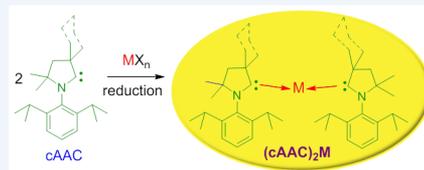


Cyclic Alkyl(amino) Carbene Stabilized Complexes with Low Coordinate Metals of Enduring Nature

Sudipta Roy, Kartik Chandra Mondal, and Herbert W. Roesky*

Institut für Anorganische Chemie, Georg-August-Universität, Tammannstrasse 4, 37077 Göttingen, Germany

CONSPECTUS: N-Heterocyclic carbenes (NHCs) are known to stabilize some metal atoms in different oxidation states mostly by their strong σ -donation. After the successful syntheses of cyclic alkyl(amino) carbenes (cAACs), they have been proven to be much more effective in stabilizing electron rich species. In cAAC, one of the σ -withdrawing and π -donating nitrogen atoms of NHC is replaced by a σ -donating quaternary carbon atom leading to a lower lying LUMO. This makes the acceptance of π -back-donation from the element bound to the carbene carbon atom of cAAC energetically more advantageous. Further evidence suggests that the carbene carbon of cAAC can use the lone pair of electrons present on the adjacent nitrogen in a more controlled way depending on the accumulation of electron density on the bound metal. It has been found that cAAC can be utilized as excellent ligand for the stabilization of a complex with three coordinate metal center [(cAAC)₂M^I-Cl; M = Fe, Co, Cr]. Complex (cAAC)₂M^{II}Cl₂ [M = Fe, Co, Cr] was prepared by reacting anhydrous M(II)Cl₂ with two equiv of cAAC followed by treatment with one equiv of KC₈ (reducing agent) to obtain (cAAC)₂M^I-Cl. The corresponding cation (cAAC)₂M⁺ was isolated when (cAAC)₂M^I-Cl was reacted with sodium-tetraarylborate (lithium) in toluene or fluorobenzene. The CV of cation (cAAC)₂M⁺ [M = Co, Fe] suggests that it can reversibly undergo one electron reduction. The cations of Co and Fe were reduced with Na(Hg) or KC₈, respectively. (cAAC)₂Co^ICl can be directly reduced to (cAAC)₂Co⁰ when reacted with one equiv of KC₈. Analogous (cAAC·)₂Zn^{II} and (cAAC)₂Mn complexes are prepared by reduction of (cAAC)MCl₂ [M = Zn, Mn] with two equiv of KC₈ in the presence of one equiv of cAAC. The square planar (cAAC)₂NiCl₂ complex was directly reduced by two equiv of LiN(*i*Pr)₂ (KC₈) to (cAAC)₂Ni⁰. The (cAAC)₂Pd⁰ and (cAAC)₂Pt⁰ complexes are prepared by substituting all four triphenylphosphines of (Ph₃P)₄M⁰ [M = Pd, Pt] by two cAACs. Cation (cAAC)₂M⁺ [M = Cu, Au] was reduced with sodium/potassium to obtain the neutral analogue [(cAAC)₂Cu, (cAAC)₂Au]. Two coordinate Zn/Mn/Cu/Au are stabilized by two neutral carbene ligands possessing radical electrons on the carbene carbon atoms, while analogous complexes of Co/Fe/Ni/Pd/Pt contain metals in the zero oxidation state. The ground electronic structure of (cAAC)₂M was thoroughly studied by theoretical calculations. In this Account, we summarize our developments in stabilizing metal complexes with low coordinate metal atoms in two, one, and most significantly in their zero oxidation states by utilizing cAACs as ligands.



INTRODUCTION

Complexes containing transition metal atoms in various oxidation states have been utilized in different areas of chemistry,¹ especially in catalysis.² Initially, olefins,³ carbon monoxide,⁴ and phosphines (PR₃)⁵ have been extensively utilized as ligands to stabilize low valent metal atoms. However, the coordination numbers of metal atoms in metal(0)-carbonyl/phosphine complexes are higher since most of them tend to obey the 18e closed-shell configuration.^{3–6} Stabilizations of metal atoms in lower oxidation states and with lower coordination numbers have been a challenging target to the chemists for decades. Latter complexes are unsaturated and hence they are highly reactive. After the first report⁷ on singlet N-heterocyclic carbenes (NHCs) by Arduengo in 1991, chemists realized that the σ -donation (M ← NHC) of an NHC is much higher than those of the previously used ligands (CO, PR₃, olefin, etc.).⁸ Subsequently, NHCs were employed to form stable complexes [NHC → MⁿL_n] with a large number of metals.^{8,9} Very soon it had been realized that a closed-shell configuration is not always necessary for a complex to become stable, since NHC can very strongly donate its lone pair to the metal center. In 1994, Arduengo et al. reported on the first

synthesis of (NHC)₂M⁰ [M = Ni, Pt] complex containing two coordinate metal(0) atom.¹⁰ A few years later synthesis of Pd⁰-analogue was developed.¹¹ (NHC)₂M⁰ [M = Ni, Pd, Pt] (Figure 1) was synthesized by reacting NHC with M⁰-phosphine¹¹ and M⁰-olefin¹⁰ or via reductive elimination of the ligands (allyl chloride and 1,3-diketone).¹² Alternatively,

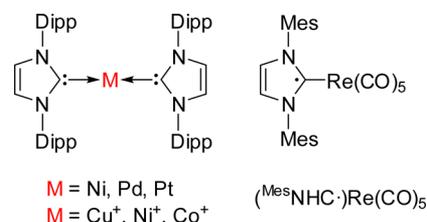


Figure 1. NHC-stabilized species (NHC)₂M, (NHC)₂M⁺ (left) and in situ generated (MesNHC·)Re(CO)₅ (right). Dipp = 2,6-diisopropylphenyl and Mes = 2,4,6-trimethylphenyl.

