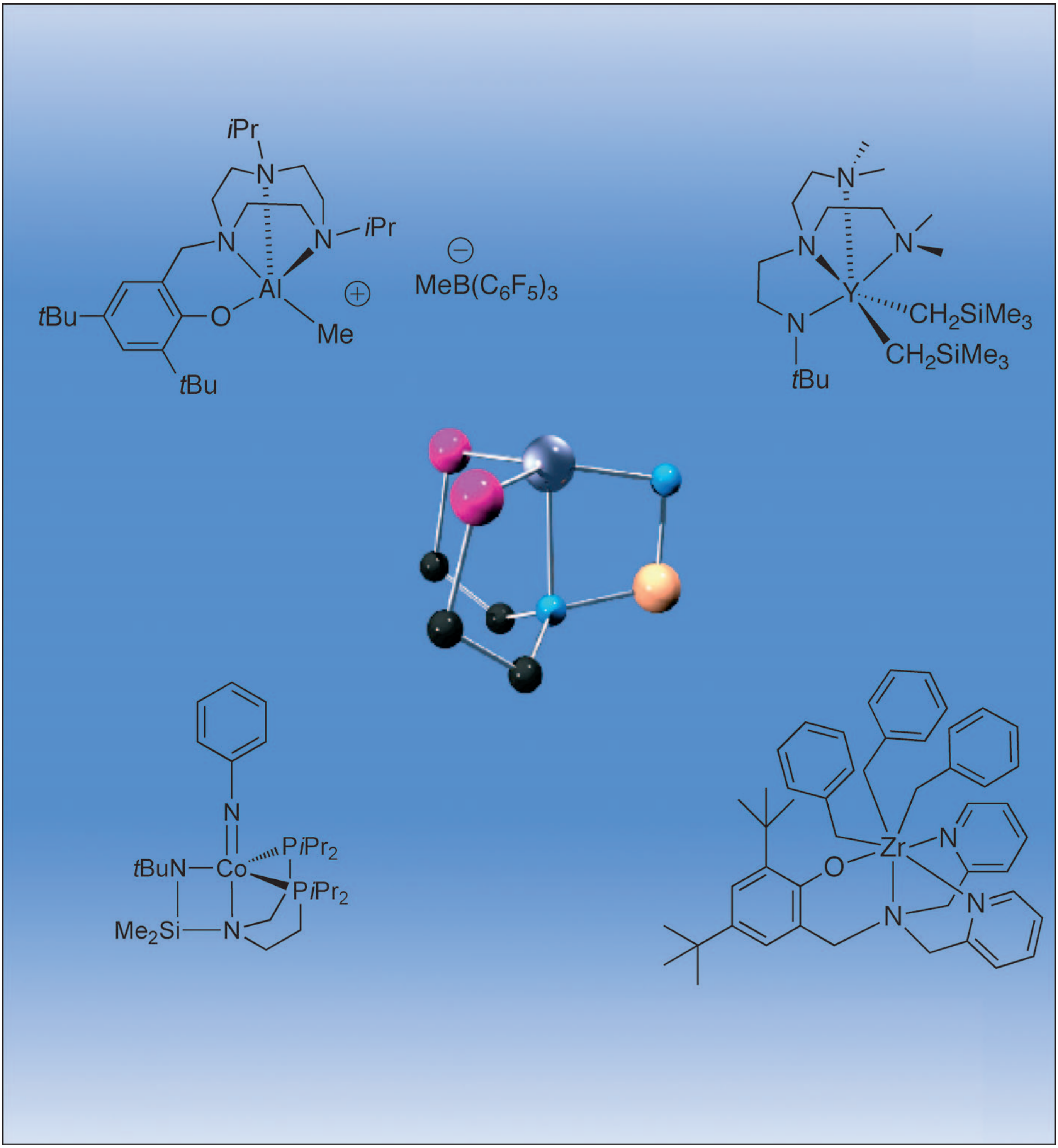
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801069

Use of Tetradentate Monoanionic Ligands for Stabilizing Reactive Metal Complexes

Wayne A. Chomitz and John Arnold*[a]



Abstract: Supporting ligand design has played a vital role in the development of coordination and organometallic chemistry. A myriad of ligands with varying charge, donor-type, and denticity have been explored in this realm. A ligand type that has garnered recent attention involves a tetradentate monoanionic (TDMA) framework. TDMA ligands have been used with p-, d-, and f-block elements to form an array of interesting new complexes with applications ranging from bioinorganic chemistry to catalysis. Complexes incorporating TDMA ligands have been shown to stabilize reactive low-valent and cationic species. Functionalized β-diiminato and TACN derivatives as well as tripodal ligands featuring both hard σ-donors as well as "mixed-donors" are covered in this review. The synthetic challenges associated with the implementation of each ligand set are discussed.

Keywords: anions · chelates · coordination modes · ligand design

Introduction

The ability of supporting ligands to solubilize and stabilize metal complexes and to direct reactivity at a metal center through steric and electronic constraints is an issue of fundamental importance in homogeneous transition-metal chemistry. In this context, donor ligands with numerous permutations of coordination number (1, 2, 3, etc.), charge (−1, −2, −3, etc.), and donor type (C, O, S, N, P, etc.) have been examined.[1] While much research and a number of reviews have focused on monodentate,[2,3] bidentate,[4–6] and tridentate[7–9] monoanionic ligands, less attention has been paid to tetradentate monoanionic (TDMA) ligands of the general formula L_3X (Figure 1).

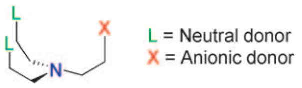


Figure 1. General TDMA ligand design.

By definition, TDMA ligands have the ability, when fully bound, to occupy four coordination sites, while tying up only one valency. The inherent higher coordination number of TDMA ligands creates the potential for hemilable behavior in which full coordination of the ligand is only achieved upon the loss of co-ligand, either through abstraction, protonation, or reduction. For instance, a change in coordination mode from tridentate to tetradentate could stabilize a transient species long enough to allow for its reaction with a substrate of choice. This change in coordination mode could also enable the isolation of species that would otherwise go undetected without the additional stabilization provided by the hemilable ligand. The intention of this review is to survey the use of nonmacrocyclic,[10–14] TDMA ligands for use with main-group, transition-metal, and f-block complexes. Cyclopentadienyl ligands exhibiting a neutral tether have been covered elsewhere and do not fall under the scope of the present review.[15]

Tetradentate β-Diiminato Ligands

Ligands incorporating β-diiminato functionalities have been known for many years.[16] These ligands are attractive due to the ready availability of their starting materials and the straightforward manner by which they are synthesized. Roesky et al. recently examined a tetradentate version of the nacnac ligand in which additional diethyl amine donor groups had been tethered to the original ligand moiety (L^a; Figure 2). Roesky and co-workers synthesized numerous Group 3 and Ln complexes supported by L^a through metathesis reactions of MX_3 (M = Sc, Y, Pr, Sm, Tb, Ho, Er, Yb; X = Cl, Br, BH_4, I) and LiL^a.[17–21] In addition, substitution reactions with $[ScCl_2(L^a)]$ and $LiN(SiMe_3)_2$ led to amide-substituted as well as ligand decomposition products. Alkylation of $[TbBr_2(L^a)]$ with two equivalents of $LiCH_2SiMe_3$ led cleanly to the dialkyl species $[Tb(CH_2SiMe_3)_2(L^a)]$, which was structurally characterized. One particularly interesting and impressive compound supported by L^a is the monoalumoxane complex $[Al(L^a)\{O\text{-}B(C_6F_5)_3\}]$ (Figure 3), the first of its kind.[22] Work by McNeil's group examined the related modified β-diiminato ligand L^b, possessing heterocyclic donor groups. The coordination compounds $[MgBr(L^b)]$, $[ZnCl(L^b)]$, and $[Cd(L^b)(OAc)]$ were synthesized and structurally characterized.[23] In each case, all four

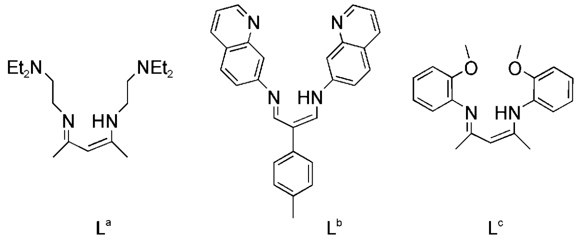


Figure 2. β-diiminato TDMA ligands.

