

Review

New tripodal N-heterocyclic carbene chelators for small molecule activation

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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(III) 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.

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

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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 coordination 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 tetradentate 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 $[\text{HIPTN}_3\text{N}]^{3-}$ (L, with $\text{N}_3\text{N}=(\text{NCH}_2\text{CH}_2)_3\text{N}$, $\text{HIPT} = 3,5-(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)\text{-C}_6\text{H}_3$) supports the molybdenum center and many of the intermediate species of a monometallic reduction of dinitrogen could be identified and isolated. These intermediates include $\text{LMo}(\text{N}_2)$ (**1**) (Fig. 1), $\text{LMo}-\text{N}=\text{N}-\text{H}$ (**2**), $[\text{LMo}=\text{N}-\text{NH}_2](\text{BAR}'_4)$ (**3**), $\text{LMo}\equiv\text{N}$ (**4**), $[\text{LMo}=\text{NH}](\text{BAR}'_4)$ (**5**), $[\text{LMo}(\text{NH}_3)](\text{BAR}'_4)$ (**6**), $\text{LMo}=\text{NH}$, and $\text{LMo}(\text{NH}_3)$. 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 N_3N framework to influence the secondary coordination sphere around the metal ions. The ligand tris(*N'*-*tert*-butylureayl)-*N*-ethyleneamine (H_6buea), with three ureayl groups forming the reactivity pocket of the $[(\text{H}_3\text{buea})\text{M}]^{n-}$ 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 $[(\text{H}_3\text{buea})\text{MO}]^{2-}$ ($\text{M} = \text{Fe}$ (**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 $[(\text{H}_3\text{buea})\text{M}]^{n-}$ 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.

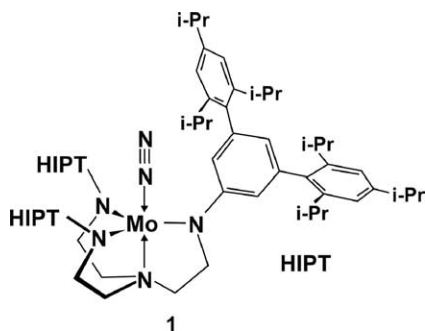


Fig. 1. The molybdenum tris(amido)amine complex $[(\text{HIPTN}_3\text{N})\text{Mo}(\text{N}_2)]$ that catalyzes the reduction of dinitrogen to ammonium.

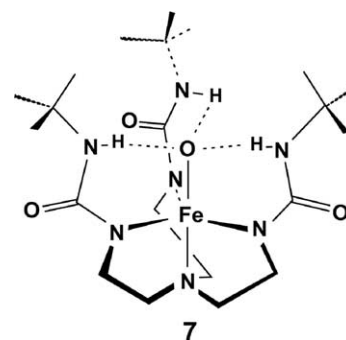


Fig. 2. The terminal iron(III) oxo complex $[(\text{H}_3\text{buea})\text{FeO}]^{2-}$ supported by a ureayl derivatized tris(amido)amine ligand.

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., N_2 , CO and NO^+), but also bind to strong π -donor ligands (e.g., NR^{2-} and N^{3-}), 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 $L_3M\equiv E$ or $L_3M=E$ species ($L = P$, $M = Fe$, Co, Ni, Cu, $E = O$, N, etc.). For instance, the complexes $[(PhBP_3)M(PMe_3)](PhBP_3=PhB(CH_2PPh_2)_3)$, $M = Co$, Fe) can aid the two-electron oxidative nitrene transfer from organic azides by forming terminal imido complexes $[(PhBP_3)M=N-p\text{-tolyl}]$ [20]. Moreover, the complexes $[(PhBP_3^{i-Pr})M]^{n+}$ ($PhBP_3^{i-Pr} = PhB(CH_2P(i-Pr)_2)_3$, $M = Fe$, Co) contain a single binding site for coordination of N_2 , diazenido (N_2Me), and imido (NR) ligands. The N_2 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 $[(PhBP_3^{i-Pr})Fe\equiv N]$ (**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 N_2 -bridged complex $[(PhBP_3^{i-Pr})Fe]_2(\mu-N_2)$, 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 $[L_3CoL']$ 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,

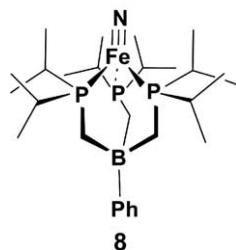


Fig. 3. The terminal iron(IV) nitrido complex $[(PhBP_3^{i-Pr})Fe\equiv N]$ supported by a tris(phosphino)borate ligand.