Received: August 17, 2015

Published: February 29, 2016

(NHC)₂Ni⁰ was prepared by metal vapor deposition.¹³ (NHC)₂Pt(0)^{10,14} was less extensively studied when it is compared with its Ni⁰,^{10,13,15} and Pd⁰-analogues.^{11,12,16} The so far known purely NHC-stabilized two coordinate M⁰ complexes were reported with Ni⁰, Pd⁰, and Pt⁰.^{10–16} The synthesis of cationic complex (NHC)₂M⁺X⁻ [M = Cu,^{17a} Au,^{17b} Co,^{17c} Ni¹⁵] with two coordinate M^I was also achieved.¹⁷ The synthesis of complex (NHC)Ni^IX [R = NR₂, NHR, alkyl] with two coordinate Ni^I was reported by Hillhouse and co-workers.¹⁸

The preparation of a complex with two coordinate Co⁰ was carried out via the reduction of (NHC)₂Co^ICl with metallic sodium or sodium-amalgam which led to the C(sp³)–H bond activation of NHC.^{17c} Synthesis of the complex (NHC)₂M⁰ [where, M = Zn–Co, Fe–Mn] to be elusive until 2011, due to the poor π -acceptance property (NHC \leftarrow M) of NHC.¹⁹

In 2005, Bertrand et al. reported on the first synthesis of cyclic alkyl(amino) carbene (cAAC)²⁰ in which one of the N atoms of NHC is replaced by one σ -donating quaternary C atom. As a result, the HOMO–LUMO energy gap is smaller in cAAC when compared with that of NHC (Figure 2).²¹

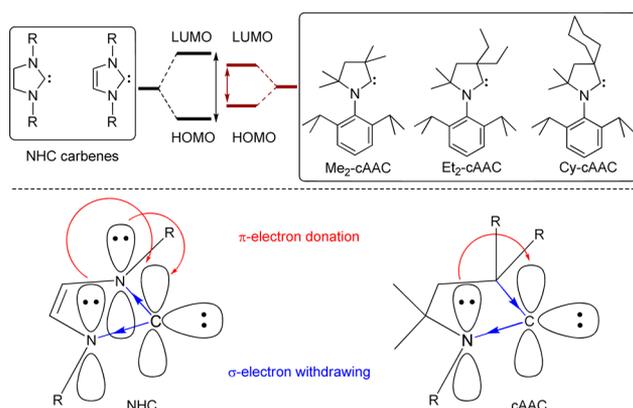


Figure 2. Comparison between NHC (left) and cAAC (right) carbenes.

Consequently, cAAC is a stronger σ -donor and better π -acceptor than NHC. This has been experimentally established by ³¹P NMR studies of carbene–phosphinidene adducts.²² cAAC cleaves strong bonds of H–H and H–NH₂, which were not achieved when NHC was employed.²³ Additionally, cAAC has also been proved to be a potential ligand for stabilizing a copious number of radical species.²⁴

As a matter of fact, complexes containing NHC centered radicals bound to a metal were not stable. Apeloig et al. could only in situ generate such a complex [(^{Mes}NHC·)Re(CO)₅] in solution at low temperature and characterize by EPR.²⁵ However, NHC stabilized 17e complex of a Ni(I)-radical has been shown to activate P₄ and chalcogenides.²⁶ The most challenging targets for the chemists were carbene supported first-row-transition-metal complexes with two-coordinate metals bound to radical centers. This could finally be achieved with the successful implementation of cAAC as π -accepting ligands.

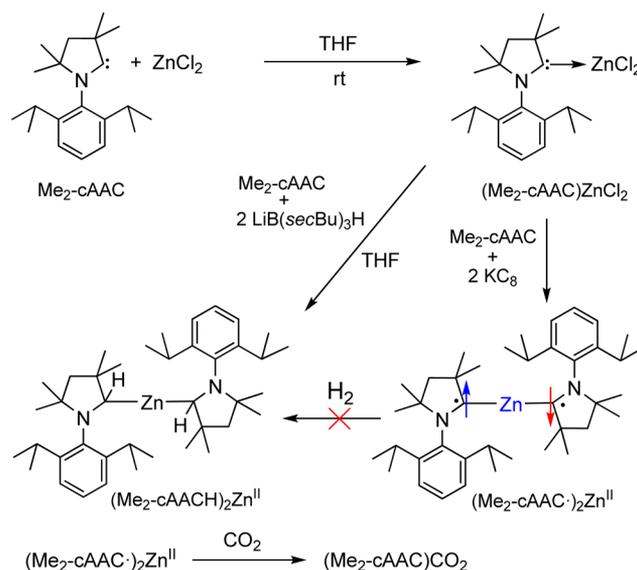
RESULTS AND DISCUSSION

Synthesis and Characterization

As a first step to synthesize the complex (cAAC)₂M with two coordinate M, initially an adduct (Me₂-cAAC)MCl₂ [M = Zn,^{27a} Mn^{27b}] was prepared by reacting commercially available