---

[a] W. A. Chomitz, Prof. Dr. J. Arnold
Department of Chemistry
University of California
Berkeley, CA, 94720-1460 (USA)
Fax: (+1) 510-666-2504
E-mail: arnold@berkeley.edu

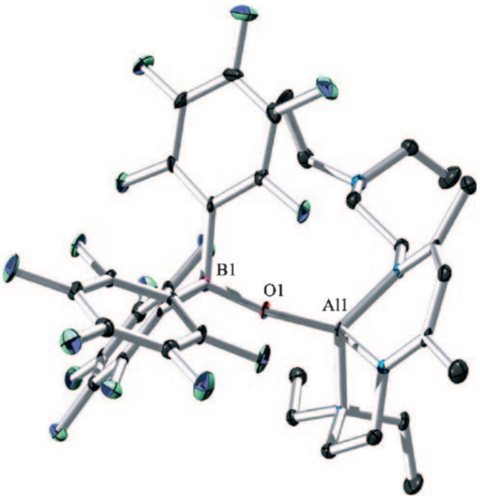


Figure 3. ORTEP diagram of $[Al(L^{a})\{O\text{-}B(C_6F_5)_3\}]$.

donors bind the metal center. In addition to neutral amine donors, ethereal donor substituted β-diiminato ligands have been synthesized and studied (L^{c}). Chisholm and co-workers examined the utility of L^{c} as a supporting ligand for a series of Mg and Zn starting materials. The coordination chemistry of complexes $[Mg(L^{c})(OtBu)]$, $[Mg(L^{c})\{N(SiMe_3)_2\}]$, $[Zn(L^{c})(OiPr)]$, and $[Zn(L^{c})\{N(SiMe_3)_2\}]$ was examined, and the activity of these complexes towards the catalytic ring opening polymerization of lactides was explored.[24]

Functionalized TACN Ligands

Monodeprotonated, 1,4,7-triazacyclononane (TACN) is a $6\,e^{-}$ tridentate monoanionic macrocyclic ligand that has been shown to be useful for supporting a variety of interesting and reactive metal complexes.[15,25–29] Conversion of the TACN ligand to a TDMA ligand is achieved by tethering an anionic functional group to one of the nitrogen donors. Tolman and co-workers began work on the phenolate substituted TACN ligands HL^{d} and HL^{e} (HL^{d} = 1-(3,5-dimethyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane; HL^{e} = 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane) to support model complexes of galactose oxidase (GAO).[30,31] The sodium salts NaL^{d} and NaL^{e} were prepared in situ upon the addition of NaH and reacted with $CuCl_2$, $Cu(O_3SCF_3)_2$, $Cu(O_2CCH_3)_2$, and $ZnCl_2$ to form the metalated products $[CuCl(L^{d/e})]$, $[Cu(L^{e})(NCCH_3)(O_3SCF_3)]$, $[Cu(L^{e})(O_2CCH_3)]$, and $[ZnCl(L^{d/e})]$. The alcohol complex $[Cu(L^{e})(OCH_2Ph)]$ was synthesized through the metathesis reaction of $L^{e}CuCl$ and $NaOCH_2Ph$. The X-ray structure reveals an O···H–C interaction of possible functional importance for the hydrogen atom abstraction involved in alcohol oxidation by GAO. In addition to $L^{d/e}$, varying substitutes at the *para* position of the phenol ring, such as OMe and SMe, were introduced to determine how the redox chemistry of the resulting complexes was affected. Also of interest was the synthesis of a Cu^{I} species supported by L^{e}. Metathesis reactions with NaL^{e} and Cu^{I} starting materials failed to yield the desired product due to disproportionation; however, the protonolysis reaction of HL^{e} and Cu^{I}–alkyl starting material led cleaning to the Cu^{I} species $[Cu(L^{e})]$ (Figure 4).[32] The reactivity of $[Cu(L^{e})]$ with O_2 was probed with the hope of elucidating the mechanism for oxidation. Weighardt et al. also examined the use of $HL^{d/e}$ for stabilizing main-group and first-row metal complexes of

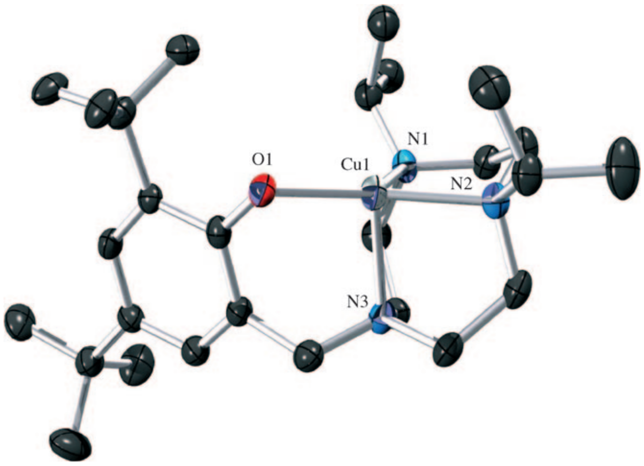


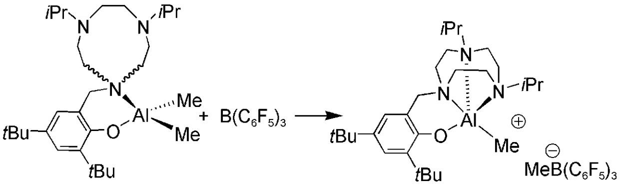
Figure 4. ORTEP diagram of $[Cu(L^{e})]$.

John Arnold received a B.Sc. in Applied Chemistry from Salford University in 1982, where he carried out research on ^{106}Ru–nitrosyl chemistry with Dr G. G. J. Boswell. He then left the UK for four years to study for his Ph.D. in Chemistry at the University of California, San Diego working under the direction of Professor T. D. Tilley. After an eighteen month postdoctoral stay with the late Professor Sir Geoffrey Wilkinson, he then spent one year as a Royal Society Research Fellow at Imperial College before moving to the University of California, Berkeley in 1989. His research interests lie across the periodic table, in the areas of inorganic and organometallic chemistry and catalysis.

Wayne A. Chomitz was born in Nashua, New Hampshire, in 1981 and grew up in Charleston, South Carolina. He attended the University of North Carolina, Chapel Hill (B.A. 2004), where he was an undergraduate researcher in the laboratory of Professor M. S. Brookhart. Wayne is currently a fifth-year graduate student in the laboratory of Professor J. Arnold at the University of California, Berkeley. His graduate research has focused on the stabilization of reactive metal–ligand fragments through ligand design.

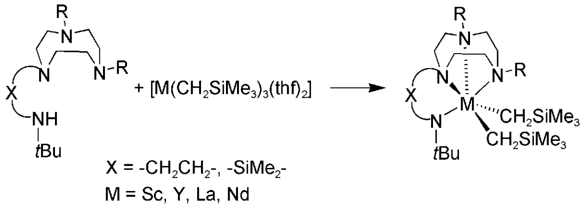
Cr^{III}, Mn^{III}, Co^{III}, Ni^{II}, Zn^{II}, and Ga^{III}.[33,34] The redox chemistry of the Co complexes $[Co(L^e)(acac)][ClO_4]$ and $[Co(L^e)(Cl_4cat)]CH_3CN$ (Cl_4cat = tetrachlorocatechol) was also probed to determine the nature and location of the radical on the reduced species.[35]

Work from Mountford et al. focused on the use of $L^{d/e}$ and L^f (HL^f = 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyl-1,4,7-triazacyclononane) for supporting hard, early metal and organometallic complexes. One of the first complexes reported was the dimethyl Al complex $[Al(L^e)Me_2]$, which exhibits hemilable behavior at the TACN moiety upon the abstraction of a methyl group with $B(C_6F_5)_3$ (Scheme 1).[36] In addition to Al chemistry, a range of trivalent main-group and transition-metal dichloride complexes were also synthesized through metathesis reactions with KL^{d-f} and metal halide starting materials MCl_3 or $MCl_3(thf)_3$ (M = Ga, In, Sc, Y, Ti, V, Cr).[37] The bis-alkyl complex $[Sc(CH_2SiMe_3)_2(L^f)]$ was synthesized by the alkylation of $[ScCl_2(L^f)]$ with two equivalents of $LiCH_2SiMe_3$ or by the protonolysis reaction of HL^f and $[Sc(CH_2SiMe_3)_3(thf)_2]$. Further reaction of $[Sc(CH_2SiMe_3)_2(L^f)]$ with two equivalents of *p*-cresol gave the bis-alkoxide $[Sc(L^f)(OAr)_2]$ (OAr = O-4-C_6H_4Me), which was structurally characterized.[38] The solid-state structure of $[Sc(L^f)(OAr)_2]$ showed the ligand fully coordinated, consistent with the NMR data (Figure 5). Mountford et al. also synthesized the Ti imido complexes $[TiCl(L^e)(NtBu)]$ and $[TiCl(L^e)(NSiMe_3)]$ as potential precursors for Ti nitride species.[39]



Scheme 1. Methyl group abstraction from $[Al(L^e)Me_2]^+$.

