate aluminium atom bound to two terminal acetylides, one novel bridging acetylide group, and the tacn amido nitrogen (see Fig. 7).

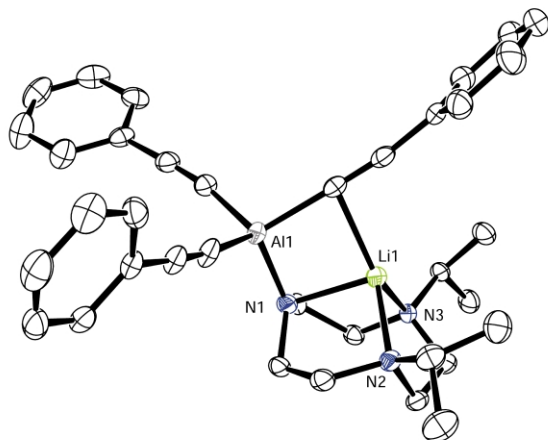


Fig. 7 ORTEP view of the structure of  $\text{Li}(\text{iPr}_2\text{tacn})\text{AlCCPh}_3$ .

The Al1–C1 bond length (1.981(3) Å) is slightly longer than the Al–C (terminal) distances (average 1.949 Å). The Al1–C1–C2 (178.1(2)°) angle is nearly linear, whereas the angles between the aluminium atom and the two terminal acetylides (174.1(2) and 169.2(2)°) deviate slightly from linearity. The Li1–C1 distance (2.230(5) Å) is only slightly longer than those found in  $(\text{iBuCCLi})_4(\text{THF})_4$  (2.19 Å). The Li1–C2 distance (2.718 Å) is long, inferring only weak electrostatic interaction between the lithium atom and the acetylide  $\pi$  electrons.

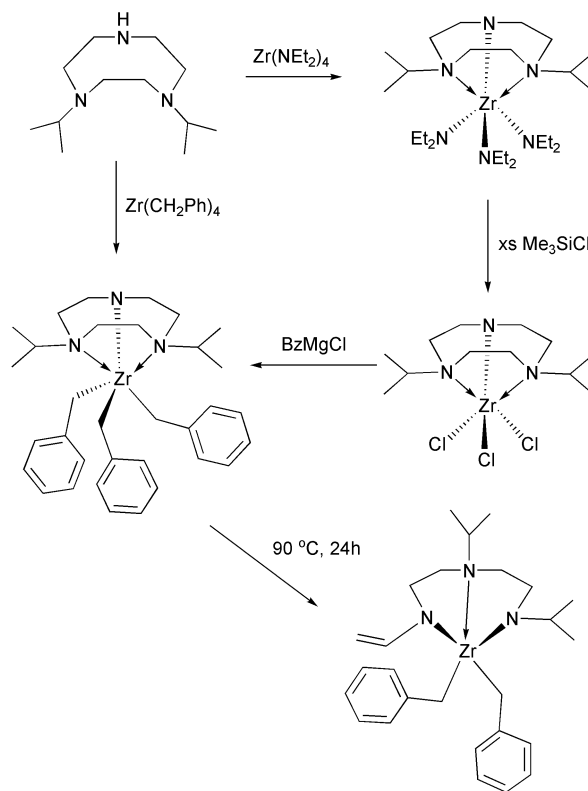
## Transition metal chemistry

Thus far, most reports of transition metal complexes involving anionic tacn ligands have been limited to early transition metals, although it is important to note that the first example of this class was a rhenium bis(amido) complex formed by deprotonation of  $\text{tacnH}_3$ .<sup>23</sup> In both cases, the aim has been to compare the coordination chemistry of  $[\text{iPr}_2\text{tacn}]^-$  with well-studied Cp and Cp\* analogs. As shown in Scheme 5, the mono-ligand trichloride complex was isolated as a yellow solid in ca. 90% overall yield by reaction of  $\text{iPr}_2\text{tacnH}$  with  $\text{Zr}(\text{NEt}_2)_4$ . Treatment with an excess of  $\text{Me}_3\text{SiCl}$  in hot toluene cleanly afforded the trichloride in pure form. The compound may also be made more directly, but in lower yield, from  $\text{iPr}_2\text{tacnLi}$  and  $\text{ZrCl}_4(\text{THF})_2$  in THF.<sup>24</sup>

As shown in Fig. 8,  $(\text{iPr}_2\text{tacn})\text{ZrCl}_3$  is monomeric in the solid state with a facially-bound tacn moiety that produces a piano-stool structure related to that found for mono-Cp zirconium trichlorides. The Zr–Cl bond *trans* to the amide of the tacn ligand is slightly longer than the two remaining Zr–Cl bonds (Zr1–Cl1 2.480(2) Å, Zr1–Cl2 2.451(2) Å, Zr1–Cl3 2.432(2) Å), but similar to those found in monocyclopentadienyl zirconium systems. The monomeric nature of the complex is in marked contrast to  $\text{CpZrCl}_3$ , which is polymeric in the solid state, or even the Cp\* analogue, which is dimeric.

The free ligand ( $\text{iPr}_2\text{tacn})\text{H}$  reacts with  $\text{Zr}(\text{CH}_2\text{Ph})_4$  in diethyl ether to form the tribenzyl species  $(\text{iPr}_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$  in good yield. The compound was also prepared from the trichloride and three equiv. of benzyl Grignard, albeit less cleanly. As expected, the complex is monomeric in the solid-state (see Fig. 9) with the tacn facially coordinated to the metal through all three nitrogens.

