New tripodal N-heterocyclic carbene chelators for small molecule activation

Xile Hu, Karsten Meyer

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, La Jolla, CA 92093-0358, USA

Received 6 June 2005; received in revised form 27 July 2005; accepted 27 July 2005

Available online 25 October 2005

Abstract

In an effort to develop new tripodal N-heterocyclic carbene (NHC) ligands for small molecule activation, two new classes of tripodal NHC ligands TIME R and TIMEN R have been synthesized. The carbon-anchored tris(carbene) ligand system TIME R (R = Me, t-Bu) forms bi- or polynuclear metal complexes. While the methyl derivative exclusively forms trinuclear 3:2 complexes [(TIME Me)2M3]3+ with group 11 metal ions, the tert-butyl derivative yields a dinuclear 2:2 complex [(TIME t-Bu)2Cu2]2+ with copper(I). The latter complex shows both "normal" and "abnormal" carbene binding modes and accordingly, is best formulated as a bis(carbene)alkenyl complex. The nitrogen-anchored tris(carbene) ligands TIMEN R (R = alkyl, aryl) bind to a variety of first-row transition metal ions in 1:1 stoichiometry, affording monomeric complexes with a protected reactivity cavity at the coordinated metal center. Complexes of TIMEN R with Cu(I)/(II), Ni(0)/(I), and Co(I)/(II)/(III) have been synthesized. The cobalt(I) complexes with the aryl-substituted TIMEN R (R = mesityl, xylyl) ligands show great potential for small molecule activation. These complexes activate for instance dioxygen to form cobalt(III) peroxo complexes that, upon reaction with electrophilic organic substrates, transfer an oxygen atom. The cobalt(I) complexes are also precursors for terminal cobalt(II) imido complexes. These imido complexes were found to undergo unprecedented intra-molecular imido insertion reactions to form cobalt(II) imine species. The molecular and electronic structures of some representative metal NHC complexes as well as the nature of the metal–carbene bond of these metal NHC complexes was elucidated by X-ray and DFT computational methods and are discussed briefly. In contrast to the common assumption that NHCs are pure σ-donors, our studies revealed non-negligible and even significant π-backbonding in electron-rich metal NHC complexes.

© 2005 Elsevier B.V. All rights reserved.

Keywords: N-Heterocyclic carbene; Tripodal ligand; Coordination compounds; Small molecule activation; X-ray structure; Bonding

Contents

1. Introduction .................................................................................. 5475
2. Carbon-anchored tris(carbene) ligand systems and their coordination chemistry ......................................................... 5477
   2.1. The TIME Me Ligand ................................................................. 5477
   2.2. The TIME t-Bu ligand and its coordination to copper(I) ............ 5478
   2.3. Nature of the metal–carbene bond ........................................... 5479
3. Nitrogen-anchored tris(carbene) ligand systems and their coordination chemistry ......................................................... 5480
   3.1. The TIMEN alkyl ligand ............................................................ 5480
   3.2. The TIMEN Ar ligand system and its coordination to cobalt .......... 5481
   3.3. Dioxygen activation and imido-transfer reactions assisted by cobalt tris(carbene) complexes ................................. 5481

* Corresponding author.
E-mail address: kmeyer@ucsd.edu (K. Meyer).

1 Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, MC 127-72, Pasadena, CA 91125, USA.

0022-328X/S - see front matter © 2005 Elsevier B.V. All rights reserved.
1. Introduction

Chelating ligands that enforce tripodal topologies at coordinated metal centers are known to provide powerful platforms for small molecule activation and often hold several advantages over mono-dentate and even bidentate ligands: (1) due to the enhanced chelating effects, tripodal ligands often bind to metal ions very strongly and can be used to stabilize reactive intermediate species with unusual electronic and geometric structures; (2) the steric bulk of tripodal ligands is highly tunable allowing for controlled reactivity at the metal center, bulky ligands are often easily synthesized; and (3) the anchoring units of tripodal ligands not only provide the ligands with additional electronic and structural flexibility, but also effectively block undesired side- and decomposition reactions. Due to these distinctive benefits, the design and development of new tripodal ligand systems has been an active area in inorganic and organometallic chemistry [1–4].