An alternative functionalized TACN ligand comes from Hessen's group, who focused on the examination of an amido tether linked by either an ethyl or a dimethylsilyl bridge to the TACN moiety.[40–43] Through protonolysis reactions between $HL^{g/h}$ (HL^g = *N-tert*-butyl-2-(4,7-dimethyl-1,4,7-triazanon-1-yl)ethylamine; HL^h = *N-tert*-butyl-2-(4,7-dimethyl-1,4,7-triazanon-1-yl)dimethylsilylamine) and $[M(CH_2SiMe_3)_3(thf)_2]$ (M = Sc, Y, La, Nd), a series of $[M(CH_2SiMe_3)_2(L^{g/h})]$ complexes were synthesized (Scheme 2).



Scheme 2. Synthesis of bis-alkyl complexes supported by amide functionalized TACN.

An X-ray diffraction study of $[Y(CH_2SiMe_3)_2(L^g)]$ revealed full coordination of the ligand, giving a six-coordinate Y complex (Figure 6). The ^1H NMR data indicate $[Y(CH_2SiMe_3)_2(L^g)]$ possesses C_s symmetry in solution, with rapid exchange of the two CH_2SiMe_3 groups. Following protonolysis with $[PhNMe_2H][B(C_6F_5)_4]$, the cationic species $[M(CH_2SiMe_3)(L^{g/h})][B(C_6F_5)_4]$ (M = Sc, Y, La, Nd) were generated in situ and were shown to be active polymerization and copolymerization catalysts with ethylene and ethylene/α-olefins, respectively. It was also determined that the stability of the complexed metal–alkyls was highly dependent on the choice of the linker arm, with the longer ethyl linker giving more thermally stable complexes.

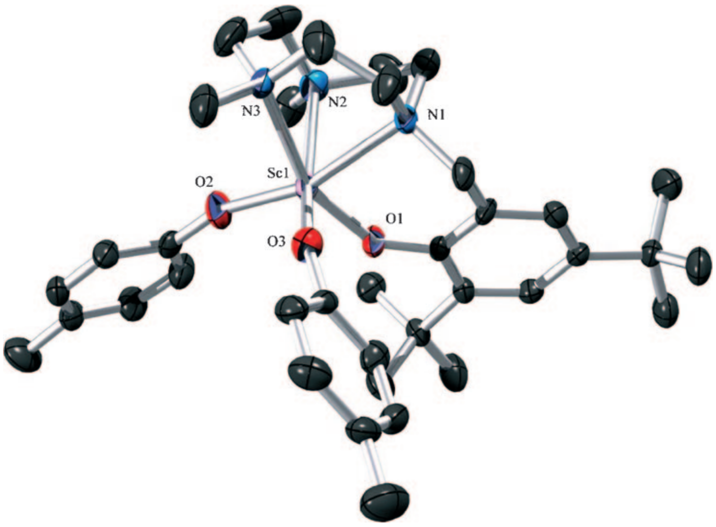


Figure 5. ORTEP diagram of $[Sc(L^f)(OAr)_2]$.

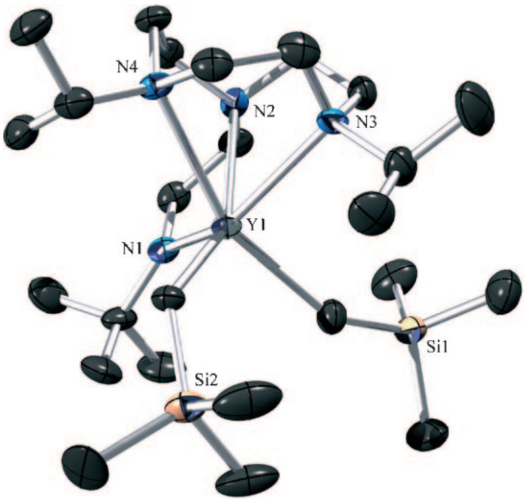


Figure 6. ORTEP diagram of $[Y(CH_2SiMe_3)_2(L^g)]$.

Tripodal Ligands

Related to functionalized TACN ligands are nitrogen-centered tripodal ligands exhibiting an "open" TACN framework. Hessen et al., curious as to how a less constrained ligand framework would affect the reactivity, began to examine the less constrained tripodal frameworks HL$^{i/j}$ (HL^{i} = *N-tert*-butylaminoethyl-bis(2-dimethylaminoethyl)amine; HL^{j} = *N-tert*-butylaminodimethylsilylbis(2-dimethylaminoethyl)amine).[44] As with functionalized TACN ligands, protonolysis of [$Y(CH_2SiMe_3)_3(thf)_2$] with HL^{i} led cleanly to the bis-alkyl complex [$Y(CH_2SiMe_3)_2(L^{i})$]. The ^{1}H NMR data suggest rapid dissociation and inversion of the neutral dimethyl amino groups; however, the X-ray diffraction study revealed full coordination of the ligand to the metal center in the solid-state (Figure 7). Upon standing at room temperature, [$Y(CH_2SiMe_3)_2(L^{i})$] was susceptible to intramolecular C–H activation at one of the dimethylamino donors, which resulted in the release of alkane and the formation of a new Y–C bond (Scheme 3). Attempts to synthesize [$Y(CH_2SiMe_3)_2(L^{j})$] resulted in the isolation of the mono-alkyl C–H activation product exclusively, again highlighting the difference in thermal stability based on linker length.

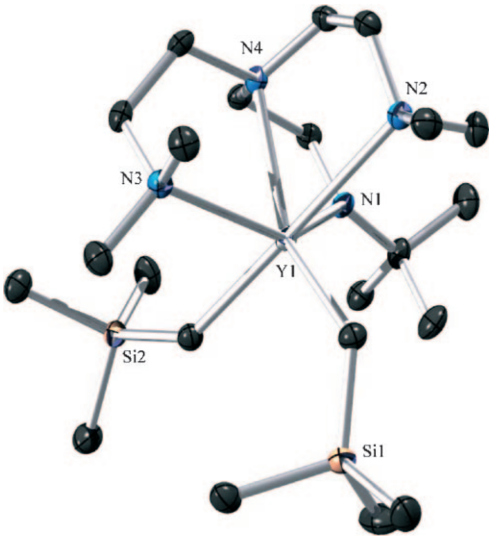
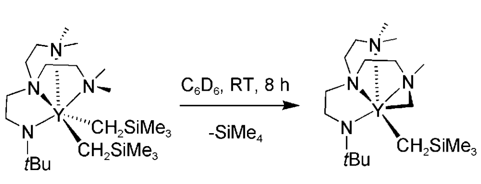


Figure 7. ORTEP diagram of [$Y(CH_2SiMe_3)_2(L^{i})$].



Scheme 3. Intramolecular C–H activation by [$Y(CH_2SiMe_3)_2(L^{i})$].