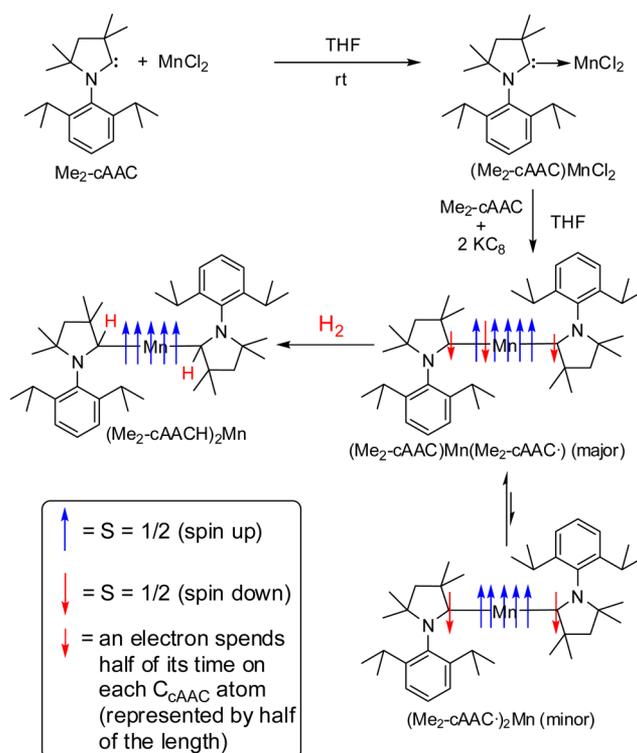
anhydrous M(II)Cl₂ with Me₂-cAAC in a 1:1 molar ratio in THF. Reduction of (Me₂-cAAC)MCl₂ with two equiv of KC₈ led to the formation of the dark blue colored (Me₂-cAAC·)₂Zn^{II} (Me₂-cAAC· = radical electron on carbene carbon atom) or dark purple solution of (Me₂-cAAC)₂Mn in low yields which were significantly increased when the reaction was carried out in the presence of another equiv of Me₂-cAAC (Schemes 1 and 2; Figure 3).²⁷ (Me₂-cAAC·)₂Zn^{II} is EPR silent, while the Mn-analogue is EPR active.

Scheme 1. Synthesis of (cAAC)₂Zn^{II}



When hydrogen gas was bubbled through the dark blue toluene solution of (Me₂-cAAC)₂Zn^{II} at rt, immediately the

Scheme 2. Synthesis of (cAAC)₂Mn



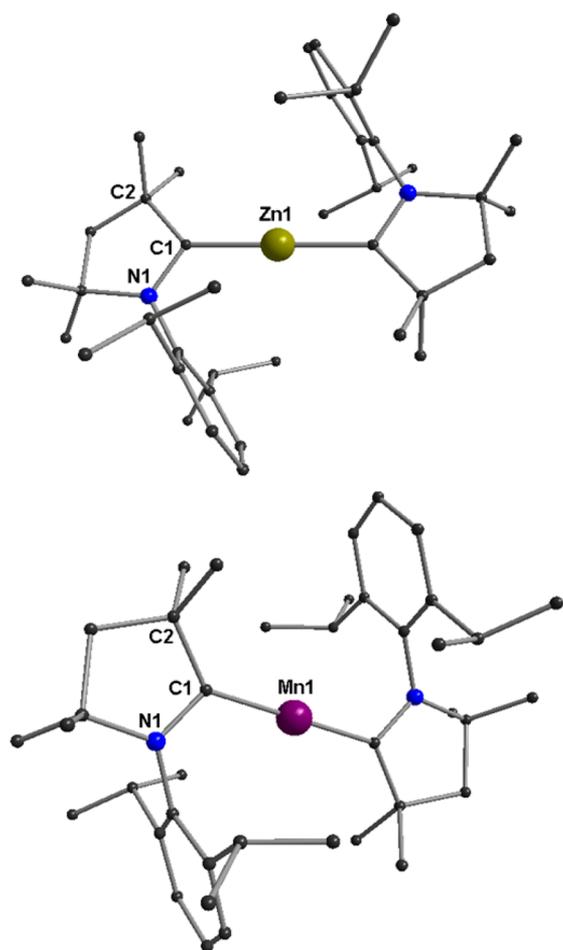


Figure 3. Molecular structures of complexes $(\text{Me}_2\text{-cAAC})_2\text{Zn}^{\text{II}}$ (top) and $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ (bottom).

solution became colorless with the deposition of black zinc metal producing $\text{Me}_2\text{-cAACH}_2$.^{21,23,24} The $(\text{Me}_2\text{-cAACH})_2\text{Zn}^{\text{II}}$ was obtained when $(\text{Me}_2\text{-cAAC})\text{ZnCl}_2$ was reacted with hydride donor $\text{LiB}(\text{sec-Bu})_3\text{H}$ in the presence of another equiv of carbene (Scheme 1).