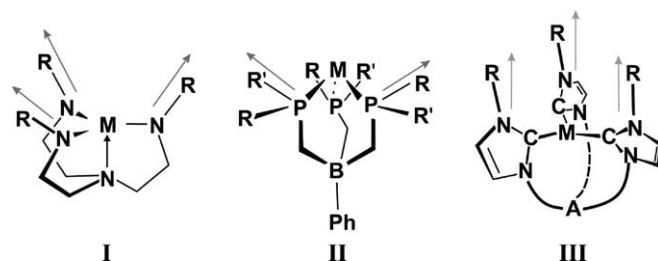


Fig. 4. Tripodal ligand scaffolds with arrows pointing in the direction of the steric bulk.

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 $[(PhBP_3^{i-Pr})Fe\equiv N]$ to form a dinitrogen bridged dinuclear species $[(PhBP_3^{i-Pr})Fe]_2(\mu-N_2)$. Also, in order to prevent $[(^A rN_3N)Mo\equiv N]$ from forming the dinuclear complex $[(^A rN_3N)Mo]_2(\mu:\eta^1, \eta^1-N_2)$, 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 sp^2 -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

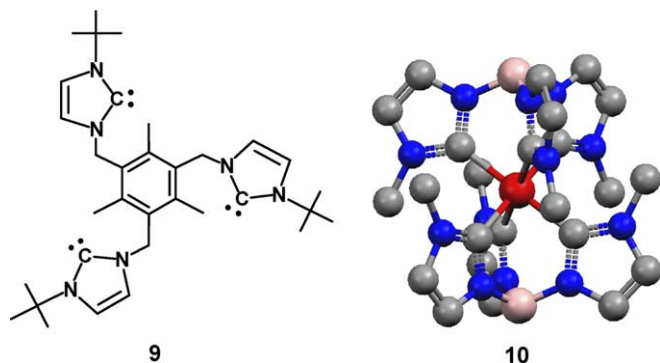


Fig. 5. Tripodal NHC ligand **9** and hexakis(carbene) complex $[L_2Fe]^+$ (**10**).

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.

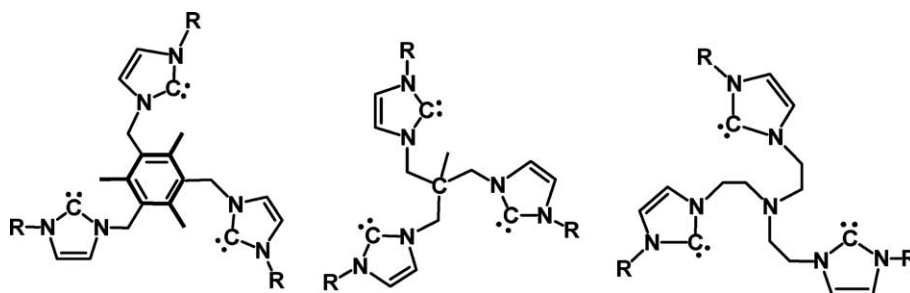
We thus decided to develop new tripodal NHC ligand systems to stabilize a single transition metal center in a coordinatively unsaturated ligand environment that would allow the binding and activation of small molecules in a controlled manner. In this review we summarize some of this exploratory work. In particular, we describe the synthesis of two new classes of tripodal NHC ligands $TIME^R$ (1,1,1-tris(3-alkylimidazol-2-ylidene)[methyl]ethane) and $TIMEN^R$ (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).