The most commonly used tripodal ligands are perhaps the tris(pyrazolyl)borate (Tp) ligand and its derivatives [1]. Metal complexes supported by tris(pyrazolyl)borate ligands have been used extensively to promote catalytic transformations such as C-H activation [5], C-C [6], C-O [7], and C-N [8] bond formation, assist dioxygen activation [9], and serve as structural mimics of metal-containing enzymes [10]. For small molecule activation, however, tripodal tris(amido)amine and tris-phosphine ligands have drawn much attention recently. The tetradeutate tris(amido)amine framework, comprising three negatively charged “hard” [11] amido donors, binds to transition metal [2,12] and main group elements [13] in 3+ or higher oxidation states. The resulting metal complexes contain a pair of degenerate π-type frontier orbitals that aid metal–ligand multi-bond formation [2] that has been proven to be essential for supporting well-defined catalytic reactions like dinitrogen reduction at a single molybdenum center [14,15]. Schrock and co-workers showed that the sterically encumbering tris(amido)amine ligand [HIPTN₃N]₃⁻ (L, with N₃N=(NCH₂CH₂)₃N, HIPT = 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃) supports the molybdenum center and many of the intermediate species of a monometallic reduction of dinitrogen could be identified and isolated. These intermediates include LMo(N₂) (1) (Fig. 1), LMo–N=N–H (2), [LMo=N=N–H₂]@[BAr₄] (3), LMo=N=N–H–(BAr₄) (5), [LMo(NH₃)][BAr₄] (6), LMo=N=NH, and LMo(NH₃). Remarkably, the same authors also demonstrated that dinitrogen can in fact be reduced catalytically by complexes 1, 2, 4, or 6 using a mild chemical reducing agent and an organic proton source [14].

The substituents on the three amido donors are often designed to alter and optimize the steric properties of the tris(amido)amine ligands. Borovik [3], for instance, have incorporated functional groups into the N₃N framework to influence the secondary coordination sphere around the metal ions. The ligand tris((N’-tert-butyleureayl)-N-ethylene)amine (H₃buea), with three ureayl groups forming the reactivity pocket of the [(H₃buea)M]^n⁺ complex, has the ability to H-bond with apical coordinating ligands, thereby stabilizing reactive intermediates. The iron(II) and manganese(II) complexes of this bio-inspired ligand mimic the function of proteins (i.e., H-bonding, immobilization, steric protection) and are competent to activate dioxygen to form the corresponding oxo complexes [(H₃buea)M]O]^n⁻ (M = Fe (7), Mn) [16]. The normally highly reactive Fe–O unit is confined within the rigid H-bond cavity (Fig. 2). Due to this stabilizing effect of the tripodal chelator, the complex was the first ever structurally characterized molecular iron species with a terminal oxo ligand. This dioxygen activation assisted by the [(H₃buea)M]^n⁻ platform beautifully illustrates the benefits and versatility of tripodal ligands for small molecule activation.

In contrast to the tris(amido)amine ligands, tripodal ligands bearing “soft” donor atoms such as sulfur [17] and phosphorus [4,18] are more suitable for stabilizing electron-rich low-valent metal centers.
Betley and Peters [4,19] showed that late metal complexes of mono anionic tris(phosphino)borate ligands not only bind to π-acceptor ligands (e.g., N₂, CO and NO⁺), but also bind to strong π-donor ligands (e.g., NR²⁻ and N³⁻), which are traditionally incompatible with “soft” metal centers [20,21]. The electronic flexibility of these ligands make them very attractive scaffolds for multi-electron redox chemistry such as dinitrogen reduction and for the synthesis of intriguing L₁M=E or L₁M=E species (L = P, M = Fe, Co, Ni, Cu, E = O, N, etc.). For instance, the complexes [(PhBP₃)₃M(PMe₃)] / PhBP₃=PhB(CH₂PPh₂)₃, M = Co, Fe) can aid the two-electron oxidative nitrene transfer from organic azides by forming terminal imido complexes [(PhBP₃)M=N-N-p-tolyl] [20]. Moreover, the complexes [(PhBP₃Pr)M]n (PhBP₃Pr = PhB(CH₂P(μ-Pr)₂), M = Fe, Co) contain a single binding site for coordination of N₂, diazenido (N₂Me), and imido (NR) ligands. The N₂ coordination by the 4-coordinate iron has been established for the formal oxidation states M(0), M(+0.5), and M(+1) [19]. Most spectacularly, the terminal iron(IV) nitrido species [(PhBP₃Pr)Fe=NN] (8) has been synthesized and spectroscopically characterized (Fig. 3) [21]. The nitrido functionality, however, is sterically not well protected and has a tendency to undergo a nitride coupling reaction to form the N₂-bridged complex [(PhBP₃Pr)FeN₂(μ-N₂)], an unprecedented six-electron redox event. The electronic properties of these strong-field tris(phosphine) ligands are also interesting. Depending on the nature of the substituents on the phosphorus donors and the axial ligands, a pseudo-tetrahedral cobalt(II) complex of the general formula [L₃CoL²⁺] can be either low spin, high spin, or exhibit spin-crossover phenomena [4,22].

Inspired by this rich chemistry of tris(amido)amine and tris(phosphine) ligands, we set out to develop N-heterocyclic carbene (NHC) analogues of these ligands. We expected tripodal NHC chelators to inherit many of the unique properties of monodentate NHC ligands and thus have very distinctly beneficial electronic and steric properties over known tripodal ligand systems. In addition, coordinated NHC ligands are less susceptible to oxidative ligand degradation than phosphine ligands and therefore are potentially advantageous for reactions such as dioxygen activation.