Tripodal ligands with other hard donors have also been examined. Kols et al. found that the protonolysis reaction of the amine mono(phenolate) ligand HL^{k} (HL^{k} = 2,4-di-*tert*-butyl-6-bis[2-(methoxy)ethyl]aminomethylphenol) with Ti(O*i*Pr)$_4$ and Zr(O*t*Bu)$_4$, led cleanly to the trialkoxides [Ti(L^{k})(O*i*Pr)$_3$] and [Zr(L^{k})(O*t*Bu)$_3$].[45] Both complexes undergo a dynamic process equilibrating the two methoxy side-arms as seen by the ^{1}H NMR spectra, and the solid-state structures confirm the presence of six-coordinate octahedral metal centers with one-side arm uncoordinated on each (Figure 8). Protonolysis of [Ti(L^{k})(O*i*Pr)$_3$] and [Zr(L^{k})(O*t*Bu)$_3$] with [$PhNMe_2H$][$B(C_6F_5)_4$] led cleanly to the highly stable bis-alkoxide complexes [Ti(L^{k})(O*i*Pr)$_2$][$B(C_6F_5)_4$] and [Zr(L^{k})(O*t*Bu)$_2$][$B(C_6F_5)_4$]. Upon the loss of alcohol and the opening of a coordination site, the previously unbound methoxy donor group coordinates to the metal center to give a fully bound TDMA ligand, demonstrating the hemilable behavior of the ligand. Kols' group also synthesized [$Zr(L^{k})(CH_2Ph)_3$] through an analogues alkane elimination reaction with HL^{k} and [$Zr(CH_2Ph)_4$]. When [$Zr(CH_2Ph)_3(L^{k})$] is allowed to react with $B(C_6F_5)_3$, a Zr–benzyl group is abstracted and the unbound methoxy donor arm coordinates once again as in compound [Zr(L^{k})(O*t*Bu)$_2$][$B(C_6F_5)_4$]. A bis-alkyl cation was also synthesized through the protonolysis of [$Zr(CH_2Ph)_3(L^{k})$] with [$PhNMe_2H$][$B(C_6F_5)_4$] (Scheme 4). Substitution of the *t*Bu groups on the phenol with Me groups was examined to determine what effect the steric bulk at those positions had on the coordination chemistry of the resulting complexes. Protonolysis of HL^{k} and HL^{l} (HL^{l} = 2,4-dimethyl-6-bis[2-(methoxy)ethyl]aminomethylphenol) with $ZnEt_2$ resulted in the isolation of [ZnEt(L^{k})] and [ZnEt(L^{l})].[46] The X-ray structure of [ZnEt(L^{k})] reveals a monomeric trigonal bipyramidal complex with the ligand fully bound. Due to the reduced steric

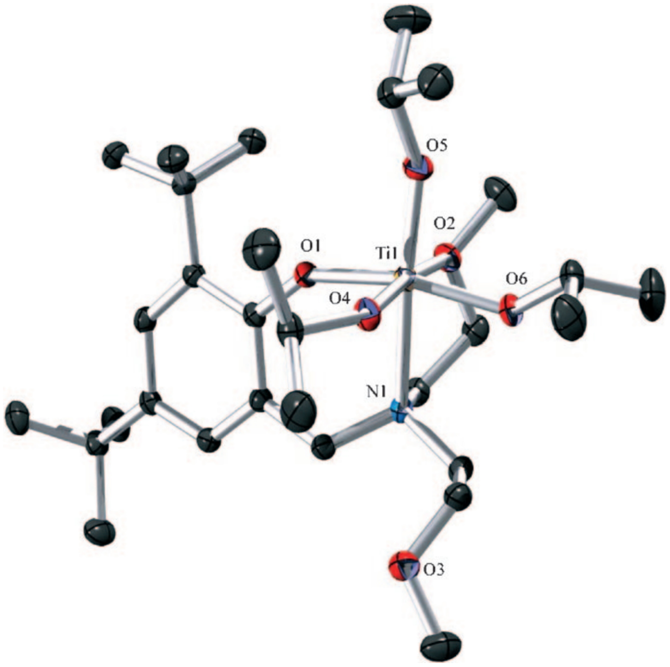
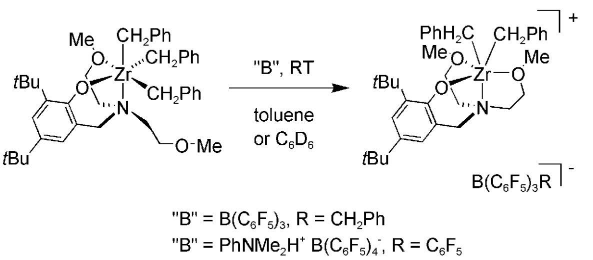


Figure 8. ORTEP diagram of [Ti(L^{k})(O*i*Pr)$_3$].



Scheme 4. Methoxy donor coordination upon Zr–C activation.

bulk on the phenol, [$ZnEt(L^l)$] is dimeric in the solid-state with bridging oxygen donors and one methoxy donor from each ligand uncoordinated. Yeldon and co-workers also examined the ability of L^k to support alkali and other first-row metals. In addition to the salt $K(L^k)$, [$Al(L^k)Me_2$], [$ZnEt(L^k)$], [$FeCl(L^k)$], and [$CoCl(L^k)$] were synthesized either through protonolysis or salt metathesis reactions.[47]

Work in the Arnold group began with an examination of the use of the phenoxytriamine ligands $HL^{m/n}$ (HL^m = 2,4-dimethyl-6-bis[2-(diethylamino)ethyl]aminomethylphenol; HL^n = 2,4-di-*tert*-butyl-6-bis[2-(diethylamino)ethyl]aminomethylphenol) with early transition metals (Figure 9), Matyjaszewski et al. previously used L^m with Cu^I for atom-transfer radical polymerization (ATRP) catalysis of *n*-butyl acrylate.[48] The Li salt was generated in situ and reacted with CuCl for use in polymerizations. Extension of this work in the Arnold group involved the synthesis and isolation of the Li, Na, and K salts of L^m and L^n. The utility of these salts towards salt metathesis reactions was probed through their reaction with [$MCl_3(thf)_3$] (M = Y, La). Salt metathesis reactions gave low yields and intractable mixtures; however, related work from Yeldon's group showed that KL^m could be reacted with [$CrCl_3(thf)_3$] to obtain [$CrCl_2(L^m)$], albeit in low yield.[47] Yeldon et al. also examined the related ligand HL^o (HL^o = 2,4-di-*tert*-butyl-6-bis[2-(dimethylamino)ethyl]aminomethylphenol), in which the diethylamino donors were replaced by dimethylamino groups. The Mg and Zn alkyl complexes [$Mg(L^o)i\Pr$] and [$ZnEt(L^o)$] were synthesized and structurally characterized.[47]

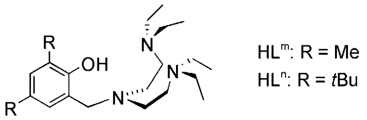


Figure 9. Phenoxytriamine ligands.

Protonolysis reactions of $HL^{m/n}$ with [$YR_3(thf)_2$] (R = CH_2SiMe_3, $N(SiMe_3)_2$, $N(SiMe_2H)_2$) were explored as alternative routes to the metalation of the TDMA ligands $L^{m/n}$. The less sterically hindered starting material [$Y\{N(SiMe_2H)_2\}_3(thf)_2$] allowed for complexation and for the synthesis of [$Y(L^{m/n})\{N(SiMe_2H)_2\}_2$].[49] Similar to the results obtained by Kol et al., the ^1H NMR data for [$Y(L^{m/n})\{N(SiMe_2H)_2\}_2$] indicated a dynamic process equilibrating the diethylamino groups was operative. An X-ray diffraction study of [$Y(L^n)\{N(SiMe_2H)_2\}_2$] elucidated the solid-state coordination geometry, showing that the Y atom lies in a five-coordinate distorted square-based pyramidal geometry with three of the four ligand donors coordinated to the metal center along with the two N-bound silylamido ligands (Figure 10). Full coordination of the ligand is likely prohibited by steric constraints. [$Y(L^{m/n})\{N(SiMe_2H)_2\}_2$] were shown to be active catalysts for the ring opening polymerization (ROP) of lactide and ε-caprolactone.