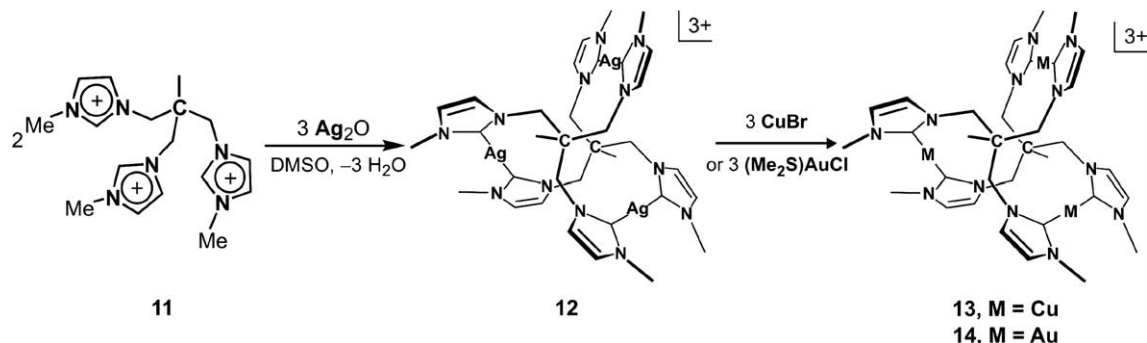
2. Carbon-anchored tris(carbene) ligand systems and their coordination chemistry

2.1. The $TIME^{Me}$ Ligand

The three pendent arms of the neo-pentane based tripodal NHC chelator 1,1,1-tris(3-alkylimidazol-2-ylidene)-[methyl]ethane ($TIME^R$) 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 ($TIME^{Me}$) could only be prepared in situ, by deprotonation of the $[H_3TIME^{Me}]^+$ (PF_6)₃ salt with a strong base. Attempts to isolate the $TIME^{Me}$ ligand were unsuccessful, and complexation of transition metals with the in situ generated carbene had limited success [29]. Metal complexes of $TIME^{Me}$ can be prepared, however, via the transmetalation method developed by Wang and Lin [30]. Treatment of $[H_3TIME^{Me}]Br_3$ (**11**) with Ag_2O in DMSO affords the trinuclear silver complex $[(TIME^{Me})_2 Ag_3](PF_6)_3$ (**12**), which serves as a carbene transfer agent and reacts with copper(I) bromide and (dimethylsulfide)gold(I) chloride to form the corresponding



Scheme 1. Tripodal N-heterocyclic carbene chelators with mesitylene (mes-carbene, left), carbon ($TIME^R$, center), and nitrogen ($TIMEN^R$, right) anchoring units.



Scheme 2. Synthesis of group 11 metal complexes of $TIME^{Me}$.

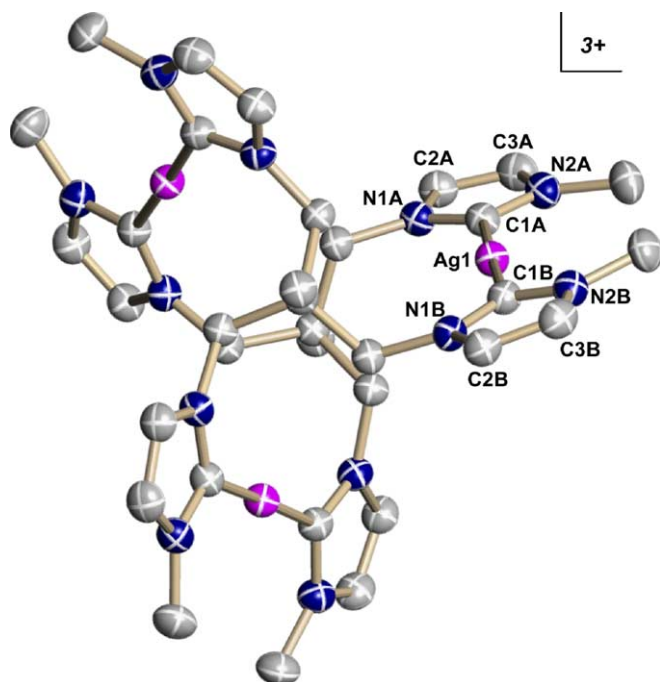


Fig. 6. Solid-state molecule structure of $[(\text{TIME}^{\text{Mc}})_2\text{Ag}_3]^{3+}$ (**12**).

copper(I) and gold(I) complexes $[(\text{TIME}^{\text{Mc}})_2\text{Cu}](\text{PF}_6)_3$ (**13**) and $[(\text{TIME}^{\text{Mc}})_2\text{Au}_3](\text{PF}_6)_3$ (**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 TIME^{Mc} 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 carbene entities 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 intramolecular metal–metal interactions in these complexes.