Two of the benzyl groups possess normal Zr–C–C bond angles (113.7(2) and 116.3(2)°) while the third displays an angle that is larger than usual (Zr1–C15–C16 133.5(2)°). The disposition of the benzyl groups is similar to that found for



Scheme 5

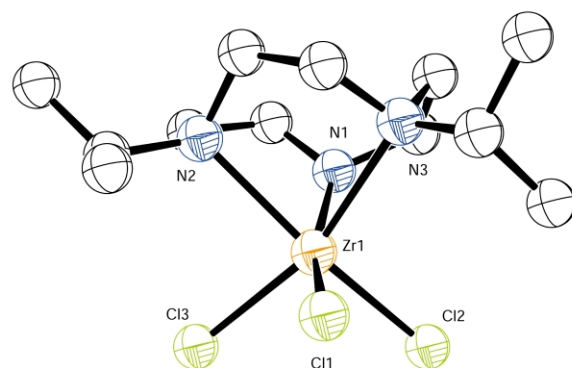


Fig. 8 ORTEP view of the structure of  $(\text{iPr}_2\text{tacn})\text{ZrCl}_3$ .

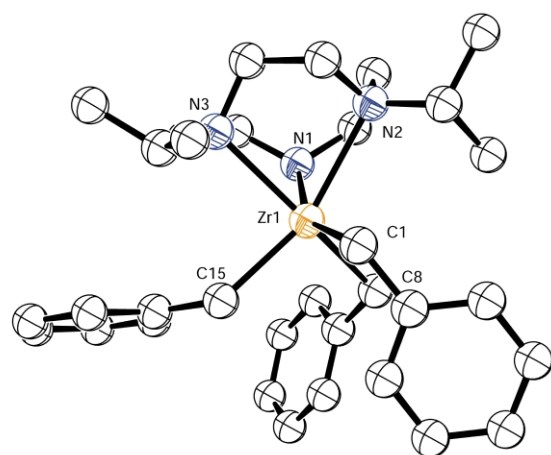


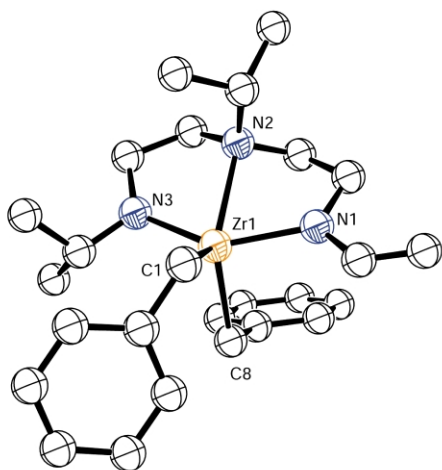
Fig. 9 ORTEP view of the structure of  $(\text{iPr}_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$ .

$\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3$ , in which a single anomalous Ti–C–C angle is believed to be due to an agostic  $\text{CH}_2\text{--Ti}$  interaction. Broadness of the benzylic methylene groups in the  $\{^1\text{H}\}^{13}\text{C}$  NMR



spectrum of the tacn derivative made resolution of the C–H coupling constant impossible; in this case, therefore, the cause of the distortion cannot be determined with certainty and crystal packing forces cannot be ruled out.<sup>25</sup>

Thermolysis of the tribenzyl resulted in elimination of one equiv. of toluene and complete conversion to a new complex. The presence of four isopropyl methyl doublets and separate multiplets for each of the methylene protons of the ligand backbone by <sup>1</sup>H NMR spectroscopy indicated a highly unsymmetrical molecule in solution. Along with <sup>13</sup>C NMR and IR data, it was determined that the tacn backbone had been cleaved at one of the C–N bonds to form an imido ligand and a new vinyl group. This was confirmed in the solid-state using X-ray diffraction, as shown in Fig. 10.

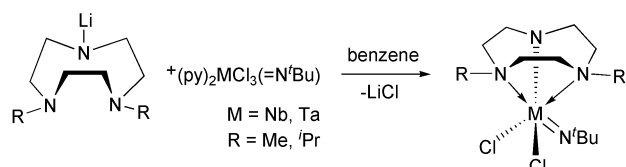


**Fig. 10** ORTEP view of the structure of  $[\text{CH}_2=\text{CHNCH}_2\text{CH}_2\text{N}(\text{iPr})\text{CH}_2\text{CH}_2\text{N}^i\text{Pr}]\text{Zr}(\text{CH}_2\text{Ph})_2$ .