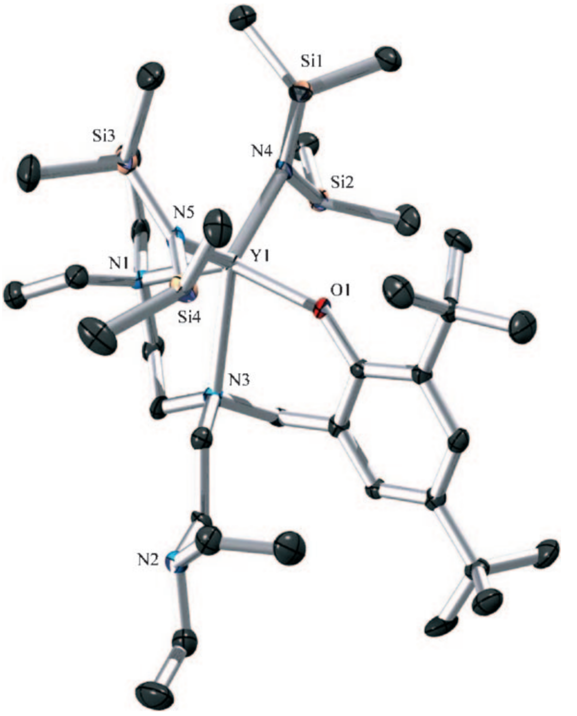


Figure 10. ORTEP diagram of [$Y(L^m)\{N(SiMe_2H)_2\}_2$].

The inability to access complexes of the general form [MLX_2] by salt metathesis reactions with $ML^{m/n}$ (M = Li, Na, K) and [$MCl_3(thf)_3$] (M = Y, La) led to the introduction of pyridyl donor groups in place of diethylamino donors in the hope that this modification would allow for the synthesis of complexes through metathesis reactions. The ligand with the requisite parameters H(BPPA) (H(BPPA) = bis(2-picolyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine) had previously been used to bind middle-to-late first-row transition metals in bioinorganic and organometallic studies. Que and co-workers first examined the unsubstituted BPPA derivative bis(2-picolyl)(2-hydroxybenzyl)amine for use with Fe as a model for the chromophoric site of purple acid phosphatates.[50] BPPA complexes of Fe and Mn were also used as structural analogues for Fe-containing intradiol cleaving catechol diooxygenases.[51,52] Coordination and organometallic complexes of Cu, Ni, and Zn have also been reported.[53–55]

The Li, Na, and K salts of BPPA were synthesized and K[BPPA] was shown to be a useful metalating reagent for main-group and transition-metal halide starting materials through the general reaction of K[BPPA] with $[MX_n(thf)_m]$ (M = Al, Ga, Ti, V, Y, Zr; X = Cl, Br; $n = 3, 4$; $m = 0, 3$).[56] The solid-state structures of $[Al(bppa)Cl_2]$, $[Ga(bppa)Cl_2]$, $[Ti(bppa)Cl_2]$, and $[V(bppa)Br_2]$ show the central atom lying in an octahedral geometry with the ligand fully bound (Figure 11). Metalation of BPPA with the larger Group 3 metal Y resulted in the chloride-bridged dimer, $[\{Y(bppa)Cl_2\}_2]$. An X-ray diffraction study of $[\{Y(bppa)Cl_2\}_2]$ reveals two symmetry related seven-coordinate Y centers each with the BPPA ligand fully bound and with one terminal and two bridging chlorides. The ^1H NMR data indicate the presence of a molecule with C_s symmetry in solution. No fluxional behavior was observed. The tetravalent complex $[Zr(bppa)Cl_3]$ was also synthesized and characterized by NMR; however, no crystallographic data were obtained. The NMR data for $[Zr(bppa)Cl_3]$ also suggest full coordination of the BPPA ligand with no fluxional behavior in solution being observed. The U complex $[U(bppa)I_3]$ was also synthesized, and one structural feature unique to this compound is a twist observed at the basal nitrogen (Figure 12), which is not observed with any of the other structurally characterized complexes supported by BPPA.

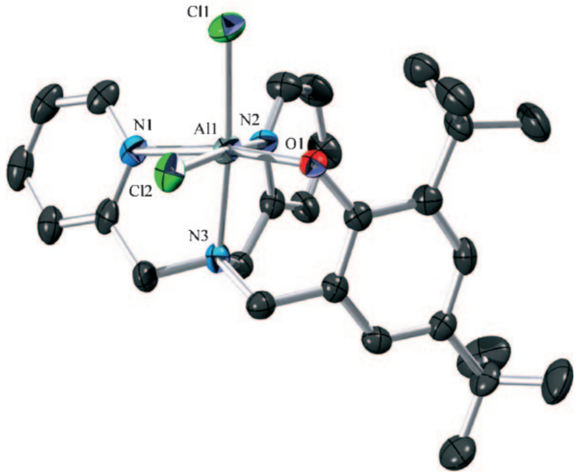


Figure 11. ORTEP diagram of $[Al(bppa)Cl_2]$.

The synthesis of $[M(bppa)R_2]$ complexes was explored as potential starting materials for $[M(bppa)R]^+$ species. Alkylation of $[\{Y(bppa)Cl_2\}_2]$ with two equivalents of $LiCH_2SiMe_3$ led to an intractable mixture of products, as did the protonolysis reaction of H(BPPA) and $[Y(CH_2SiMe_3)_3(thf)_2]$. Addition of H(BPPA) to a solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ in pentane at −70 °C resulted in the formation of a colorless precipitate; however upon warming, the reaction mixture turned forest green and finally dark red. $[Zr(bppa)R_3]$ was next targeted as a desirable complex to determine whether a metal–alkyl species could be isolated and potentially aid in identifying the cause of the decomposition of the initial product from the reaction with Y. Though alkylation of $[Zr(bppa)Cl_3]$ failed to yield the desired product, the protonolysis reaction of H(BPPA) and $[Zr(CH_2Ph)_4]$ did lead to the isolation of $[Zr(bppa)(CH_2Ph)_3]$ (Figure 13).

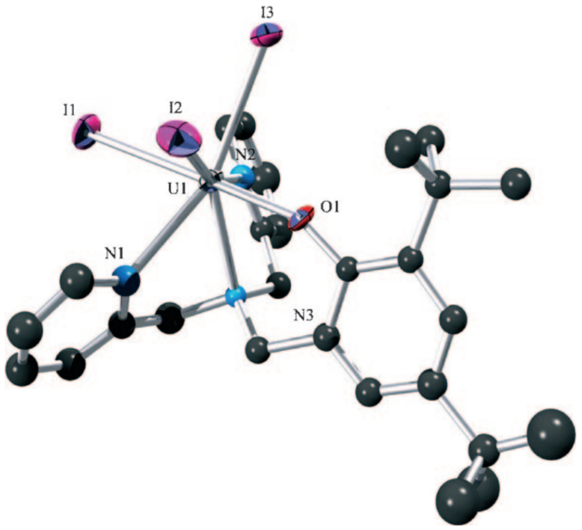


Figure 12. ORTEP diagram of $[U(bppa)I_3]$.

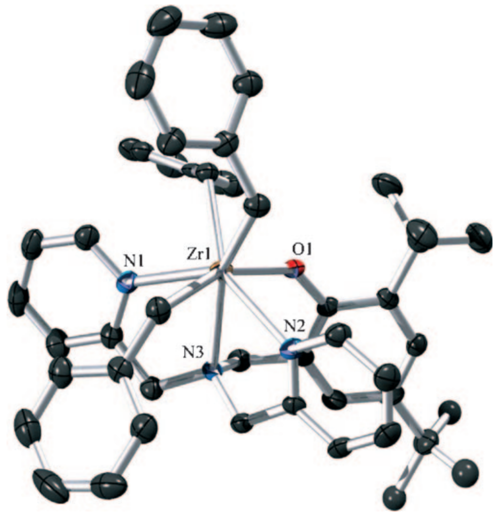
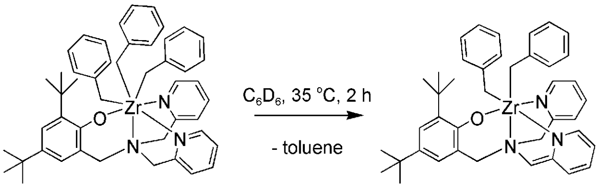


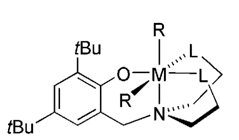
Figure 13. ORTEP diagram of $[Zr(bppa)(CH_2Ph)_3]$.

$[Zr(bppa)(CH_2Ph)_3]$ was found to be stable in the solid-state at room temperature and in solution at −40 °C; however when an NMR sample of $[Zr(bppa)(CH_2Ph)_3]$ in C_6D_6 was allowed to warm to room temperature, the solution color quickly changed from bright orange to dark red. The resulting ^1H NMR spectrum displayed a new set of resonances for an asymmetric molecule as well as the presence of one equivalent of toluene. A series of 1D and 2D NMR experiments were used to identify the metal containing product as $[Zr(bppa')(CH_2Ph)_2]$ (Scheme 5), which results from the intramolecular deprotonation of a 2-picolyl proton by the benzyl group on the metal similar to what was observed by Hessen et al. for $L^{i/j}$ (above), leading to the conversion of



Scheme 5. Transformation of BPPA.