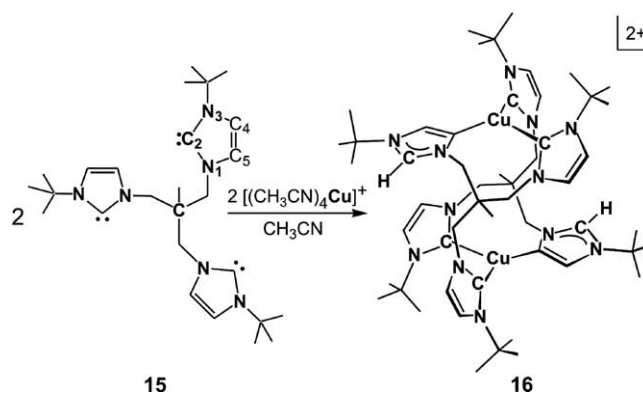
2.2. The $\text{TIME}^{\text{t-Bu}}$ ligand and its coordination to copper(I)

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 TIME ligand by synthesizing the *tert*-butyl derivative $\text{TIME}^{\text{t-Bu}}$.

Deprotonation of the imidazolium salt $[\text{H}_3\text{TIME}^{\text{t-Bu}}](\text{PF}_6)_3$ with three equivalents of potassium *tert*-butoxide

yielded the free carbene $\text{TIME}^{\text{t-Bu}}$ (**15**), which was isolated and fully characterized [35]. Reaction of one equivalent of **15** with $[(\text{CH}_3\text{CN})_4\text{Cu}](\text{PF}_6)$ affords the copper complex $[(\text{TIME}^{\text{t-Bu}})_2\text{Cu}_2](\text{PF}_6)_2$ (**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 carbene ligands 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].



Scheme 3. Synthesis of the bis(carbene)alkenyl complex $[(\text{TIME}^{\text{t-Bu}})_2\text{Cu}_2](\text{PF}_6)_2$ (**16**).

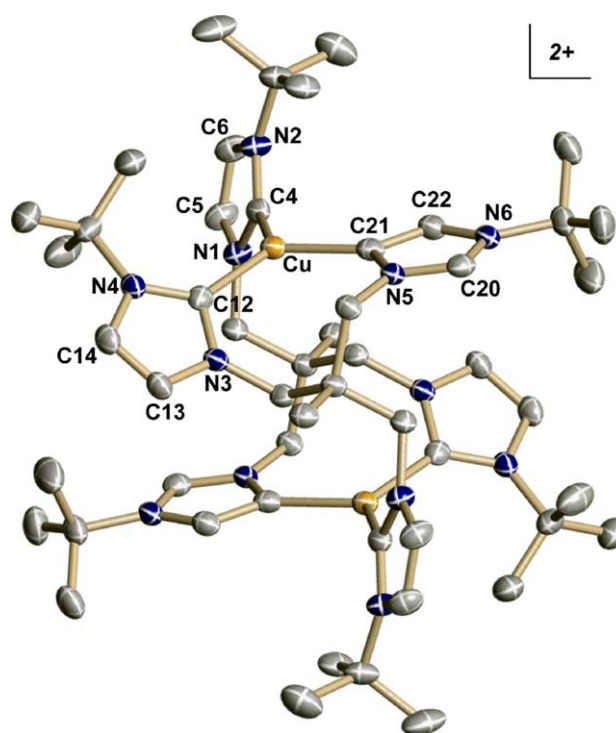


Fig. 7. Solid-state molecular structure of $[(\text{TIME}^{\text{t-Bu}})_2\text{Cu}_2]^{2+}$ (**16**).

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^{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_3 and L_2 fragment of the M_3L_2 complexes. Analysis of the corresponding molecular orbitals (MOs) allows for deriving σ - and π -back-bonding models for the metal–ligand electronic interactions involved. For example, the complex $[(\text{TIME}^{\text{Me}})_2\text{Cu}_3](\text{PF}_6)_3$ (**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 $3d_z^2 + 4s$ hybrid orbitals, as well as the empty $4p_z$ orbitals of the metal fragment. The π -backbonding results from interaction of partially empty π/π^* orbitals of the ligand fragment with the filled $3d_{xz/yz}$ metal orbitals. Representative σ - and π -orbitals are shown in Fig. 8.

This π -bonding contribution between the metal ions and NHC ligands is not limited to complex **13**. In fact, calculations on complex **12**, **14**, and a D_{2d} -symmetric bis-carbene complex $\text{Pd}(\text{CN}_2\text{Bu}_2\text{C}_2\text{H}_2)_2$ (**17**) [39], also revealed varying degrees of π -interactions.