Recent studies suggest that the seemingly “soft” NHCs not only bind to the “soft”, electron-rich metal fragments, but are also capable to stabilize the “hard”, electron-deficient metal centers [23–25]. In fact, NHCs can coordinate to virtually every metal in the periodic table, in both low and high oxidation states [23]. The newly developed tripodal NHC ligands thus are complementary to both the Schrock-type tris(amido)amine ligand system and the Peters-type tris(phosphino)borate ligand system.

The geometries of most other tripodal ligand systems are regulated by the various organic substituent directly linked to the donor atoms (Fig. 4, Types I and II). Upon coordination these substitutes often point away from the metal center. This in turn leaves the reactive site of the complex wide open (see arrows in Fig. 4) encouraging binuclear decomposition of reactive species. Accordingly, Betley and Peters [21] report that the bulky iso-propyl derivatized tris(phosphino)-borate ligand does not prevent dimerization of the highly reactive terminal nitrido complex [(PhBP₃Pr)Fe=NN] to form a dinitrogen bridged dinuclear species [(PhBP₃Pr)FeN₂(μ-N₂)]. Also, in order to prevent [(ArN₃N)Mo=NN] from forming the dinuclear complex [([(ArN₃N)Mo]=N]₂ [μ:η¹:N₁=N₂]], Yandulov and Schrock [14] had to introduce three exceedingly bulky hexa-isopropyl terphenyl substituents at the tris(amido)amine ligand. The synthesis of these “ultra-bulky” ligand derivatives is often challenging and time-consuming.

In contrast, the sterics of tripodal NHC ligands are controlled by the substituents at the imidazole N3 position (Fig. 4, Type III). We could show that in metal complexes of tripodal NHC ligands the substituents on the sp²-hybridized ring nitrogen can align perpendicularly to the coordinated metal centers, thereby forming a deep (5–6 Å), well-protected cavity for ligand binding. Therefore, less bulky alkyl or aryl substituents are sufficient to stabilize reactive species.

Prior to our work, only two tripodal NHC ligand systems were known. The mesitylene-anchored tris(carbene) ligand (Fig. 5, 9) was the only isolated tris(carbene) ligand [26], yet metal complexation had not been achieved with this ligand. Nakai and co-workers [27] thoroughly investigated the coordination chemistry of 9 and its derivatives and found that the cavity of this ligand system can only host exceptionally large metal ions, such as the thallium(I) cation. Attempts to synthesize transition metal complexes of derivatives of 9 were unsuccessful. Fehlhammer et al. [28] synthesized and reported the lithium salts of carbene

![Fig. 3. The terminal iron(IV) nitrido complex ([(PhBP₃Pr)Fe=NN] supported by a tris(phosphino)borate ligand.](Image 305x630 to 549x724)
analogues of tris(pyrazolyl)borate-type ligands. These monoanionic ligands tend to form transition metal complexes with two tripodal ligand molecules chelating one metal ion (Fig. 5, 10) [28]. The resulting hexakis(carbene) complexes contain coordinatively saturated metal ions and no additional ligand binding and inner-sphere redox events were observed. Furthermore, the free carbene ligands are very reactive and could not be isolated to date.

We thus decided to develop new tripodal NHC ligand systems to stabilize a single transition metal center in a coordinatively unsaturated ligand environment that would allow the binding and activation of small molecules in a controlled manner. In this review we summarize some of this exploratory work. In particular, we describe the synthesis of two new classes of tripodal NHC ligands TIME\textsuperscript{R} (1,1,1-tris(3-alkylimidazol-2-ylidene)[methyl]ethane) and TIMEN\textsuperscript{R} (tris-[2-(3-alkylaryl-imidazol-2-ylidene)ethyl]amine, “N” for “amine” anchor) and their coordination to transition metal ions. The reactivity of certain tris(carbene) complexes with respect to small molecule activation as well as some interesting findings on the nature of metal–NHC bond are also reported (see Scheme 1).

2. Carbon-anchored tris(carbene) ligand systems and their coordination chemistry

2.1. The TIME\textsuperscript{Me} Ligand

The three pendent arms of the neo-pentane based tripodal NHC chelator 1,1,1-tris(3-alkylimidazol-2-ylidene)-[methyl]ethane (TIME\textsuperscript{Me}) are anchored by a single carbon atom and the resulting binding cavity has the appropriate size to host a transition metal ion. The imidazolium precursors of the free monodentate carbenes are accessible following the methods reported by Dias and Jin [26] for the preparation of mesitylene-anchored tris(carbene) ligand 9. The methyl derivative of the ligand (TIME\textsuperscript{Me}) could only be prepared in situ, by deprotonation of the [H\textsubscript{3}TIME\textsuperscript{Me}]-[PF\textsubscript{6}]\textsubscript{3} salt with a strong base. Attempts to isolate the TIME\textsuperscript{Me} ligand were unsuccessful, and complexation of transition metals with the in situ generated carbene had limited success [29]. Metal complexes of TIME\textsuperscript{Me} can be prepared, however, via the transmetallation method developed by Wang and Lin [30]. Treatment of [H\textsubscript{3}TIME\textsuperscript{Me}]Br\textsubscript{3} (11) with Ag\textsubscript{2}O in DMSO affords the trinuclear silver complex [(TIME\textsuperscript{Me})\textsubscript{2}Ag\textsubscript{3}][PF\textsubscript{6}]\textsubscript{3} (12), which serves as a carbene transfer agent and reacts with copper(I) bromide and (dimethylsulfide)gold(I) chloride to form the corresponding...
copper(I) and gold(I) complexes \([\text{TIME}^\text{Me}_2\text{Cu}]_3\text{PF}_6\) (13) and \([\text{TIME}^\text{Me}_2\text{Au}_3\text{PF}_6\) (14) (Scheme 2) [29,31].