BPPA to a dianion. Reaction of [Zr(bppa)$(CH_2Ph)_3$] with $[H(Et_2O)_2][B(C_6F_5)_4]$ resulted in the formation of the thermally stable cationic species [Zr(bppa)$(CH_2Ph)_2$]$[B(C_6F_5)_4]$. Related work from Bercaw's group examined the tripodal TMDA ligands $L^{k/n-p}$ as well as BPPA with Group 3 metal alkyl complexes for use as ethylene polymerization catalysts (Figure 14).[57] Through protonolysis reactions of $HL^{k/n-p}$ and $[MR_3(thf)_2]$ (M = Sc, Y; R = CH_2SiMe_3, CH_2SiMe_2Ph), a series of LMR_2 complexes were isolated. Attempts to synthesize [Y(bppa)$(CH_2SiMe_3)_2$] were hampered by decomposition. Bercaw et al. also observed deprotonation of the 2-picolyl proton resulting in the transformation of BPPA into a divalent ligand with the dialkyl Sc analogue (above). The bis-alkyl complexes were probed as precatalysts for ethylene polymerization with $[PhNMe_2H][B(C_6F_5)_4]$ and MAO as initiators. Only mild activity was observed in all cases, likely due to the instability of the resulting cationic species.



M = Sc, Y

$L^k = OCH_3$, $L^o = NMe_2$, $L^n = NEt_2$, $L^p = SCMe_3$

R = CH_2SiMe_2Ph, CH_2SiMe_3

Figure 14. Group 3 metal-alkyl complexes supported by alternative TDMA ligands

"Mixed-Donor" Tripodal Ligands

The seminal findings of Fryzuk et al. demonstrated that "mixed-donor" ligands (containing N and P donors) were able to stabilize early-metal–alkyl and –alkylidene complexes as well as low-oxidation-state early metal species.[58,59] The recent work of Mindiola et al. and Ozerov et al. have further shown neutral P*i*Pr$_2$ donor groups to be compatible with reactive early-metal–alkyl, –alkylidene, and –alkylidyne fragments.[60–62] Given this precedence, a "mixed-donor" tripodal TDMA ligand was synthesized. The resulting ligand, $H[N_2P_2]$ (in which $H[N_2P_2]$ = *N-tert*-butylaminodimethylsilylbis(2-di-isopropylphosphinoethyl)amine), can be synthesized in a straight-forward manner on a multigram scale. $Li[N_2P_2]$ was shown to be a useful starting material for the synthesis of a wide range of first-row transition-metal compounds by means of salt metathesis reactions. The first-row metal-halide complexes $[TiCl_2(N_2P_2)]$, $[VBr_2(N_2P_2)]$, $[CrCl_2(N_2P_2)]$, $[MnCl(N_2P_2)]$, $[FeCl(N_2P_2)]$, $[CoCl(N_2P_2)]$, and $[NiBr(N_2P_2)]$ were synthesized and isolated in good yields following the reaction of the metal halide starting material $[MX_3(thf)_3]$ (M = Ti, V, Cr; X = Cl, Br) or MX_2 (M = Mn, Fe, Co, Ni; X = Cl, Br) with $Li[N_2P_2]$.[63] All but the V analogue were structurally characterized, and one feature of these complexes that was revealed from the X-ray diffraction studies was the different coordination modes observed in the solid-state: κ^3-N_2P, κ^3-NP_2, and κ^4-N_2P_2. The electronic and geometric preferences of the metal center appear to dictate the coordination mode of the ligand with more electropositive metals such as Ti preferring coordination of the two harder nitrogen donors over the two phosphine donors (κ^3-N_2P). The converse is true of later metal derivatives such as Mn, Fe, and Co, which all lie in distorted tetrahedral environments with the basal nitrogen uncoordinated (κ^3-NP_2). The solid-state magnetic moments of all the first-row complexes are high spin.

The reduction chemistry of selected complexes supported by the N_2P_2 ligand was explored and resulted in the isolation of the new bridging dinitrogen complexes $[\{TiCl(N_2P_2)\}_2(\mu\text{-}N_2)]$, $[\{Mn(N_2P_2)\}_2(\mu\text{-}N_2)]$, and $[\{Fe(N_2P_2)\}_2(\mu\text{-}N_2)]$ as well as the low-valent monomeric Co^I species $[Co(N_2P_2)]$ (Figure 15).[64,65] Alkylation of $[\{TiCl(N_2P_2)\}_2(\mu\text{-}N_2)]$with two equivalents of $LiCH_2SiMe_3$ led to the isolation of the bis-alkyl bridging dinitrogen complex $[\{TiCH_2SiMe_3(N_2P_2)\}_2(\mu\text{-}N_2)]$ and was the first alkylation of a bridging dinitrogen complex reported. The N–N bond length in $[\{Mn(N_2P_2)\}_2(\mu\text{-}N_2)]$ (1.208(6) Å) is significantly longer than the N–N distance observed in the only other previously known example of a bridging N_2 complex of Mn, $[\{Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2\}_2(\mu\text{-}N_2)]$ (1.118(7) Å). The elongation of the N–N bond likely results from the substitution of π-acidic CO groups for highly basic σ-donors. Unlike $[\{TiCl(N_2P_2)\}_2(\mu\text{-}N_2)]$ and $[\{Mn(N_2P_2)\}_2(\mu\text{-}N_2)]$, the N_2 moiety in $[\{Fe(N_2P_2)\}_2(\mu\text{-}N_2)]$ appears to be labile in solution and the solid-state. When ex-

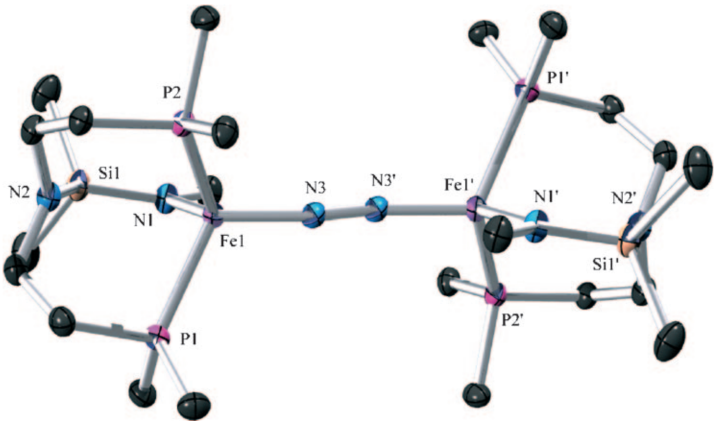
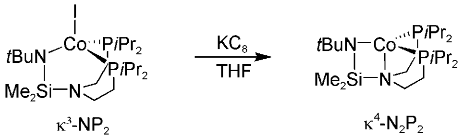


Figure 15. ORTEP diagram of $[\{Fe(N_2P_2)\}_2(\mu\text{-}N_2)]$.

posed to vacuum, dark red [{Fe(N_2P_2)}$_2$(μ-N_2)] changes color to green. The dark red color returns on re-exposure to an atmosphere of N_2. The N–N bond length in [{Fe(N_2P_2)}$_2$(μ-N_2)] is similar to related bridging N_2 complexes (1.166(3) Å). In contrast to the results obtained for the reduction of the Ti, Mn, and Fe analogues, reduction of [CoI(N_2P_2)] resulted in the isolation of monomeric [Co(N_2P_2)]. Following the loss of halide, a change in the coordination mode of the N_2P_2 ligand from κ^3-NP_2 to κ^4-N_2P_2 occurs (Scheme 6).



Scheme 6. Reduction of [CoI(N_2P_2)].