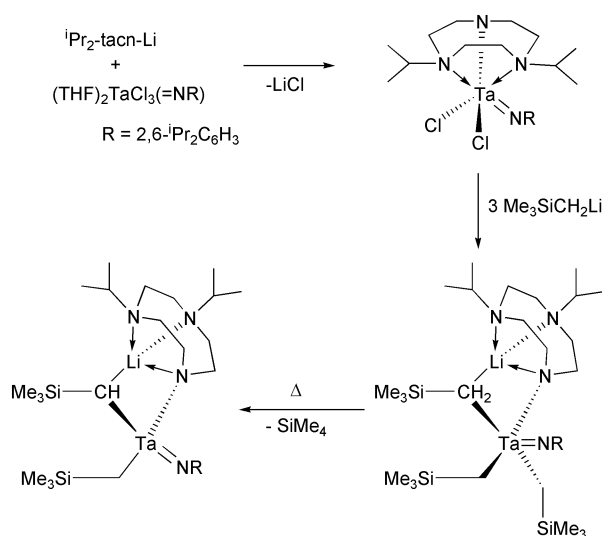
In this molecule, the zirconium center is coordinated by two benzyl groups and a new tacn-derived pincer ligand in which the original anionic, macrocyclic, diamino-amido ligand has been transformed into a dianionic, acyclic, diamido-amino moiety incorporating a pendant vinyl group (C15–C16). The zirconium center is distorted trigonal bipyramidal, with N1 and N3 occupying the axial sites. Both amido nitrogens display trigonal planar geometries and short zirconium–nitrogen amido interactions (Zr1–N1 2.131(5) Å, Zr1–N3 2.043(5) Å) relative to the longer Zr1–N2 (amino) bond (2.410(5) Å). The elimination reaction appears to be general: (<sup>i</sup>Pr<sub>2</sub>tacn)ZrCl<sub>3</sub> reacted with three equiv. of RLi (R = Me, CH<sub>2</sub>SiMe<sub>3</sub> or Ph) to form the respective  $[\text{CH}_2=\text{CHNCH}_2\text{CH}_2\text{N}(\text{iPr})\text{CH}_2\text{CH}_2\text{N}^i\text{Pr}]\text{ZrR}_2$ , with elimination of the corresponding alkane, in each case. A mechanism involving a benzyldiene intermediate formed by  $\alpha$ -hydrogen abstraction was ruled out on the basis of a thermolysis experiment using the deuterated complex (<sup>i</sup>Pr<sub>2</sub>tacn)Zr(CD<sub>2</sub>C<sub>6</sub>D<sub>5</sub>)<sub>3</sub>, which afforded only C<sub>7</sub>D<sub>7</sub>H.

A series of tantalum and niobium complexes incorporating R<sub>2</sub>tacn<sup>−</sup> and imido ligands has been reported that provides a system that is comparable, electronically, to the metallocene dichloride species of group 4. (Imido and Cp<sup>−</sup> ligands are isolobal; both are 1 $\sigma$ , 2 $\pi$  donors.) Mountford and coworkers were the first to report both tantalum and niobium complexes of the general type (R<sub>2</sub>tacn)MCl<sub>2</sub>(N<sup>i</sup>Bu) (R=Me, <sup>i</sup>Pr) which were prepared in benzene as shown in Scheme 6.<sup>5</sup>

Using related methodology, a close analog was prepared independently.<sup>26,27</sup> Treatment of (THF)<sub>2</sub>TaCl<sub>3</sub>(=NAr) [Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] with <sup>i</sup>Pr<sub>2</sub>tacnLi gave (<sup>i</sup>Pr<sub>2</sub>tacn)TaCl<sub>2</sub>(=NAr) in moderate yield as a yellow, crystalline solid (Scheme 7). The reactivity of this complex has been extensively investigated for comparison to the Zr tacn complexes described above and to group 4 metallocene chemistry. Spectroscopic investigations, using a combination of <sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C-DEPT and <sup>13</sup>C-<sup>1</sup>H HMQC

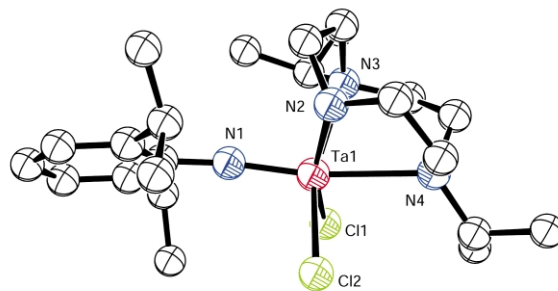


**Scheme 6**



**Scheme 7**

NMR, led to the assignment of a pseudo-octahedral coordination geometry with the tridentate <sup>i</sup>Pr<sub>2</sub>tacn ligand coordinated facially and the imido ligand oriented *trans* to an amino donor from the <sup>i</sup>Pr<sub>2</sub>tacn. This geometry is consistent with what might be expected on the basis of electronic considerations where, due to the *trans* effect of the  $\pi$ -donor imido ligand, one would expect the relatively weakly  $\sigma$ -donating amino ligand to be oriented *trans* to the latter. The solid-state structure (Fig. 11)

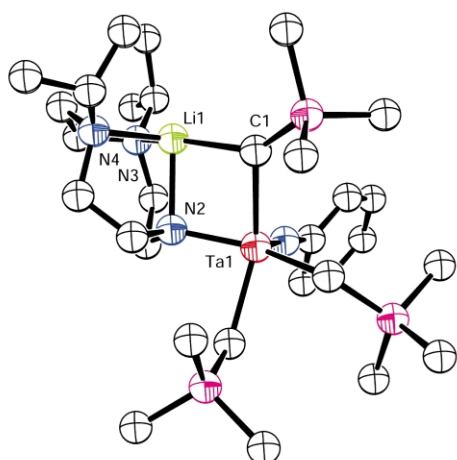


**Fig. 11** ORTEP view of the structure of (<sup>i</sup>Pr<sub>2</sub>tacn)TaCl<sub>2</sub>[N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)].

confirms the above interpretation. At 1.783(3) Å, the Ta–N(imido) bond length falls well within the range observed previously for terminal Ar–N=Ta species. Notably, the Ta–N(amino) bond *trans* to the imido group (2.512(4) Å) is elongated in comparison to the *cis* amino bond (2.403(3) Å).