X-ray diffraction analysis revealed iso-structural geometries for all three trinuclear complexes. In each complex, three metal ions are coordinated to two molecules of the \text{TIME}^\text{Me} ligand (Fig. 6). Each metal ion is coordinated to two carbenoid carbon atoms, each of which stems from a different ligand. The structure exhibits a \(D_3\) symmetry with the threefold axis passing through the anchoring C atoms of the two ligands.

The metal–carbene bond distances in these complexes (2.082(2) Å for Ag, 1.9124(16) Å for Cu, and 2.035(12) Å for Au) are within the range of reported values for typical group 11 metal NHC complexes [32–34]. The metal carbenes are almost linear, with a C–M–C bond angle of 178.56(13), 177.70(9), and 177.7(6) for Ag, Cu, and Au, respectively. The imidazole units in the structures of 12–14 exhibit structural parameters typically observed for coordinated NHC ligands. There are no inter- or intra-molecular metal–metal interactions in these complexes.

### 2.2. The \text{TIME}^{\text{t-Bu}} ligand and its coordination to copper(I)

The formation of trinuclear complexes 12–14 reflects the tendency of group 11 metal ions to form linear, two-coordinate complexes. As a result, the metal centers of these complexes are not situated in a well-protected cavity as desired. In order to prevent the formation of polynuclear species, we decided to increase the steric bulk at the \text{TIME}^\text{Me} ligand by synthesizing the \text{t}er\text{-}t\text{u}t\text{-}b\text{u}l\text{y}l derivative \text{TIME}^{\text{t-Bu}}.

Deprotonation of the imidazolium salt \([\text{H}_3\text{TIME}^{\text{t-Bu}}]_3\text{PF}_6\) with three equivalents of potassium \text{t}er\text{-}t\text{u}t\text{-}b\text{u}l\text{y}l yielded the free carbene \text{TIME}^{\text{t-Bu}} (15), which was isolated and fully characterized [35]. Reaction of one equivalent of 15 with \([\text{CH}_3\text{CN}]_2\text{Cu}_3\text{PF}_6\) affords the copper complex \([\text{TIME}^{\text{t-Bu}}]_3\text{Cu}_3\text{PF}_6\) (16) (Scheme 3).

The X-ray crystallographic analysis of 16 reveals a dimeric structure, in which two copper ions are coordinated to two ligand molecules (Fig. 7). Each copper ion is situated in a trigonal planar carbene/alkenyl carbon ligand environment. Two carbenes stem from one chelator, while a third carbon is provided by the pendent arm of a second chelator, which, with its two remaining pendent arms, coordinates to a symmetry-related second copper center. The average Cu–C bond distance is 1.996(1) Å, consistent with that of other reported Cu(I) carbene complexes [34].
Interestingly, the X-ray structure of 16 reveals the existence of an “alkenyl” binding mode within the Cu–C entity. Two of the three carbon chelators coordinated to the copper ion are “normal” diamino carbene centers, i.e., the C2 carbon of the imidazole rings (Scheme 3). The third carbon chelator formally is the C5 backbone atom of the imidazole ring structure. The carbon donor can thus be considered an alkenyl functionality; a formulation which is further supported by NMR spectroscopy [35]. Although this type of metal binding to N-heterocyclic carbene ligands was previously reported for complexes synthesized directly from imidazolium salts [36], this is the first example of this binding mode generated by metal coordination to the free carbene starting material.

2.3. Nature of the metal–carbene bond

In recent years, NHCs were almost exclusively referred to as pure σ-donors [23,25]. This is merely based on the fact that in most metal NHC complexes, the metal–carbene bond distances are close to that of a “normal” single bond [23]. In general, there is a lack of rigorous theoretical studies on metal NHC complexes, especially on the electronic nature of metal–carbene bonds. Nevertheless, several studies suggest various degrees of π-bonding in transition metal NHC complexes [37,38]. We applied DFT computational methods to thoroughly study the electronic structures of the TIME\textsuperscript{Me} group 11 metal complexes 12–14 and related late metal NHC complexes [29]. In this study, we applied orbital diagram and energy decomposition analyses to elucidate the nature of the metal–carbene bond.