The nature of the M–C_{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 va-

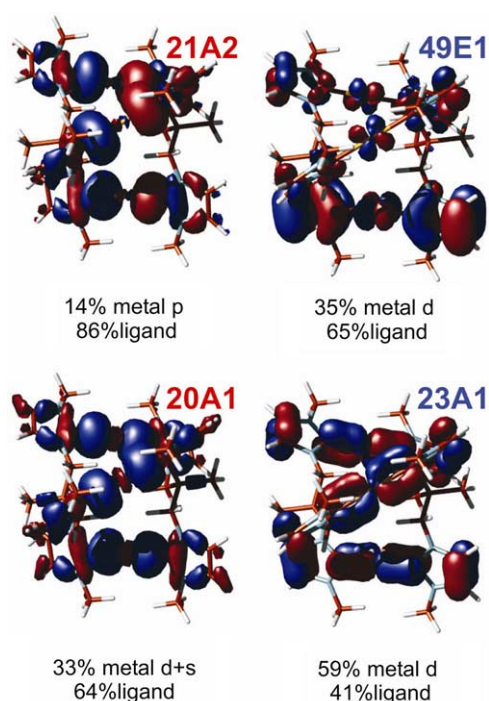


Fig. 8. Representative σ - and π -type molecular orbitals of $[(\text{TIME}^{\text{Me}})_2\text{Cu}_3]^{3+}$ (**13**).

lue) in **17** is 2.2, and the π -bonding contributes 30% to the overall stabilizing orbital interaction energy (calculated with D_{2h} -symmetric model complexes $\text{M}(\text{IM}^{\text{Me}}\text{C})_2$). 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 $[\text{Cp}(\text{NHC})\text{Ir}=\text{CH}_2]$ [38]. Our calculations of the latter iridium complex established 20% π -backbonding in the NHC–Ir fragment. A Schrock-type metal–carbene fragment $\{\text{M}=\text{CH}_2\}$ 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 $(\text{IM}^{\text{Mes}}\text{C})_2\text{M}$ (with $\text{IM}^{\text{Mes}}\text{C} = 1,3$ -dimesitylimidazol-2-ylidene, $\text{M} = \text{Ni}(0)$, $\text{Ag}(I)$, and I^+). These complexes are iso-structural and

possess the same set of NHC ligands. It was found that from I^+ (electron poor, not capable of π -backbonding) to Ag^+ (less electron-rich, capable of π -backbonding) to $Ni(0)$ (electron-rich, very capable of π -backbonding), the average C–N bond lengths of the NHC fragments increase from 1.346 Å in $[(IM^{Mes}C)_2I]^+$, to 1.358 Å in $[(IM^{Mes}C)_2Ag]^+$, to 1.375 Å in $[(IM^{Mes}C)_2Ni]$. This was attributed to decreased nitrogen-carbene π -bonding as a result of increased π -backbonding from the metal to NHC ligand. We synthesized the $Ni(0)$ and $Ni(I)$ complexes of the tripodal NHC ligand $TIMEN^{t-Bu}$ 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 π -backbonding in the $Ni(0)$ complex.

Since the publication of our work on this topic, a few other reports emerged confirming the presence of π -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 $R_2C \leftarrow ML_n \pi$ back-donation in complexes with N-heterocyclic carbenes is not substantially lesser than in classical Fischer carbene complexes bearing two π donor groups R. Lin et al. [44] prepared $Au(I)$ NHC complexes and found that the elongated N–C_{carbene} bond distances in these complexes are consistent with non-negligible metal–NHC π -backbonding.

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

3.1. The $TIMEN^{alkyl}$ ligand

The fact that tripodal carbene ligands $TIME^{Me}$ and bulky $TIME^{t-Bu}$ do not form simple tridentate κ^3 complexes reflects a fundamental problem associated with this class of ligands. Examination of the backbones of these *neo*-pentane-based, carbon-anchored tripodal ligands reveals possible reasons for the lack of 1:1 complex formation. A hypothetical κ^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).

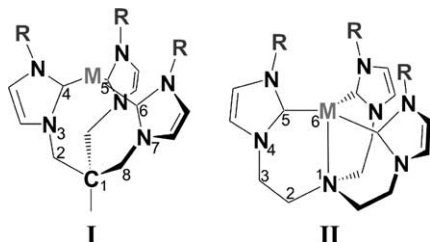


Fig. 9. Structural models of carbon- and nitrogen-anchored tris(carbene) metal complexes.