Unlike the simple alkylation observed in complexes with cyclopentadienyl ligands, alkylation of the latter species using Me<sub>3</sub>SiCH<sub>2</sub>Li invariably results in the consumption of not two, but three equivalents of the Li salt to generate (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>(ArN=)Ta( $\mu$ -CH<sub>2</sub>SiMe<sub>3</sub>)( $\mu$ - $\eta$ <sub>1</sub>: $\eta$ <sub>3</sub>-<sup>i</sup>Pr<sub>2</sub>tacn)Li as small yellow crystals from diethyl ether. The compound is fluxional in solution at room temperature, giving a <sup>1</sup>H NMR spectrum consistent with a time-averaged mirror plane in the <sup>i</sup>Pr<sub>2</sub>tacn ligand. Cooling to as low as −84 °C led only to broad peaks for the methyl groups, rather than resolution of the chemically inequivalent protons.

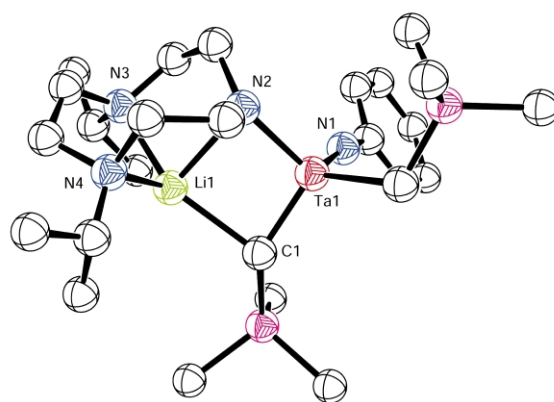
The X-ray structure of this compound (Fig. 12), shows a  ${}^i\text{Pr}_2\text{tacn}$  ligand bound in a *monodentate* fashion to the tantalum



**Fig. 12** ORTEP view of the structure of  $(\text{Me}_3\text{SiCH}_2)_2[\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(\mu\text{-CH}_2\text{SiMe}_3)(^i\text{Pr}_2\text{tacn})\text{Li}$  (phenyl  ${}^i\text{Pr}$  groups omitted for clarity).

via the anionic nitrogen atom and tridentate to the lithium ion. Additionally, a carbon atom from a  $\text{Me}_3\text{SiCH}_2$  anion bridges between the lithium and tantalum ions, a rare bonding mode in tantalum chemistry.<sup>28</sup> Finishing out the coordination sphere of the tantalum are two alkyl ligands and the aryl imido group. The tantalum is in a pseudo-square pyramidal environment with the imido group occupying the axial coordination site and the tantalum atom located 0.6 Å above the basal square plane. The  $\text{Ta}=\text{NR}$  bond length (1.723(7) Å) is the shortest observed crystallographically for a tantalum bound aryl imido. The  $\text{Ta}-\text{C}_{\text{br}}$  bond length (2.320(7) Å) is substantially longer than the  $\text{Ta}-\text{C}_{\text{term}}$  bonds (2.15(1) and 2.24(1) Å) which are well within the usual range of bond lengths (2.03–2.29 Å).

In contrast to the Zr alkyl species described above, the Ta complex undergoes  $\alpha$ -hydrogen abstraction upon gentle heating, resulting in the clean formation of a new alkylidene complex *via* elimination of  $\text{SiMe}_4$ . The crystal structure, shown in Fig. 13, shows a geometry very similar to the trialkyl precursor, with a pseudo-tetrahedral tantalum coordinated by the anionic nitrogen from  ${}^i\text{Pr}_2\text{tacn}$ , one imido ligand, one alkyl group, and the carbon from a bridging alkylidene moiety. The

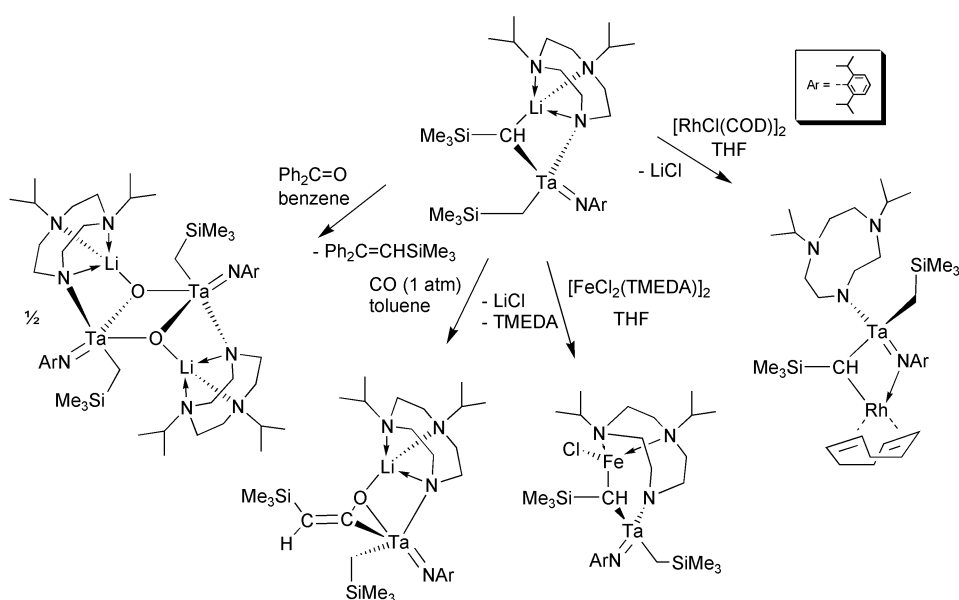


**Fig. 13** ORTEP view of the structure of  $(\text{Me}_3\text{SiCH}_2)[\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(\mu\text{-CHSiMe}_3)(^i\text{Pr}_2\text{tacn})\text{Li}$  (phenyl  ${}^i\text{Pr}$  groups omitted for clarity).