The metal–ligand interactions of 12–14 were analyzed using a “fragment approach”. This approach is based on a molecular orbital interaction diagram comprising the M\textsubscript{1} and L\textsubscript{1} fragment of the M\textsubscript{1}L\textsubscript{2} complexes. Analysis of the corresponding molecular orbitals (MOs) allows for deriving σ- and π-backbonding models for the metal–ligand electronic interactions involved. For example, the complex [(TIME\textsuperscript{Me})\textsubscript{2}Cu\textsubscript{3}](PF\textsubscript{6})\textsubscript{3} (13) this qualitative molecular orbital diagram reveals both σ-bonding and π-backbonding between the metal and the ligand fragments [29]. The σ-bonding results from interaction of the filled σ-orbitals of the ligand fragment with the partially empty 3d\textsubscript{z2} + 4s hybrid orbitals, as well as the empty 4p\textsubscript{x} orbitals of the metal fragment. The π-backbonding results from interaction of partially empty π/π\textsuperscript{*} orbitals of the ligand fragment with the filled 3d\textsubscript{xy/yz} metal orbitals. Representative σ- and π-orbitals are shown in Fig. 8.

This π-backbonding contribution between the metal ions and NHC ligands is not limited to complex 13. In fact, calculations on complex 12, 14, and a D\textsubscript{2h}-symmetric bis-carbene complex Pd(CN\textsubscript{2}Bu\textsubscript{2}C\textsubscript{5}H\textsubscript{5})\textsubscript{2} (17) [39], also revealed varying degrees of π-interactions.

The nature of the M–C\textsubscript{carbene} bond in complexes 12–14 and 17 was additionally explored using the Ziegler and Rauk energy-decomposition schemes [29,40]. According to this analysis, the ratio of σ-donation/π-backdonation (d/b value) in 17 is 2.2, and the π-bonding contributes 30% to the overall stabilizing orbital interaction energy (calculated with D\textsubscript{2h}-symmetric model complexes M(IM\textsuperscript{Me}C\textsubscript{5}H\textsubscript{5})\textsubscript{2}). For complexes 12–14, the d/b ratios are approximately 5.6, 4.4, and 5.8, respectively. Thus, in these less electron-rich compounds, the π-bonding contributes to approximately 15–18% of the overall stabilizing orbital interaction energy [29].

The foregoing study leads to the conclusion that, unlike commonly assumed, NHCs are not only excellent σ-donors, but also fairly good π-acceptors. Although, the covalent bonding energy represents only a fraction of the total metal-NHC bonding energy, it is important to recognize these potential π-acceptor properties of NHC ligands.

In complexes of electron rich metal centers, π-backbonding can be significant and often contributes up to 20–30% of the orbital interaction energy of a metal NHC complex, e.g., in palladium complex 17 or in iridium complex [Cp(NHC)Ir=CH\textsubscript{2}] [38]. Our calculations of the latter iridium complex established 20% π-backbonding in the NHC–Ir fragment. A Schrock-type metal–carbene fragment {M=CH\textsubscript{2}} can be seen as a benchmark example for σ-bonding/π-backbonding interactions in a carbene–metal fragment. It has previously been established that for this fragment the π-backbonding contributes 25% to the covalent bonding energy [38].

Additionally, there is structural evidence for the existence of π-bonding interactions in electron-rich metal NHC complexes. For example, Arduengo et al. [32,41] prepared a series of bis(carbene) complexes (IM\textsuperscript{Me}C\textsubscript{5}H\textsubscript{5})\textsubscript{2}M (with IM\textsuperscript{Me}C\textsubscript{5}H\textsubscript{5} = 1,3-dimesitylimidazol-2-ylidene, M = Ni(0), Ag(I), and I\textsuperscript{−}). These complexes are iso-structural and
possess the same set of NHC ligands. It was found that from I⁺ (electron poor, not capable of \(\pi\)-backbonding) to Ag⁺ (less electron-rich, capable of \(\pi\)-backbonding) to Ni(0) (electron-rich, very capable of \(\pi\)-backbonding), the average C–N bond lengths of the NHC fragments increase from 1.346 Å in [(IM\(_{12}\)C\(_3\))I]\(^+\), to 1.358 Å in [(IM\(_{12}\)mes-C\(_2\))Ag]\(^+\), to 1.375 Å in [(IM\(_{12}\)mes-C\(_2\))Ni]. This was attributed to decreased nitrogen-carbene \(\pi\)-bonding as a result of increased \(\pi\)-backbonding from the metal to NHC ligand.

We synthesized the Ni(0) and Ni(I) complexes of the tris(carbene) ligand TIMEN\(_{3}\)alu and, for the Ni(0) complex, found a significant shorter Ni–C bond distance (vide infra) [42]. We attribute this to a higher degree of \(\pi\)-backbonding in the Ni(0) complex.