Ab initio calculations showed that $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ has a quartet ($S = 3/2$) spin ground state having two spin conformers.^{27b} The minor conformer is represented as $(\text{Me}_2\text{-cAAC}\cdot)_2\text{Mn}$, while $(\text{Me}_2\text{-cAAC})\text{Mn}(\text{Me}_2\text{-cAAC}\cdot)$ is the major conformer (Scheme 2).^{27b} When H_2 gas was bubbled through a toluene solution of $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ at rt, an immediate color change of the reaction solution was observed and a flesh-colored crystalline precipitate was obtained which was characterized as the hydrogenated product $(\text{Me}_2\text{-cAACH})_2\text{Mn}^{\text{II}}$ (Scheme 2). $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ was the only complex of the series of $(\text{cAAC})_2\text{M}$ which was able to activate and split the H–H bond without dissociation.^{27b}

A similar synthetic strategy was not successful with CuCl_2 since cAAC reduces CuCl_2 to CuCl . Hence, $\text{Et}_2\text{-cAAC}$ was reacted with CuI in a 2:1 molar ratio to obtain $(\text{Et}_2\text{-cAAC})_2\text{Cu}^+\text{I}^-$ in 75% yield (Scheme 3).²⁸ Cyclic voltammetry (CV) showed one electron reduction of $(\text{Et}_2\text{-cAAC})_2\text{Cu}^+\text{I}^-$ (Figure 4, left). The chemical synthesis of $(\text{Et}_2\text{-cAAC})_2\text{Cu}$ was indeed achieved when $(\text{Et}_2\text{-cAAC})_2\text{Cu}^+\text{I}^-$ was treated with one equiv of sodium. Analogous $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ was isolated as dark green needles from a toluene solution when a 2:1:2 molar mixture of $\text{Me}_2\text{-cAAC}:\text{CuCl}_2:\text{KC}_8$ was reacted (Scheme 3).

Scheme 3. Syntheses of $(\text{cAAC})_2\text{Cu}^+$ and $(\text{cAAC})_2\text{Cu}$

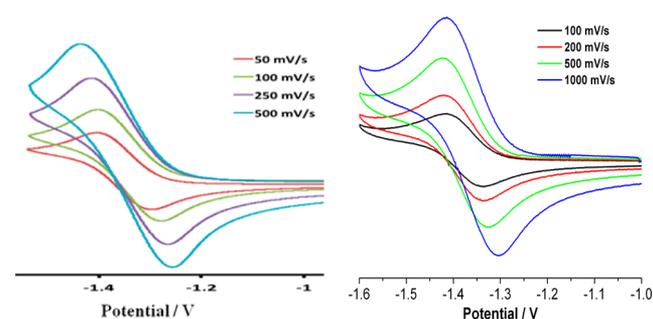
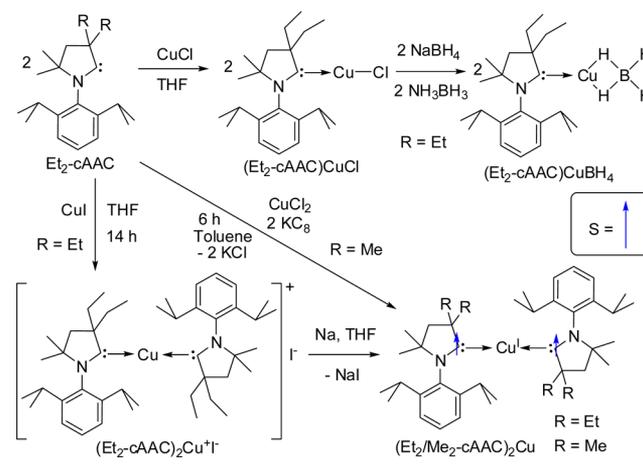


Figure 4. CV of $(\text{Et}_2\text{-cAAC})_2\text{Cu}^+\text{I}^-$ (left) and $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ (right) containing 0.1 M $n\text{Bu}_4\text{NPF}_6$ as an electrolyte.

This reaction possibly proceeds via formation of carbene-radical anion ($\text{cAAC}\cdot^-$) intermediate which replaces the chlorides of CuCl_2 . However, the yield of $(\text{cAAC})_2\text{Cu}$ is found to be only 7–35%. The CV of $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ exhibited one electron quasi-reversible process at $E_{1/2} = -1.35$ V (Figure 4, right) like the $\text{Et}_2\text{-cAAC}$ -analogue.²⁸

$(\text{Et}_2/\text{Me}_2\text{-cAAC})_2\text{Cu}$ was characterized by EPR (Figure 5) spectroscopy which suggested a three-centered carbene/copper/carbene description of $[(\text{cAAC}\cdot)\text{Cu}^1(\text{cAAC})]$ or $(\text{cAAC})\text{Cu}^1(\text{cAAC}\cdot)$ with a predominant carbene radical character.²⁸