Accordingly, the nitrogen-anchored tris(carbene) ligand system $\text{tris}[2-(3\text{-alkylimidazol-2-ylidene)ethyl]amine$ ($TIMEN^{alkyl}$) was synthesized. The imidazolium precursors $[H_3TIMEN^R]^3+$ 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 $TIMEN^{alkyl}$.

Monomeric copper(I) tris(carbene) complexes can be prepared by reacting $TIMEN^{alkyl}$ with copper(I) salts. The X-ray structures of $[(TIMEN^R)Cu]^+$ complexes (R = *tert*-butyl (**21**), benzyl (Bz, **22**)) show that the $TIMEN^R$ ligand coordinates to the copper(I) ion via the three carbene carbon atoms in the predicted κ^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 $[(TIMEN^{t-Bu})Cu]^+$ is well-shielded by the three sterically encumbering *tert*-butyl groups. This steric congestion is largely reduced in the analogous complex $[(TIMEN^{Bz})Cu]^+$. Electrochemical measurements show that the complexes exhibit a reversible Cu(I)/Cu(II) couple at 0.11 and –0.1 V versus Fc/Fc⁺ for **21** and **22**, respectively. Accordingly, the complex $[(TIMEN^{Bz})Cu]^{2+}$ could be synthesized, isolated and spectroscopically characterized. However, all Cu(I) complexes $[(TIMEN^{alkyl})Cu]^+$ 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 $[(TIMEN^{t-Bu})Ni]$ (**23**) was prepared by reacting $TIMEN^{t-Bu}$ with $Ni(COD)_2$ [42] and reaction of **23** with CH_2Cl_2 yields the $Ni(I)$ complex $[(TIMEN^{t-Bu})Ni]Cl$ (**24**). Interestingly, the molecular structures of these two nickel com-

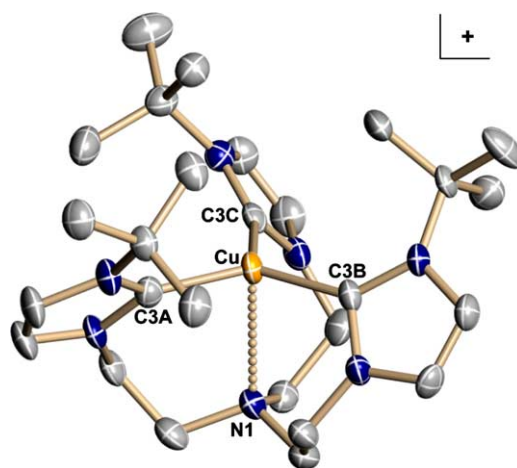


Fig. 10. Solid-state molecular structure of $[(TIMEN^{t-Bu})Cu]^+$ (**21**).

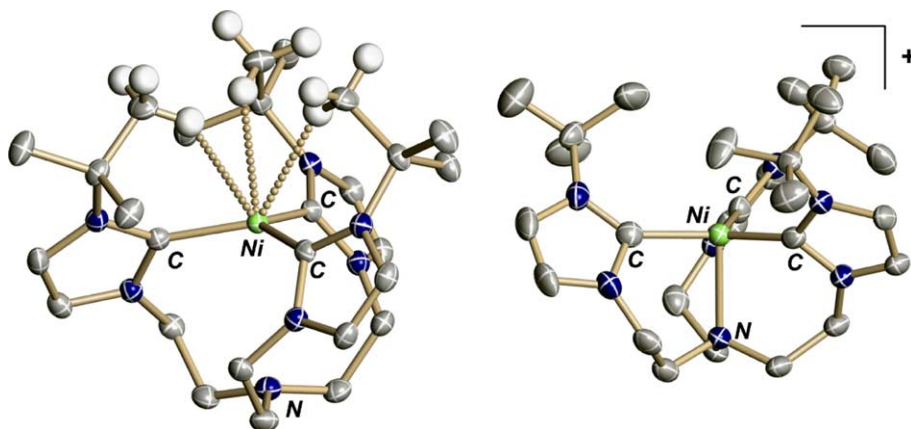


Fig. 11. Solid-state molecular structure of $[(\text{TIMEN}^{t\text{-Bu}})\text{Ni}]$ (**23**) and $[(\text{TIMEN}^{t\text{-Bu}})\text{Ni}]^+$ (**24**).