Since the publication of our work on this topic, a few other reports emerged confirming the presence of \(\pi\)-bonding in metal NHC complexes. For instance, Frenking et al. [43] carried out similar DFT studies on group 11 metal NHC complexes and concluded that the R\(_2\)C \(\rightarrow\) ML\(_n\) \(\pi\) back-donation in complexes with N-heterocyclic carbenes is not substantially lesser than in classical Fischer carbene complexes bearing two \(\pi\) donor groups R. Lin et al. [44] prepared Au(I) NHC complexes and found that the elongated N–C\(_{\text{carbene}}\) bond distances in these complexes are consistent with non-negligible metal–NHC \(\pi\)-backbonding.

3. Nitrogen-anchored tris(carbene) ligand systems and their coordination chemistry

3.1. The TIMEN\(_{\text{alkyl}}\) ligand

The fact that tripodal carbene ligands TIME\(_{\text{Me}}\) and bulky TIME\(_{\text{Bu}}\) do not form simple tridentate \(\kappa^3\) complexes reflects a fundamental problem associated with this class of ligands. Examination of the backbones of these neo-pentane-based, carbon-anchored tripod ligands reveals possible reasons for the lack of 1:1 complex formation. A hypothetical \(\kappa^3\) complex of TIME would contain three eight-membered rings (Fig. 9, I) with much lower stability than the more commonly observed five-, six- or seven-membered rings formed, for instance, by poly(pyrazolyl)borate or poly(phosphine) ligands. In order to overcome these inherent deficits of TIME, we sought to incorporate a coordinating atom at the anchoring position of the carbene tripod, engendering ligands that favor 1:1 metal complexation by forming three stable six-membered rings (Fig. 9, II).

![Fig. 9. Structural models of carbon- and nitrogen-anchored tris(carbene) metal complexes.](image)

Accordingly, the nitrogen-anchored tris(carbene) ligand system tris[2-(3-alkylimidazol-2-ylidene)ethyl]amine (TIME\(_{\text{alkyl}}\)) was synthesized. The imidazolium precursors [H\(_3\)TIME\(_{\text{alkyl}}\)]\(^+\) were prepared by quaternization of functionalized N-alkylimidazoles with tris(2-chloroethyl)amine. Deprotonation of the imidazolium salts with potassium tert-butoxide yields the free carbenes TIMEN\(_{\text{alkyl}}\).

Monomeric copper(I) tris(carbene) complexes can be prepared by reacting TIMEN\(_{\text{alkyl}}\) with copper(I) salts. The X-ray structures of [(TIME\(_{\text{alkyl}}\)Cu)]\(^+\) complexes (R = tert-butyl (21), benzyl (Bz, 22)) show that the TIMEN\(_{\text{alkyl}}\) ligand coordinates to the copper(I) ion via the three carbene carbons in the predicted \(\kappa^3\)-fashion (Fig. 10) [45].

The Cu–C distances of 1.95–2.00 Å compare well with bond distances found for other Cu(I) NHC complexes [34]. The cuprous center is located in the plane of the three carbenes, with the sum of the three C–Cu–C angles close to 360°. The Cu–N(anchor) distances in complexes 21 and 22 range from 2.4–2.6 Å, suggesting that the interaction between the anchoring nitrogen atom and the copper center is non-significant. The space filling model shows that the copper center in complex [(TIME\(_{\text{alkyl}}\)Cu)]\(^+\) is well shielded by the three sterically encumbering tert-butyl groups. This steric congestion is largely reduced in the analogous complex [(TIME\(_{\text{alkyl}}\)Cu)]\(^+\). Electrochemical measurements show that the complexes exhibit a reversible Cu(I)/Cu(II) couple at 0.11 and −0.1 V versus Fe/Fe\(^+\) for 21 and 22, respectively. Accordingly, the complex [(TIME\(_{\text{alkyl}}\)Cu)]\(^+\) could be synthesized, isolated and spectroscopically characterized. However, all Cu(I) complexes [(TIME\(_{\text{alkyl}}\)Cu)]\(^+\) have proven to be inert toward additional ligand binding and activation of small molecules. This suggests that copper(I) complexes with the strongly electron-donating tris(carbene) ligand are electronically saturated and unreactive.