The coordination chemistry of this N_2P_2 ligand with larger second-row metals was explored through the reaction of Li[N_2P_2] with [$ZrCl_4$(thf)$_2$], and [$ZrCl_3$(N_2P_2)] was isolated as a colorless solid. No crystallographic data have been obtained to-date; however, the ^{31}P NMR spectrum contains two non-equivalent phosphorous resonances at 2.59 and 16.38 ppm. These data, along with the ^{1}H NMR spectrum, suggest that the ligand coordinates κ^3-N_2P as was seen with [$TiCl_2$(N_2P_2)] (above). Reduction of [$ZrCl_3$(N_2P_2)] with two equivalents of KC_8 in thf resulted in the formation of the side-on bridged dinitrogen complex [{ZrCl(N_2P_2)}$_2$(μ-η^2:η^2-N_2)] (Figure 16). The ^{31}P NMR spectrum displaces resonances for two isomers in solution with one phosphine donor coordinated (17.08 and 14.46 ppm) and one uncoordinated (1.54 and 0.07 ppm) with similar resonances to those observed for the parent species, [$ZrCl_3$(N_2P_2)]. [{ZrCl(N_2P_2)}$_2$(μ-η^2:η^2-N_2)] contains an extremely long N–N bond length of 1.576(9) Å.

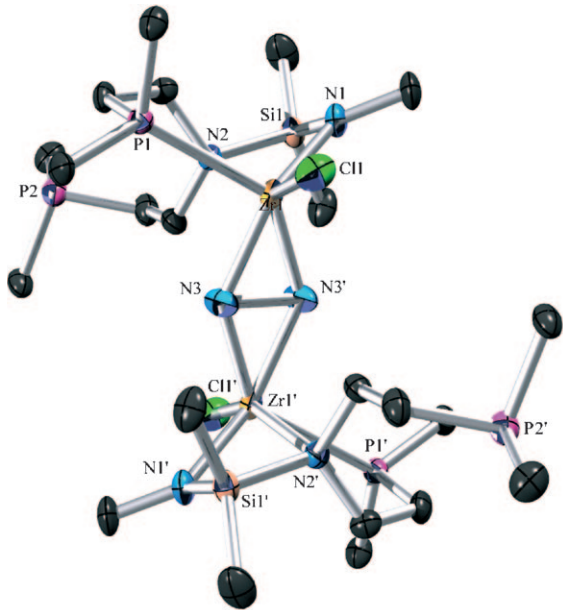


Figure 16. ORTEP diagram of [{ZrCl(N_2P_2)}$_2$(μ-η_2:η_2-N_2)].

The Co^I species [Co(N_2P_2)] was found to react with arylazides to form species with metal-imido character. The addition of phenylazide to a solution of [Co(N_2P_2)] at low temperature resulted in the formation of a dark green precipitate. When allowed to warm to room temperature, the green suspension quickly turned to a dark red solution. Two products were isolated from the reaction mixture following fractional crystallization. The major product, [Co(NHPh)(N_2P_2)], resulted from an imido assisted hydrogen-atom abstraction from the *t*Bu group of the ligand (Figure 17). The second product, [Co{PhN=P*i*Pr_2(CH_2)$_2$NPh}{*t*BuNHSiMe_2N(CH_2)$_2$P*i*Pr_2}], formed following the oxidation of one of the neutral phosphines, followed by C–N bond cleavage and protonation of the original amide functionality of the ligand (Figure 18). The yields of [Co(NHPh)(N_2P_2)] and [Co{PhN=P*i*Pr_2(CH_2)$_2$NPh}{*t*BuNHSiMe_2N(CH_2)$_2$P*i*Pr_2}] were found to be solvent dependent, with the product distribution being attributed to a combination of the BDE of the C–H bonds of the solvent as well as the polarity of the reaction medium. The conversion of 1,2-diphenylhydrazine to azobenzene in the presence of [Co(N_2P_2)] and an arylazide further supported the proposed hydrogen-atom abstraction by a transient Co^{III} imido species. When the green suspension was exposed to an atmosphere of CO at low temperature and allowed to warm, a yellow suspension formed. The Co^I complex [Co(CO)$_2${*t*BuN(C=O)SiMe_2N(CH_2CH_2P*i*Pr_2)$_2$}] and OCNPh were isolated, demonstrating the ability of the Co^{III} imido to perform intermolecular group transfer (Figure 19).

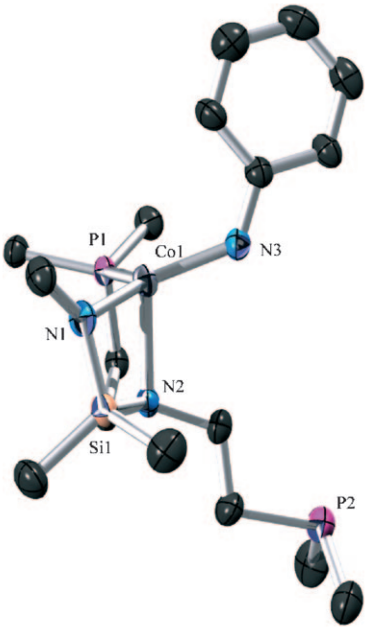


Figure 17. ORTEP diagram of [Co(NHPh)(N_2P_2)].

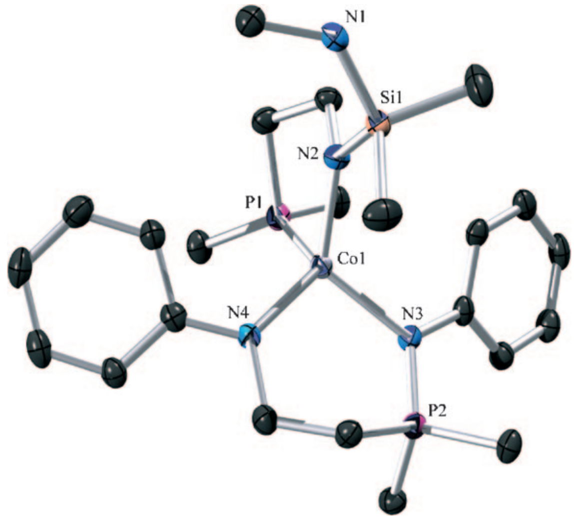


Figure 18. ORTEP diagram of [Co{PhN=P*i*Pr$_2$(CH$_2$)$_2$NPh}{*t*BuNHSiMe$_2$N(CH$_2$)$_2$P*i*Pr$_2$}].

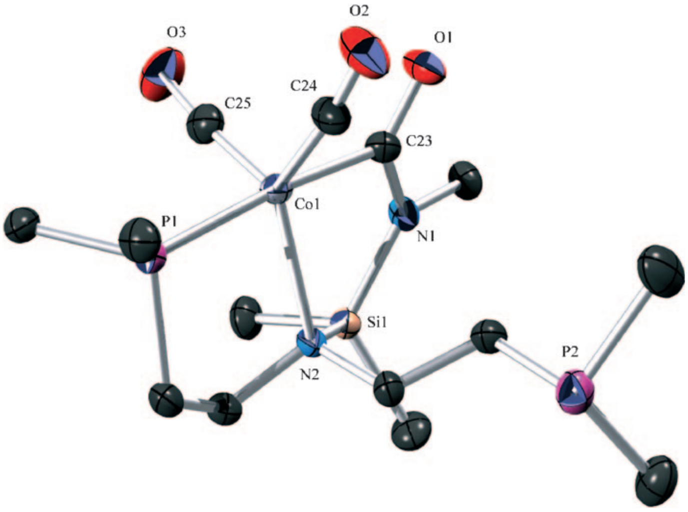


Figure 19. ORTEP diagram of [Co{*t*BuN(C=O)SiMe$_2$N(CH$_2$CH$_2$P*i*Pr$_2$)$_2$}(CO)$_2$].

Conclusions

Recent studies by a number of research groups have demonstrated that TDMA ligands are competent supporting ligands for a wide range of main-group, transition-metal, and f-block chemistry, and substantial progress has been made in these areas to date. Under certain conditions, TDMA ligands allow for the stabilization and isolation of cationic metal–alkyl species as well as reduced metal complexes. Stabilization of these species is achieved either by maintaining a high electron count around the metal center, by providing steric bulk and coordination saturation, or by providing additional donor groups that exhibit hemilable behavior.

Acknowledgements

We are grateful to the US-NSF, DOE, ACS-PRF and AFOSR for financial support of our work.