plexes **23** and **24** differ significantly (Fig. 11). The $\text{TIMEN}^{t\text{-Bu}}$ ligand of **23** is tridentate and coordinates to the nickel center only through the three carbene chelators ($d(\text{Ni}-\text{N}) = 3.204 \text{ \AA}$). In complex **24**, however, $\text{TIMEN}^{t\text{-Bu}}$ coordinates in a tetradentate fashion and additionally binds to the nickel center via the anchoring nitrogen atom ($d(\text{Ni}-\text{N}) = 2.22 \text{ \AA}$). 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 $1.892(1) \text{ \AA}$ for Ni(0) (**23**) and $1.996(4) \text{ \AA}$ for Ni(I) (**24**) is also noteworthy. The short Ni–C distance of $1.892(1) \text{ \AA}$ for the bigger Ni(0) center might be due to a substantially higher degree of π -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 Fc/Fc^+ , 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 tripod 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 $\text{TIMEN}^{\text{iso-Pr}}^{\text{O}}$ isopropyl derivative are currently underway.

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

The foregoing data show the strong shielding effect of the bulky organic substituents of the $\text{TIMEN}^{t\text{-Bu}}$ 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^{Ar} with low-valent cobalt ions.

Reaction of TIMEN^{Ar} with a suitable cobalt(I) precursor, i.e., $\text{Co}(\text{PPh}_3)_3\text{Cl}$, yields the $[(\text{TIMEN}^{\text{Ar}})\text{Co}]\text{Cl}$ ($\text{Ar} = \text{xyl}$ (**25**), mesityl) target complexes [46]. In both compounds, the cobalt(I) centers are in a distorted trigonal-pyramidal ligand environment of three carbenoid carbons 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(I) complex $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{CO})]^+$ 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_3), yields cobalt(II) species $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{X})]^+$, ($\text{X} = \text{Cl}^-$, 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 $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{NCCH}_3)]^{2+}$.

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. Noteworthy, 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 $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{N}_3)]^+$.

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

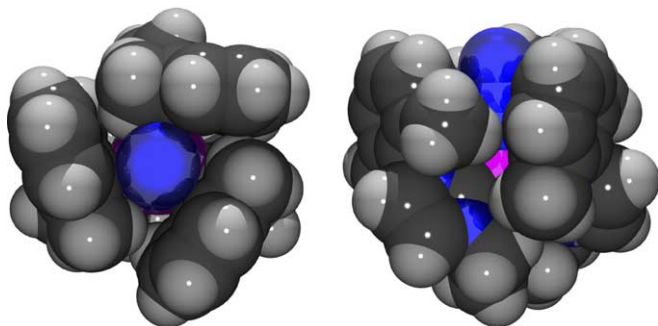


Fig. 12. Space-filling model of $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{N}_3)]^+$ illustrating the cylindrical cavity in complexes of $[(\text{TIMEN}^{\text{xyl}})\text{M}(\text{L})]$.

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 $[(\text{TIMEN}^{\text{xyl}})\text{Co}]\text{Cl}$ (**25**) reacts cleanly with dioxygen at room temperature to form a 1:1 cobalt dioxygen adduct $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{O}_2)]^+$ (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 $^{18}\text{O}_2$ 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 $1.429(3)\text{ \AA}$. 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 π^* orbital.

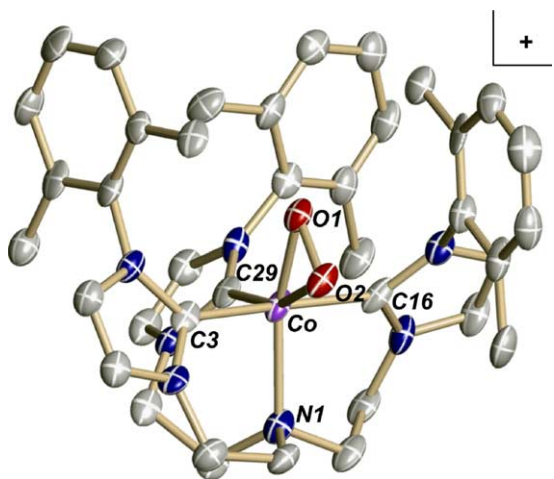


Fig. 13. Solid-state molecular structure of $[(\text{TIMEN}^{\text{xyl}})\text{Co}(\text{O}_2)]^+$ (**26**).