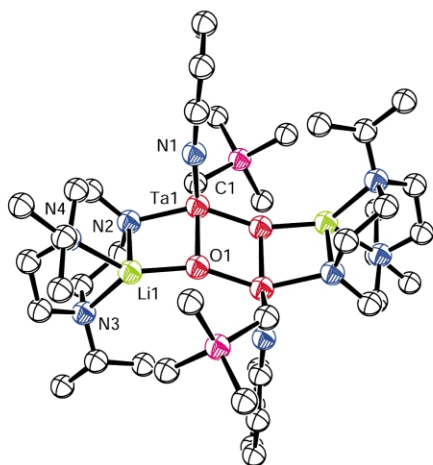
$\text{Ta}-\text{N}(\text{imido})$  and  $\text{Ta}-\text{C}_{\text{term}}$  bond lengths are essentially unchanged whereas the  $\text{Ta}-\text{N}(\text{amido})$  bond (2.05(3) Å) is lengthened slightly. The  $\text{Ta}-\text{C}_{\text{br}}$  bond (1.93(6) Å) is significantly shorter whereas the  $\text{Li}-\text{C}_{\text{br}}$  bond (2.23(6) Å) remains almost unchanged.

The kinetics of this transformation were determined using  ${}^1\text{H}$  NMR spectroscopy in the range 50–100 °C. An Arrhenius plot yielded values of  $\Delta G^\ddagger = 113(2)$  kJ mol<sup>-1</sup>,  $\Delta H^\ddagger = 109(2)$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -11.9(1)$  J mol<sup>-1</sup> K<sup>-1</sup>. It was noted that the magnitude of the transition state entropy is lower than that observed in related  $\alpha$ -abstraction reactions. On the basis of this data, a simple first-order intramolecular decomposition reaction mechanism, perhaps assisted electronically by the lithium ion, was assumed.

The alkylidene,  $(\text{Me}_3\text{SiCH}_2)(\text{ArN})\text{Ta}(\mu\text{-CHSiMe}_3)(^i\text{Pr}_2\text{tacn})\text{Li}$ , was shown to undergo a wide range of reactions.<sup>26,29</sup> Some of these are typical of traditional alkylidenes, whereas others were quite unique to this system (Scheme 8). For example, the compound reacted cleanly with 1 equiv. of benzophenone, liberating  $\text{Me}_3\text{SiCH}=\text{CPh}_2$  and forming the oxo compound,  $[(\text{Me}_3\text{SiCH}_2)(\text{ArN}=\text{O})\text{Ta}(\mu\text{-O})(^i\text{Pr}_2\text{tacn})\text{Li}]_2$ . As shown in Fig. 14, the compound is dimeric, with each oxo ligand spanning one Li and two Ta atoms. The dimer is held together by the commonly observed  $\text{Ta}_2\text{O}_2$  metallocycle, with normal  $\text{Ta}-\text{O}$  bond lengths (1.978(6) and 2.060(6) Å). The  $\text{Ta}-\text{N}(\text{imido})$  bond length (1.812(8) Å), though longer than in the alkylidene, is otherwise unremarkable.

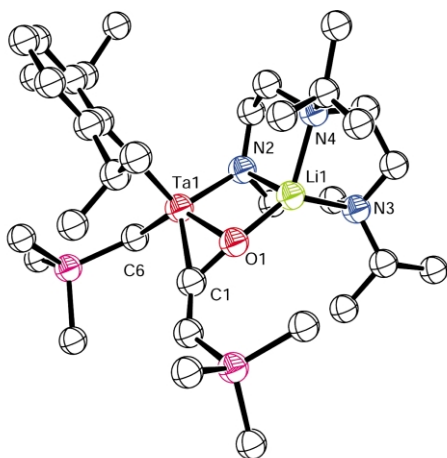


**Scheme 8**



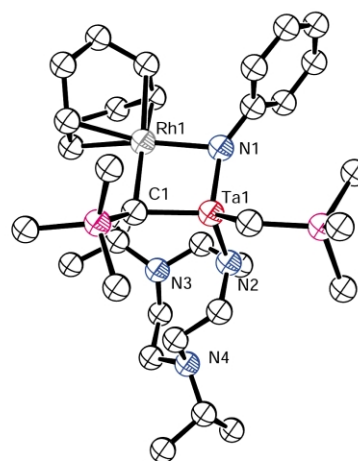
**Fig. 14** ORTEP view of the structure of  $[(\text{Me}_3\text{SiCH}_2)[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(\mu\text{-O})(i\text{Pr}_2\text{tacn})\text{Li}]_2$  (phenyl  $i\text{Pr}$  groups omitted for clarity).

Also in typical alkylidene-like fashion, the compound reacts with carbon monoxide (1 atm) at ambient temperature to form the ketene complex shown in Scheme 8. X-Ray diffraction on crystals grown from saturated octane confirm the connectivity as shown in Fig. 15. The ketene ligand is coordinated  $\eta_2\text{-}(C,O)$  to Ta and  $\eta_1\text{-O}$  to Li. Again, the bridging structure of the  $i\text{Pr}_2\text{tacn}^-$  is retained, with virtually no change in the remaining metal–ligand bond lengths.