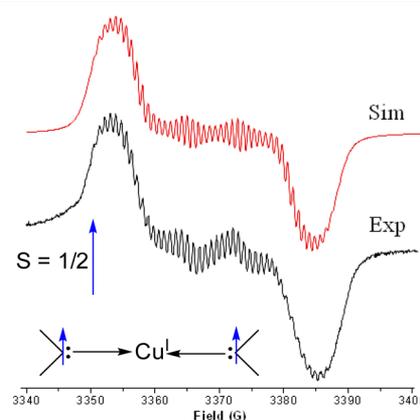
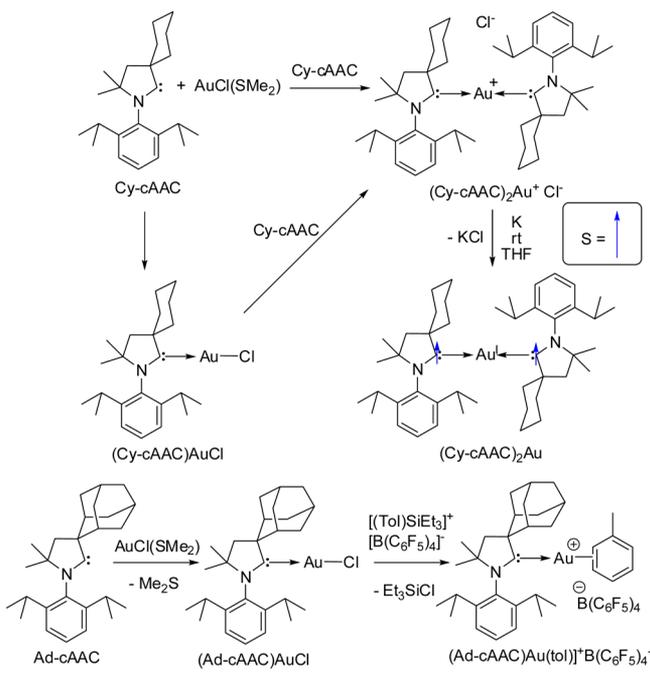


Figure 5. Experimental/simulated EPR spectra of $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ at rt.

The synthesis and isolation of $(\text{Me}_2\text{-cAAC})_2\text{Ag}$ remained unsuccessful until now. Theoretical calculations suggested that cAAC ligands in $(\text{cAAC})_2\text{M}$ have stronger π -accepting properties compared to their σ -donating abilities. The bond dissociation (cAAC-M) energies are in the order of $\text{Au} > \text{Cu} > \text{Ag}$.²⁹

Similarly, $(\text{Cy-cAAC})_2\text{Au}^+\text{Cl}^-$ was readily obtained when $\text{AuCl}(\text{SMe}_2)$ was treated with two equiv of Cy-cAAC. The CV of this cationic compound showed a reversible one-electronic process at -2.24 V. The air/moisture sensitive green colored neutral complex $(\text{Cy-cAAC})_2\text{Au}$ was synthesized in 44% yield when $(\text{Cy-cAAC})_2\text{Au}^+\text{Cl}^-$ was reduced by potassium metal (Scheme 4).³⁰ The electronic structure of $(\text{Cy-cAAC})_2\text{Au}$ is also analogous to that of $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ (Figure 6).^{28,30}

Scheme 4. Synthesis of $(\text{Cy-cAAC})_2\text{Au}^+$ and $(\text{Cy-cAAC})_2\text{Au}$



$(\text{Ad-cAAC})\text{AuCl}$ was possible to prepare by the reaction of $\text{AuCl}(\text{SMe}_2)$ with sterically demanding Ad-cAAC instead of Cy-cAAC. $(\text{Ad-cAAC})\text{AuCl}$ was converted to solvent coordinated cationic complex $[(\text{Ad-cAAC})\text{Au}(\text{tol})]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (Scheme 4).

Reduction of $(\text{bulky-cAAC})\text{AuCl}$ with a suspension of lithium sand produced the air and moisture sensitive light brown crystals of dinuclear complex $(\text{bulky-cAAC})_2\text{Au}_2$ (Scheme 5),³⁰ having a Au_2 unit with a Au-Au bond. The Au-C bond of $(\text{bulky-cAAC})_2\text{Au}_2$ is significantly longer than that of $(\text{Cy-cAAC})_2\text{Au}$.

$(\text{Me}_2\text{-cAAC})_2\text{Ni}^{31}$ was obtained as a dark purple complex when $(\text{Me}_2\text{-cAAC})_2\text{NiCl}_2$ was reduced with the hydride donor lithiumdiisopropylamide (LiNiPr_2) in 1:2 molar ratio (Scheme 6).³¹ LiNiPr_2 acts both as a hydride-donor and as a base. The crystals of $(\text{Me}_2\text{-cAAC})_2\text{Ni}^0$ (Figure 7) are stable at -32 °C for months but at rt they slowly decompose after 1 week.