The analogous nickel(0) tris(carbene) complex [(TIME\(_{\text{Bu}}\)Ni)]\(^+\) (23) was prepared by reacting TIMEN\(_{\text{Bu}}\) with Ni(COD)\(_2\) [42] and reaction of 23 with CH\(_2\)Cl\(_2\) yields the Ni(I) complex [(TIME\(_{\text{Bu}}\)Ni)]Cl (24). Interestingly, the molecular structures of these two nickel com-

![Fig. 10. Solid-state molecular structure of [(TIME\(_{\text{Bu}}\)Ni)]\(^+\) (21).](image)
plexes 23 and 24 differ significantly (Fig. 11). The TIMEN\textsuperscript{t}-Bu ligand of 23 is tridentate and coordinates to the nickel center only through the three carbene chelators (d(Ni–N) = 3.204 Å). In complex 24, however, TIMEN\textsuperscript{t}-Bu coordinates in a tetradentate fashion and additionally binds to the nickel center via the anchoring nitrogen atom (d(Ni–N) = 2.22 Å). This observation strongly supports our theory that the nexus nitrogen can function as an electron pool supplying two additional electrons for metal centers in higher oxidation states. The difference between the Ni–C bond distance of 1.892(1) Å for Ni(0) (23) and 1.996(4) Å for Ni(I) (24) is also noteworthy. The short Ni–C distance of 1.892(1) Å for the bigger Ni(0) center might be due to a substantially higher degree of \( \pi \)-backbonding in this complex.

The cyclic voltammogram of complex 23 shows two quasi-reversible Ni(0)/(I) and Ni(I)/(II) redox waves at \(-2.5\) and \(-1.1\) V versus Fe/Fe\textsuperscript{2+}, respectively. Unfortunately, the two-electron oxidized complexes could be isolated. This is likely due to structural rearrangements during the electron-transfer, which are not easily accommodated by the ridged tripodal ligand environment. We are now looking for alternative routes to these complexes, which, if accessible, might provide useful platforms for activating small molecules via one- and two-electron redox chemistry. Attempts to synthesize the Ni(0) complex with the less bulky TIMEN\textsuperscript{iso-pro} isopropyl derivative are currently underway.

3.2. The TIMEN\textsuperscript{Ar} ligand system and its coordination to cobalt

The foregoing data show the strong shielding effect of the bulky organic substituents of the TIMEN\textsuperscript{t}-Bu ligand, resulting in a lack of reactivity and small molecule activation with these complexes. With complexes of other alkyl derivatives, we encountered different problems. For example, complexes of the benzyl derivative are often oily and do not crystallize, complexes of the iso-propyl derivatives, on the other hand, have a fairly reactive C–H bond near the metal center and are difficult to purify and isolate, and complexes of the methyl derivative have trimeric structures. We thus decided to investigate the chemistry of aryl-substituted TIMEN ligands. We first studied the coordination chemistry of TIMEN\textsuperscript{Ar} with low-valent cobalt ions.

Reaction of TIMEN\textsuperscript{Ar} with a suitable cobalt(1) precursor, i.e., Co(PPh\textsubscript{3})\textsubscript{3}Cl, yields the \([\text{TIMEN}^{\text{Ar}}\text{Co}]\text{Cl} (\text{Ar} = \text{xyl}) (25)\), target complexes \([46]\). In both compounds, the cobalt(1) centers are in a distorted trigonal-pyramidal ligand environment of three carbene donors and the anchoring nitrogen. The cobalt centers are coordinatively unsaturated and react with a variety of small molecules. Accordingly, 25 reacts with carbon monoxide gas, yielding the cobalt(1) complex \([\text{TIMEN}^{\text{xyl}}\text{Co(CO)}]\text{+} with an axial carbonyl ligand. In addition, reaction of 25 with one-electron oxidizers, such as benzyl chloride, methylene chloride or trimethylsilyl azide (TMS-N\textsubscript{3}), yields cobalt(II) species \([\text{TIMEN}^{\text{xyl}}\text{Co}(X)]\text{+} (X = \text{Cl}^-, \text{N}_3^-)\) with axial halide and pseudo-halide ligands, respectively. The weakly bound chloro ligand can be replaced by coordinating solvent molecules, thereby furnishing, for instance, the acetonitrile complex \([\text{TIMEN}^{\text{xyl}}\text{Co(NCCH}_3\text{)}]\text{2+}\).

X-ray crystallographic analysis shows that the cobalt centers in these complexes all have distorted trigonal-pyramidal coordination geometry consisting of three carbene donors and the external ligands. The anchoring nitrogen atom of these complexes is not coordinated. Note-worthy, the cylindrical cavity (Fig. 12), formed by the three arene substituents in these complexes, enforces a linear coordination mode for the typically bent azido ligand in \([\text{TIMEN}^{\text{xyl}}\text{Co(N}_3\text{)}]\text{+}\).

All these cobalt(I)/(II) complexes have high-spin electronic configurations. They exhibit well-defined, threefold symmetrical, paramagnetic \(^1\text{H}\) NMR spectra. The room temperature magnetic moments are about 3.6 \( \mu_B \) for the cobalt(I) complexes and 4.2–4.8 \( \mu_B \) for the cobalt(II) complexes.

3.3. Dioxygen activation and imido-transfer reactions assisted by cobalt tris/(carbene) complexes

The above-mentioned coordinatively and electronically unsaturated cobalt tris-carbene complexes fulfill the basic
requirements for small molecule activation via an inner sphere redox mechanism. We are particularly interested in their possible application for oxygen and nitrogen atom transfer reactions.