**Fig. 15** ORTEP view of the structure of  $(\text{Me}_3\text{SiCH}_2)[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(i\text{Pr}_2\text{tacn})\text{Li}[\eta_2\text{-C},O:\eta_1\text{-O-C}(\text{O})=\text{CHSiMe}_3]$ .

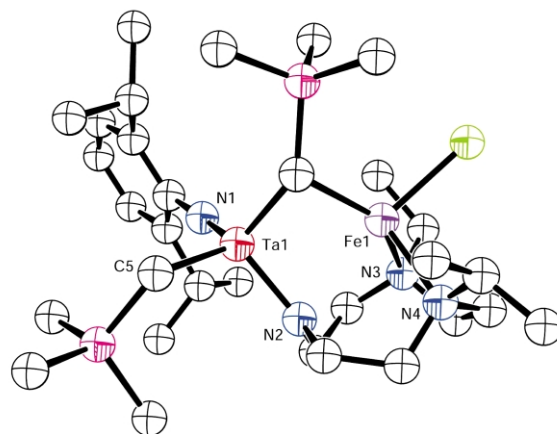
The above reactions proceed with retention of the Li ion due, at least in part, to the lack of a suitable leaving group. In another series of reactions, the lithium ion was encouraged to depart using common metathesis chemistry. In this way, some unusual heterobimetallic transition metal systems were prepared, in which two metals in close proximity are linked by single-atom bridges. For example, reaction of the alkylidene with  $[\text{RhCl}(\text{COD})]_2$  (COD = 1,5-cyclooctadiene) in toluene afforded  $(\text{Me}_3\text{SiCH}_2)(i\text{Pr}_2\text{tacn})(\text{Me}_3\text{SiCH})\text{Ta}(\text{NAr})\text{Rh}(\text{COD})$ , the X-ray structure of which (Fig. 16) shows a Ta–Rh bimetallic compound in which the alkylidene and imido groups bridge the metal centers. The pseudo-tetrahedral coordination of the tantalum is completed by a monodentate  $\text{tacn}^-$  ligand (the first example of its kind for a transition metal) and the remaining alkyl group, while the Rh(I), still bound to COD, resides in its preferred square planar environment. The Ta–N(imido) bond distance is lengthened to 1.871(5) Å, a value indicative of double-bond character and the Rh–N(imido) bond length (2.123(5) Å) falls in the range of values observed for dative rhodium–nitrogen interactions. The fact that the  $\text{tacn}$  ligand



**Fig. 16** ORTEP view of the structure of  $(\text{Me}_3\text{SiCH}_2)(i\text{Pr}_2\text{tacn})(\text{Me}_3\text{SiCH})\text{Ta}[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]\text{Rh}(\text{COD})$  (phenyl  $i\text{Pr}$  groups omitted for clarity).

remains monodentate in solution and the solid state was ascribed to steric effects since, electronically, the tantalum center is still quite unsaturated in this complex.

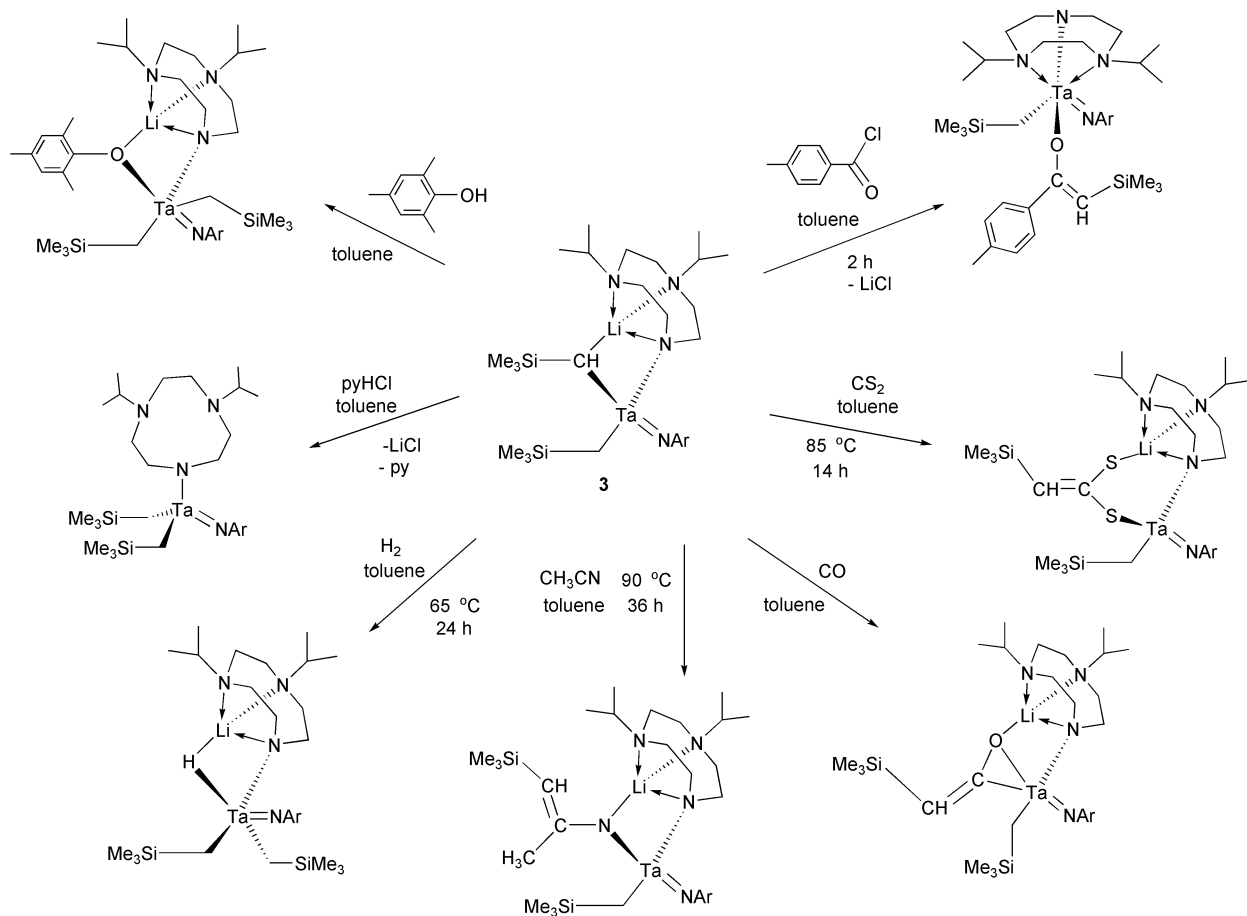
A new type of heterobimetallic complex was obtained when  $(\text{Me}_3\text{SiCH}_2)(\text{ArN})\text{Ta}(\mu\text{-CHSiMe}_3)(i\text{Pr}_2\text{tacn})\text{Li}$  was treated with  $[\text{FeCl}_2(\text{TMEDA})]_2$  in tetrahydrofuran (Scheme 8). The compound is paramagnetic, with a solution magnetic susceptibility of  $\mu_{\text{eff}} = 4.2 \mu_{\text{B}}$  that is consistent with high-spin  $d_6$  Fe(II). The structure was confirmed using X-ray diffraction to be  $(\text{Me}_3\text{SiCH}_2)(\text{ArN})\text{Ta}(\text{CHSiMe}_3)(i\text{Pr}_2\text{tacn})\text{FeCl}$  (Fig. 17). The iron