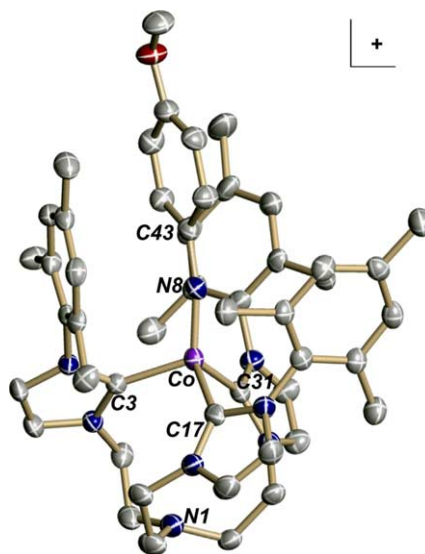


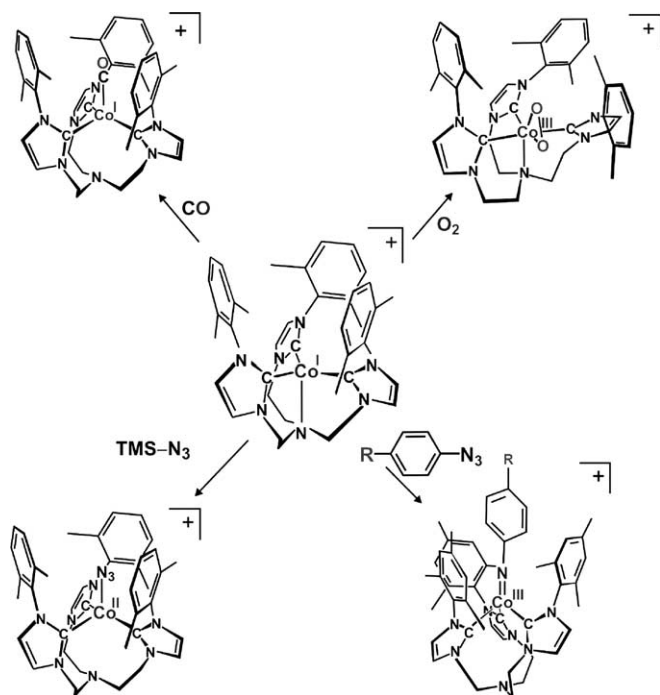
Fig. 14. Solid-state molecular structure of $[(\text{TIMEN}^{\text{Mes}})\text{Co}(\text{N}(p\text{-PhOMe}))]^+$ (**27**).

philic reactivity of **26** was further confirmed by DFT calculations, which showed that the HOMO of **26** mainly consists of the dioxygen π^* orbital.

The cobalt(I) complexes also react with aryl azides to form terminal cobalt(III) imido complexes $[(\text{TIMEN}^{\text{Ar}})\text{Co}(\text{NAr}^{\text{R}})]\text{Cl}$ (Ar = xyl, mes, R = *p*-PhMe, *p*-PhOMe) at $-35\text{ }^\circ\text{C}$. The crystal structure of $[(\text{TIMEN}^{\text{Mes}})\text{Co}(\text{N}(p\text{-PhOMe}))]^+$ (**27**) shows a pseudo-tetrahedral geometry featuring a tridentate $\text{TIMEN}^{\text{Mes}}$ ligand with a short Co–N_{imido} bond ($1.675(2)\text{ \AA}$) (Fig. 14) [47]. This short distance, together with an almost linear Co–N–C angle of $168.6(2)^\circ$, 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 $-35\text{ }^\circ\text{C}$. In solution at room temperature, however, the imido group readily inserts into one of the cobalt-carbene bonds as established by ^1H 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 $[(\text{TIMEN}^{\text{aryl}})^*\text{Co}]^{2+}$, 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 $[(\text{TIMEN}^{\text{Ar}})\text{Co}(\text{NAr}^{\text{R}})]\text{Cl}$ 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



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

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 [(TIMEN^{Ar})Co(NAr^R)]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.

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 κ^3 fashion, rendering the coordinated metal centers well-protected in reactivity pockets. Particularly promising are the aryl-substituted TIMEN^{Ar} 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.

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