The $(\text{cAAC})_2\text{Pd}$ and $(\text{cAAC})_2\text{Pt}$ were successfully synthesized substituting four triphenylphosphine ligands of $(\text{Ph}_3\text{P})_4\text{M}^0$ [$\text{M} = \text{Pd}, \text{Pt}$] by two cAACs (Scheme 7)³² by exploiting the fact that cAAC is a stronger σ -donor than Ph_3P . The dark green solution of $(\text{Cy-cAAC})_2\text{Pd}^0$ was stored at -32

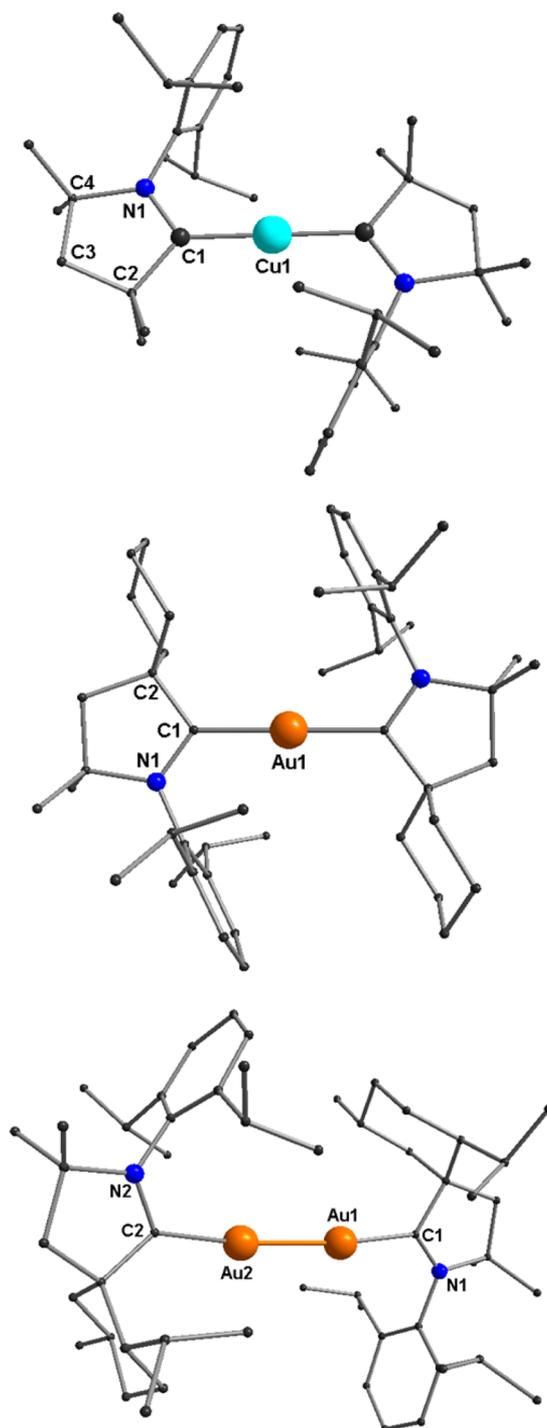
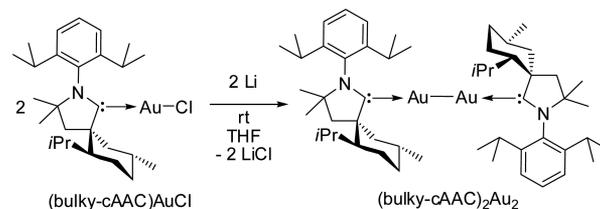
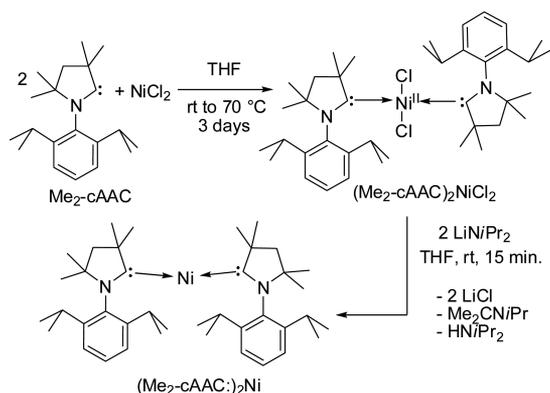


Figure 6. Molecular structures of complexes $(\text{Me}_2\text{-cAAC})_2\text{Cu}$ (top), $(\text{Cy-cAAC})_2\text{Au}$ (middle), and $(\text{bulky-cAAC})_2\text{Au}_2$ (bottom).

Scheme 5. Synthesis of $(\text{cAAC})_2\text{Au}_2$



Scheme 6. Synthesis of (cAAC)₂Ni

$^\circ\text{C}$ to form dark maroon rods of (Cy-cAAC)₂Pd·THF in 84% yield. The changes in the C–Pd–C angles (from 166.94 $^\circ$ to 172.75 $^\circ$) have been attributed to the drastic changes in the color.³²

Similarly, the light yellow solution of (Ph₃P)₄Pt was reacted with cAAC in a 1:5 molar ratio to obtain a dark orange solution of (cAAC)₂Pt⁰ (Scheme 7, Figure 7). ¹⁹⁵Pt NMR (~ –4200/–4300 ppm) resonance of (cAAC)₂Pt⁰ was found to be upfield shifted when compared with that of the NHC analogue (NHC)₂Pt⁰ (~ –1196 ppm).¹⁰

The CV (Figure 8) showed a one-electron quasi-reversible oxidation at $E_{1/2} = -0.60$ V (Pd) and $E_{1/2} = -0.07$ V (Pt) vs (Cp*₂Fe)/(Cp*₂Fe)⁺, indicating the formation of the stable cationic species (cAAC)₂M⁺ (M = Pd, Pt; Scheme 8).³²

cAAC forms an adduct with CoCl₂ in a much faster rate when compared with that of NiCl₂. (Me₂-cAAC)₂Co₂Cl₄ was isolated as a light violet-blue crystalline powder when Me₂-cAAC and CoCl₂ were reacted in a 1:1 molar ratio (Scheme 9).³³ It slowly decomposes to (Me₂-cAACH)[(Me₂-cAAC)Co(μ-Cl)₂Cl(Li)_{0.5}]₂ in THF. (Me₂-cAAC)₂Co^ICl (Figure 9, top) with three coordinate cobalt(I) was obtained when a 1:2 molar mixture of (Me₂-cAAC)₂Co₂Cl₄ and Me₂-cAAC was reduced with two equiv of KC₈.^{33,34} The red needles of (Me₂-cAAC)₂Co^ICl are stable in an inert atmosphere for months.