We found that a solution of [(TIMENxyl)Co]Cl (25) reacts cleanly with dioxygen at room temperature to form a 1:1 cobalt dioxygen adduct [(TIMEN(\(^{18}\)O)xyl)Co(O\(^2\))]+ (Fig. 13, 26). Infra-red, NMR, and X-ray crystallography establish the side-on binding mode of the coordinated peroxo ligand. The \(^{16}\)O–\(^{16}\)O stretching frequency is 890 cm\(^{-1}\), and is shifted to 840 cm\(^{-1}\) in a \(^{18}\)O\(^2\) substituted sample. The crystal structure shows a hexa-coordinated cobalt(III) ion situated in a pseudo-octahedral ligand environment.

The dioxygen ligand is bound side-on, with a O–O distance of 1.429(3) Å. The coordination sphere is completed by the three carbenoid carbons and the anchoring nitrogen atom of the carbene tripod. The formation of this octahedral complex with TIMEN is remarkable as it underlines the great structural flexibility of this type of ligand system.

The coordinated dioxygen in 26 is nucleophilic and reacts with electron-poor organic substrates such as benzoyl chloride, malonitrile, and tetracyanoethylene to transfer one single oxygen atom. A mechanism involving a homolytic Co–O bond cleavage has been proposed [46]. The nucleophilic reactivity of 26 was further confirmed by DFT calculations, which showed that the HOMO of 26 mainly consists of the dioxygen \(\pi^*\) orbital.

The cobalt(1) complexes also react with aryl azides to form terminal cobalt(III) imido complexes [(TIMEN(\(^{18}\)O)Ar)Co(NArR)]Cl (Ar = xyl, mes, R = p-PhMe, p-PhOMe) at –35 °C. The crystal structure of [(TIMEN(\(^{18}\)O)mes)Co(N(p-PhOMe))]\(^{2+}\) (27) shows a pseudo-tetrahedral geometry featuring a tridentate TIMENMes ligand with a short Co–Nimido bond (1.675(2) Å) [47]. This short distance, together with an almost linear Co–N–C angle of 168.6(2)°, is indicative of strong multiple bond character within the Co–NAr entity. According to our DFT studies, this bond is better formulated as a double bond [47]. The imido complexes are stable in solid-state and in solution at –35 °C. In solution at room temperature, however, the imido group readily inserts into one of the cobalt-carbene bonds as established by \(^1\)H NMR spectroscopy and X-ray crystallography.

We propose that the immediate reaction product is a cobalt(I) imine species, which further disproportionates to form cobalt(II) imine complexes [(TIMENAr\(^2\)]*Co\(^{2+}\), metallic cobalt(0) species, and unidentified organic side-products. The kinetic data indicate that the reaction rate is faster for the more electron-deficient imido species, thus suggesting the reaction to proceed via an electrophilic attack of the imido group on the Co–C bond.

Few terminal late metal imido complexes have been prepared recently [20,48,49], but the intramolecular imido insertion reactions as seen for [(TIMENAr)Co(NAr\(^2\)]Cl are unprecedented. The electrophilic Co–NAr functionality of these complexes differs substantially from those of terminal imido complexes supported by tris(phosphino)borate or diphosphine ligands. The latter complexes are nucleophilic and react with CO to form isocyanates. In fact, the imido species reported here are more closely related to a...
The aryl-substituted TIMENAr ligands that give rise to protected in reactivity pockets. Particularly promising are reactions of previously reported transient tris(pyrazolyl)borate cobalt imido complex that undergoes intra-molecular C–H activation to form a cobalt amido complex [49]. Reactions of tris(carbene) [(TIMENAr)Co(NArR)]Cl with an excess of nucleophiles, such as styrene and imidazole-2-ylidene, did not result in intra-molecular imido transfer. This can be explained by the inaccessibility of the cobalt imido functionality for substrates in complexes of xylene and mesitylene functionalized NHC ligands. We believe, however, that sterically less crowded systems have the potential to effect N-group transfer reactions to nucleophilic organic substrates, such as normal alkenes.

A scheme depicting reactions of complex 23 with various small molecules is shown in Scheme 4.

Scheme 4. Selected reactivities of cobalt(I) tris(carbene) complex 23.

4. Summary

In conclusion, we have developed two novel tripodal NHC ligand systems and studied their coordination to transition metals. The carbon-anchored ligands TIME normally form polynuclear species while the nitrogen anchored ligands TIMEN can coordinate to transition metals in a 1:1 $\kappa^2$ fashion, rendering the coordinated metal centers well-protected in reactivity pockets. Particularly promising are the aryl-substituted TIMENAr ligands that give rise to coordinatively and electronically unsaturated transition metal complexes. The cobalt complexes of these ligands show interesting reactivities toward dioxygen and organic azides. Although catalytic oxygen and nitrogen atom transfer reactions have not been achieved with these complexes, they do have the potential for further modification and optimization. The coordination chemistry of tris(carbene) ligands and their reactivity studies remains a central topic of our research.

References