**Fig. 17** ORTEP view of the structure of  $(\text{Me}_3\text{SiCH}_2)[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(\text{CHSiMe}_3)(i\text{Pr}_2\text{tacn})\text{FeCl}$ .

atom is in a pseudo-tetrahedral environment with the bridging  $\text{tacn}^-$  ligand now coordinated in a *bidentate* fashion (through the two amino nitrogens). The anionic nitrogen of the  $\text{tacn}^-$  ligand does not appear to interact with the iron appreciably, exhibiting a nearly trigonal planar environment (sum of angles =  $359(2)^\circ$ ), even though the Ta–N(amido) bond length (1.995(9) Å) is typical of a Ta–N single bond. The Ta–C<sub>br</sub> bond length (2.02(1) Å) is much shorter than the Fe–C<sub>br</sub> distance (2.18(1) Å) and is most likely due to a greater Ta–C bond order.

The reactivity of  $(\text{Me}_3\text{SiCH}_2)(\text{ArN})\text{Ta}(\mu\text{-CHSiMe}_3)(i\text{Pr}_2\text{tacn})\text{Li}$  with proton sources was also described recently. Reaction with 2,4,6-trimethylphenol proceeded rapidly at room temperature to afford the aryloxide shown in Scheme 9. This behavior is comparable to that of  $(\text{Me}_3\text{CCH}=\text{O})\text{Ta}(\text{Me}_3\text{CCH}_2)_3$ , which reacts with two equivalents of TpOH [Tp =  $(\text{C}_6\text{H}_4)_3\text{C}_2\text{HOH}$ ] to yield  $(\text{Me}_3\text{CCH}_2)_3\text{Ta}(\text{OTp})_2$ . In both cases, the nucleophilic alkylidene moiety is protonated by the weakly acidic alcohol.



Scheme 9

Reaction of the alkylidene and pyridinium chloride resulted in quantitative conversion to the dialkyl species  $(\text{Me}_3\text{Si-CH}_2)_2(\text{ArN}=\eta_1\text{-Pr}_2\text{tacn})\text{Ta}$ . This result can be compared with that of HCl with the more typical alkylidene  $(\text{Me}_3\text{CCH}=\text{Ta}(\text{Me}_3\text{CCH}_2)_3)$  which yields  $(\text{Me}_3\text{CCH}_2)_4\text{TaCl}$ . Thus, the presence of lithium in the former case plays a key role in determining the fate of the reaction and the final products. Interestingly, the dialkyl tacn complex was also obtained by reaction of the  $\mu$ -alkyl species with an equivalent of pyridinium chloride. In accord with this behavior, addition of  $\text{LiCH}_2\text{SiMe}_3$  regenerated the  $\mu$ -alkyl quantitatively.

Exposure of the alkylidene to  $\text{H}_2$  results in protonation to again form an alkyl ligand but, more interestingly, the hydride counter ion is retained in a bridging fashion, bound to the tantalum and lithium atoms. The pale yellow compound is stable for weeks as a solid, but slowly decomposes in solution. The  $^1\text{H}$  NMR spectrum of this compound exhibits a  $^1\text{H}$  resonance for the hydride at 11.13 ppm as a 1 : 1 : 1 : 1 quartet ( $^1J$  14.7 Hz). This splitting, due to a coupling between H and  $^7\text{Li}$  ( $S = 3/2$ ), is matched by the appearance of a doublet with an identical  $^1J_{\text{LiH}}$  at 3.63 ppm in the  $^7\text{Li}$  NMR spectrum (Fig. 18).