The CV of (Me₂-cAAC)₂Co^ICl showed a one-electron quasi-reversible reduction at $E_{1/2} = -0.57$ V vs (Cp*₂Fe)/(Cp*₂Fe)⁺, indicating the feasible formation of the dicarbene-cobalt(0) complex. Indeed, the chemical synthesis of (Me₂-cAAC)₂Co⁰ was achieved when a 1:1 molar mixture of (Me₂-cAAC)₂Co(I)Cl and KC₈ was reacted in THF. The air and moisture sensitive complex (Me₂-cAAC)₂Co⁰ (Figure 9, bottom) was isolated as dark blue needles in 98% yield (Scheme 9).³⁴ It was characterized by EI-MS spectrometry and EPR spectroscopy.³⁴

Synthesis of three coordinate Fe(I)-analogue (Et₂-cAAC)₂M^ICl [M = Fe] was easily achieved by reduction of the in situ generated (Et₂-cAAC)₂M^{II}Cl₂ complex with one equiv of sodium amalgam. The corresponding cationic species [(Et₂-cAAC)₂M]⁺(BAR^F₂₄)[–]³⁵ (Figure 10) was prepared by dechlorination of (Et₂-cAAC)₂M^ICl with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate (Na⁺BAR^F₂₄[–]) (Scheme 10). The neutral (Et₂-cAAC)₂Fe⁰ complex (d⁸, S = 1) was obtained by one electron reduction (KC₈) of its cationic analogue leading to the isolation of a dark green powder of (Et₂-cAAC)₂Fe⁰ in 89% yield.³⁵ Similarly, the neutral and cationic Co(I)-analogues were synthesized (Scheme 10). The CV of [(Et₂-cAAC)₂Co]⁺(BAR^F₂₄)[–] exhibited a reversible reduction at

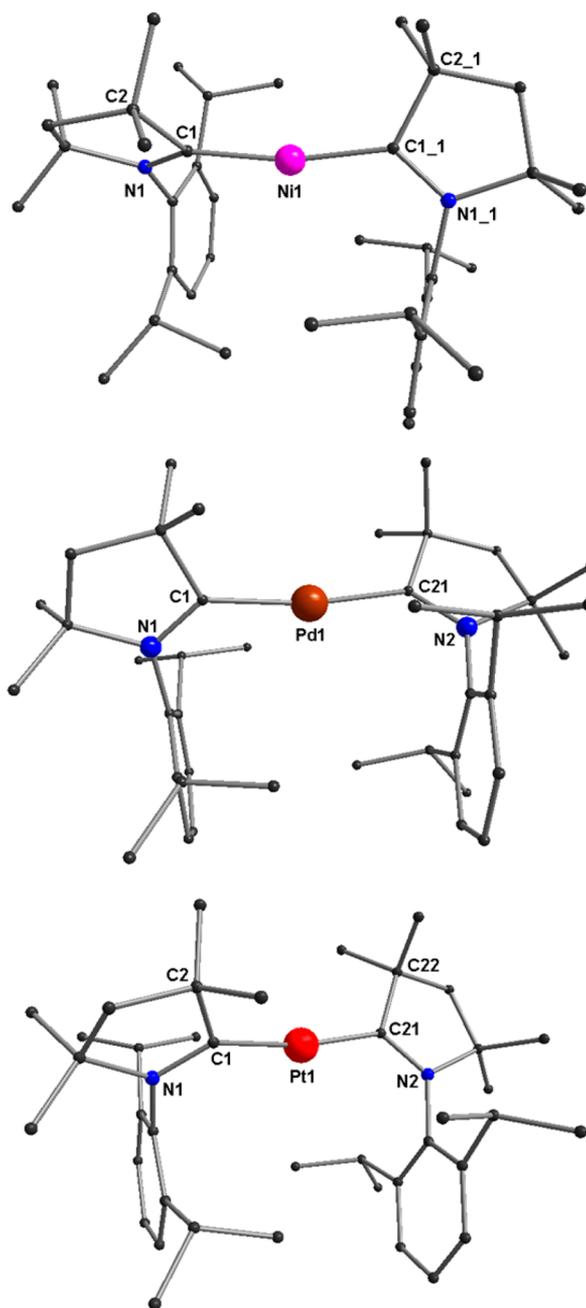
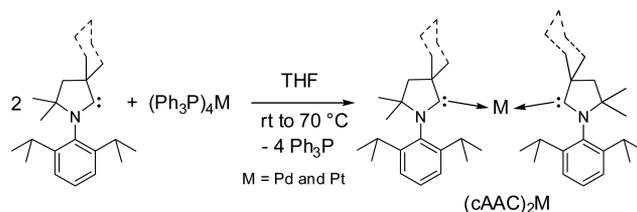


Figure 7. Molecular structures of complexes (Me₂-cAAC)₂Ni (top), (Me₂-cAAC)₂Pd (middle), and (Me₂-cAAC)₂Pt (bottom).