---

[1] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.
[2] P. P. Power, *J. Organomet. Chem.* **2004**, *689*, 3904–3919.
[3] J. R. Fulton, A. W. Holland, D. J. Fox, R. G. Bergman, *Acc. Chem. Res.* **2002**, *35*, 44–56.
[4] F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481.
[5] P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141.
[6] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3065.
[7] C. Janiak, *Coord. Chem. Rev.* **2006**, *250*, 66–94.
[8] L. C. Liang, *Coord. Chem. Rev.* **2006**, *250*, 1152–1177.
[9] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943–980.
[10] J. L. Karn, D. H. Busch, *Inorg. Chem.* **1969**, *8*, 1149–1153.
[11] C. M. Che, S. T. Mak, W. O. Lee, K. W. Fung, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **1988**, 2153–2159.
[12] M. V. Baker, B. W. Skelton, A. H. White, C. C. Williams, *Organometallics* **2002**, *21*, 2674–2678.
[13] S. Autzen, H. G. Korth, R. Boese, H. de Groot, R. Sustmann, *Eur. J. Inorg. Chem.* **2003**, 1401–1410.
[14] M. Ohashi, M. Konkol, I. D. Rosal, R. Poteau, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2008**, *130*, 6920–6921.
[15] P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404–2433.
[16] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3066.
[17] A. M. Neculai, H. W. Roesky, D. Neculai, J. Magull, *Organometallics* **2001**, *20*, 5501–5503.
[18] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, H. G. Schmidt, M. Noltemeyer, *J. Organomet. Chem.* **2002**, *643*, 47–52.
[19] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, R. Herbst-Irmer, *Organometallics* **2003**, *22*, 2279–2283.
[20] G. B. Nikiforov, H. W. Roesky, T. Labalm, D. Vidovic, D. Neculai, *Eur. J. Inorg. Chem.* **2003**, 433–436.
[21] A. M. Neculai, D. Neculai, H. W. Roesky, J. Magull, *Polyhedron* **2004**, *23*, 183–187.
[22] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, B. Walfort, D. Stalke, *Angew. Chem.* **2002**, *114*, 4470–4472; *Angew. Chem. Int. Ed.* **2002**, *41*, 4294–4296.
[23] J. M. Fritsch, K. A. Thoreson, K. McNeill, *Dalton Trans.* **2006**, 4814–4820.
[24] M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2005**, *44*, 8004–8010.
[25] C. M. Cui, G. R. Giesbrecht, J. A. R. Schmidt, J. Arnold, *Inorg. Chim. Acta* **2003**, *351*, 404–408.
[26] G. R. Giesbrecht, C. M. Cui, A. Shafir, J. A. R. Schmidt, J. Arnold, *Organometallics* **2002**, *21*, 3841–3844.
[27] J. Schmidt, J. Arnold, *Organometallics* **2002**, *21*, 3426–3433.
[28] B. Qian, L. Henling, J. Peters, *Organometallics* **2000**, *19*, 2805–2808.
[29] J. A. R. Schmidt, G. R. Giesbrecht, C. M. Cui, J. Arnold, *Chem. Commun.* **2003**, 1025–1033.
[30] J. L. Schneider, J. A. Halfen, V. G. Young, W. B. Tolman, *New J. Chem.* **1998**, *22*, 459–466.
[31] J. A. Halfen, B. A. Jazdzewski, S. Mahapatra, L. M. Berreau, E. C. Wilkinson, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1997**, *119*, 8217–8227.
[32] B. A. Jazdzewski, A. M. Reynolds, P. L. Holland, V. G. Young, S. Kaderli, A. D. Zuberbuhler, W. B. Tolman, *J. Biol. Inorg. Chem.* **2003**, *8*, 381–393.
[33] J. Müller, A. Kikuchi, E. Bill, T. Weyhermuller, P. Hildebrandt, L. Ould-Moussa, K. Wieghardt, *Inorg. Chim. Acta* **2000**, *297*, 265–277.
[34] A. Sokolowski, J. Muller, T. Weyhermuller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **1997**, *119*, 8889–8900.

[35] A. Sokolowski, B. Adam, T. Weyhermuller, A. Kikuchi, K. Hildenbrand, R. Schnepf, P. Hildebrandt, E. Bill, K. Wieghardt, *Inorg. Chem.* **1997**, *36*, 3702–3710.
[36] D. A. Robson, L. H. Rees, P. Mountford, M. Schroder, *Chem. Commun.* **2000**, 1269–1270.
[37] S. Y. Bylikin, D. A. Robson, N. A. H. Male, L. H. Rees, P. Mountford, M. Schroder, *J. Chem. Soc. Dalton Trans.* **2001**, 170–180.
[38] M. E. G. Skinner, B. R. Tyrrell, B. D. Ward, P. Mountford, *J. Organomet. Chem.* **2002**, *647*, 145–150.
[39] J. D. Gardner, D. A. Robson, L. H. Rees, P. Mountford, *Inorg. Chem.* **2001**, *40*, 820–824.
[40] S. Bambirra, D. van Leusen, C. G. J. Tazelaar, A. Meetsma, B. Hessen, *Organometallics* **2007**, *26*, 1014–1023; C. G. J. Tazelaar, A. Meetsma, B. Hessen, *Organometallics* **2007**, *26*, 1014–1023.
[41] S. Bambirra, A. Meetsma, B. Hessen, A. P. Bruins, *Organometallics* **2006**, *25*, 3486–3495.
[42] S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2001**, 637–638.
[43] C. G. J. Tazelaar, S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* **2004**, *23*, 936–939.
[44] S. Bambirra, S. J. Boot, D. van Leusen, A. Meetsma, B. Hessen, *Organometallics* **2004**, *23*, 1891–1898.
[45] S. Groysman, E. Sergeeva, I. Goldberg, M. Kol, *Inorg. Chem.* **2005**, *44*, 8188–8190.
[46] S. Groysman, E. Sergeeva, I. Goldberg, M. Kol, *Eur. J. Inorg. Chem.* **2006**, 2739–2745.
[47] A. R. F. Cox, V. C. Gibson, E. L. Marshall, A. J. P. White, D. Yeldon, *Dalton Trans.* **2006**, 5014–5023.
[48] Y. Inoue, K. Matyjaszewski, *Macromolecules* **2003**, *36*, 7432–7438.
[49] I. Westmoreland, J. Arnold, *Dalton Trans.* **2006**, 4155–4163.
[50] S. Yan, L. Que, L. Taylor, O. Anderson, *J. Am. Chem. Soc.* **1988**, *110*, 5222–5224.
[51] R. Viswanathan, M. Palaniandavar, T. Balasubramanian, T. P. Muthiah, *Inorg. Chem.* **1998**, *37*, 2943–2951.
[52] N. Reddig, D. Pursche, B. Krebs, A. Rompel, *Inorg. Chim. Acta* **2004**, *357*, 2703–2712.
[53] Y. Shimazaki, S. Huth, S. Karasawa, S. Hirota, Y. Naruta, O. Yamauchi, *Inorg. Chem.* **2004**, *43*, 7816–7822.
[54] A. Trösch, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **1998**, 827–832.
[55] R. Uma, R. Viswanathan, M. Palaniandavar, M. Lakshminarayanan, *J. Chem. Soc. Dalton Trans.* **1994**, 1219–1226.
[56] W. A. Chomitz, S. G. Minasian, A. D. Sutton, J. Arnold, *Inorg. Chem.* **2007**, *46*, 7199–7209.
[57] S. C. Marinescu, T. Agapie, M. W. Day, J. E. Bercaw, *Organometallics* **2007**, *26*, 3264–3264.
[58] M. D. Fryzuk, S. S. H. Mao, M. J. Zaworotko, L. R. Macgillivray, *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337.
[59] M. D. Fryzuk, T. S. Haddad, S. J. Rettig, *J. Am. Chem. Soc.* **1990**, *112*, 8185–8186.
[60] B. C. Bailey, H. J. Fan, J. C. Huffman, M. H. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 8781–8793.
[61] L. C. H. Gerber, L. A. Watson, S. Parkin, W. Weng, B. M. Foxman, O. V. Ozerov, *Organometallics* **2007**, *26*, 4866–4868.
[62] W. Weng, L. Yang, B. M. Foxman, O. V. Ozerov, *Organometallics* **2004**, *23*, 4700–4705.
[63] W. A. Chomitz, S. F. Mickenberg, J. Arnold, *Inorg. Chem.* **2008**, *47*, 373–380.
[64] W. A. Chomitz, J. Arnold, *Chem. Commun.* **2007**, 4797–4799.
[65] W. A. Chomitz, J. Arnold, *Chem. Commun.* **2008**, 3648–3650.