The remainder of the  $^1\text{H}$  NMR spectrum was broad at room temperature, indicating fluxionality, which can be resolved by cooling to  $-2^\circ\text{C}$ . The low temperature spectrum was interpreted as involving a square pyramidal coordination sphere in which the imido ligand is axial and the two alkyl ligands are oriented in a *cis* fashion. The fluxionality seen at room temperature was attributed to a square-pyramidal/trigonal bipyramidal equilibrium. In the  $^2\text{H}$  NMR spectrum of the product prepared from  $\text{D}_2$ , resonances at 11.13 (br, s) and 0.52 ppm (br, d) were assigned to the bridging deuteride and the  $\text{CDHSiMe}_3$  group, respectively.

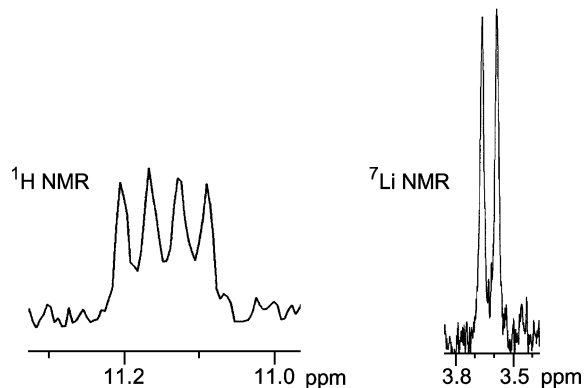
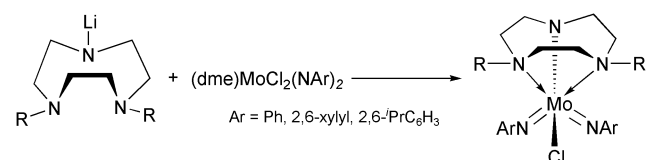


Fig. 18 NMR Spectra ( $^1\text{H}$  and  $^7\text{Li}$ ) of  $(\text{Me}_3\text{SiCH}_2)_2[\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]\text{-Ta}(^i\text{Pr}_2\text{tacn})(\text{LiH})$ .

The reactions shown in Scheme 10 were employed in the preparation of the first molybdenum complexes with anionic



Scheme 10

tacn ligands.<sup>5</sup> These compounds exhibit  $C_s$  symmetry in solution, with the amide N-donor *trans* to the chloride ligand, as determined by  $^1\text{H}$  NMR spectroscopy. The X-ray structure of one example,  $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2(^i\text{Pr}_2\text{tacn})\text{MoCl}$ , is shown in



Fig. 19 (only one of the two independent molecules is displayed). Most notable are the long Mo–N(amine) distances, which are the longest of any molybdenum complex bearing a (neutral) tacn ligand. The normal range of values is on the order 2.18–2.48 Å, whereas in the anionic tacn complex they lie in the range 2.520–2.644 Å. It is believed that excessive steric crowding in the molecule is responsible for this bond lengthening.

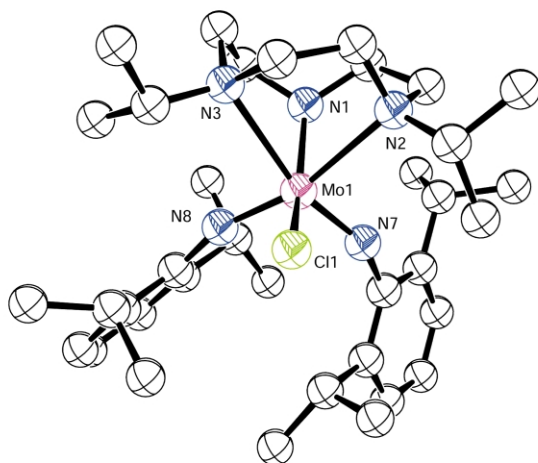


Fig. 19 ORTEP view of the structure of  $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2(\text{Pr}_2\text{tacn})\text{MoCl}$ .

## Summary and conclusions

The ability of the anionic tacn moiety to support novel organometallic chemistry with early transition metals is now well established. For the most part, the tacn ligand is a relatively innocent spectator that shields one face of a metal complex, providing it with stability and low molecular weight, at least in the case of the well-studied  $i\text{Pr}$  derivative. Nevertheless, there are now clear cases where hemilabile behavior, involving  $\eta^3\text{-}\eta^1$  interactions, is observed. Electronically, the  $\eta^3$ -coordination mode may involve donation of six or eight electrons to the metal center, depending on whether the latter is able to accommodate a  $\pi$ -bond involving the amido nitrogen lone pair in addition to the three  $\sigma$ -bonds (two from the amino nitrogens; one from the amido). Under certain circumstances, the tacn moiety displays decidedly 'guilty' behavior when it becomes intimately involved as a reactive species, leading to ring opening and formation of an N-vinyl, diamide-amido dianion.

As shown in this review, the focus has thus far been on electropositive, early transition metals. Extending this work to lanthanides and to more electron-rich metal systems may lead to some interesting new chemistry, especially for the latter species where the ability of anionic tacn ligands to engage in hemilabile behavior might lead to catalytic reactivity.

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