Scheme 7. Synthesis of (cAAC)₂Pd and (cAAC)₂Pt

$E_{1/2} = -1.79$ V.³⁵ The chemical reduction of the cation (Et₂-cAAC)₂Co⁺ to the neutral (Et₂-cAAC)₂Co⁰ was carried out utilizing one equiv of sodium amalgam which was not successful for the NHC-analogues.^{17c}

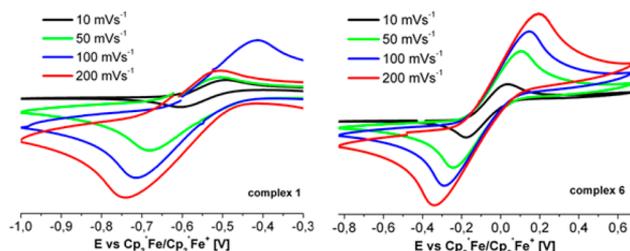
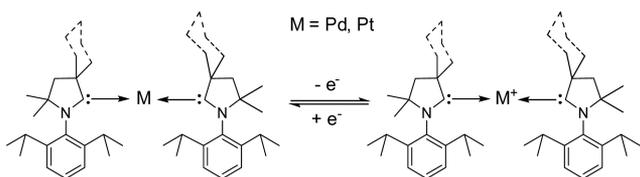
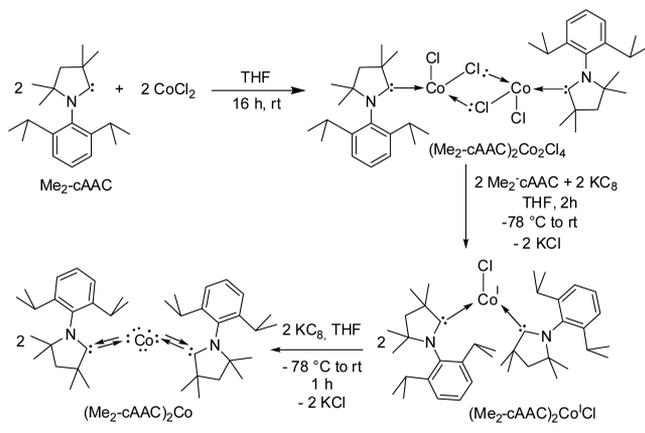


Figure 8. CV of THF solutions of $(\text{Cy-cAAC})_2\text{Pd}$ (left) and $(\text{Me}_2\text{-cAAC})_2\text{Pt}$ (right).

Scheme 8. Reversible One Electron Oxidation of $(\text{cAAC})_2\text{Pd}$ and $(\text{cAAC})_2\text{Pt}$



Scheme 9. Synthesis of $(\text{cAAC})_2\text{Co}$ Complex



The temperature dependent UV–vis spectra of $(\text{Et}_2\text{-cAAC})_2\text{Fe}^0$ showed that it reversibly binds with N_2 below -80°C (Bertrand et al.).³⁶

The reduction of $(\text{Et}_2\text{-cAAC})_2\text{Fe}^0$ with KC_8 at -95°C in diethyl ether in the presence of 18-crown-6 led to the isolation of dark brown crystals of $[(\text{Et}_2\text{-cAAC})_2\text{Fe}(\text{N}_2)][\text{K}(18\text{-crown-6})]$ (Scheme 11).³⁶

In order to synthesize the two coordinate cationic species $[(\text{Me}_2\text{-cAAC})_2\text{M}]^+$ [$\text{M} = \text{Fe}, \text{Cr}$], initially $(\text{Me}_2\text{-cAAC})_2\text{M}^{\text{II}}\text{Cl}_2$ was isolated and subsequently reduced (Scheme 12) to $(\text{Me}_2\text{-cAAC})_2\text{M}^{\text{I}}\text{Cl}$ species by utilizing one equiv of KC_8 .^{37,38} Both $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}\text{Cl}$ and $(\text{Me}_2\text{-cAAC})_2\text{Cr}^{\text{I}}\text{Cl}$ were converted to the corresponding cations $[(\text{Me}_2\text{-cAAC})_2\text{M}]^+\text{B}(\text{R}^{\text{F}}_{20})_4^-$ using lithium and sodium borate, respectively (Scheme 12).^{37,38} The dechlorination of $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}\text{Cl}$ in toluene produced $[(\text{Me}_2\text{-cAAC})_2\text{Fe}]^+\text{B}(\text{R}^{\text{F}}_{20})_4^-$, while the chromium analogue was only obtained when 1,3-difluorobenzene was used as solvent under argon atmosphere with prolonged stirring of the reaction solution.³⁷

■ STRUCTURAL DESCRIPTION

Structurally, each metal atom of $(\text{Me}_2\text{-cAAC})_2\text{M}^{\text{I}}\text{Cl}$ [$\text{M} = \text{Co}, \text{Fe}, \text{Cr}$] is coordinated by one chlorine and two carbene carbon atoms (Figures 9 and 11).^{34–38} The C–M–C bond angles are

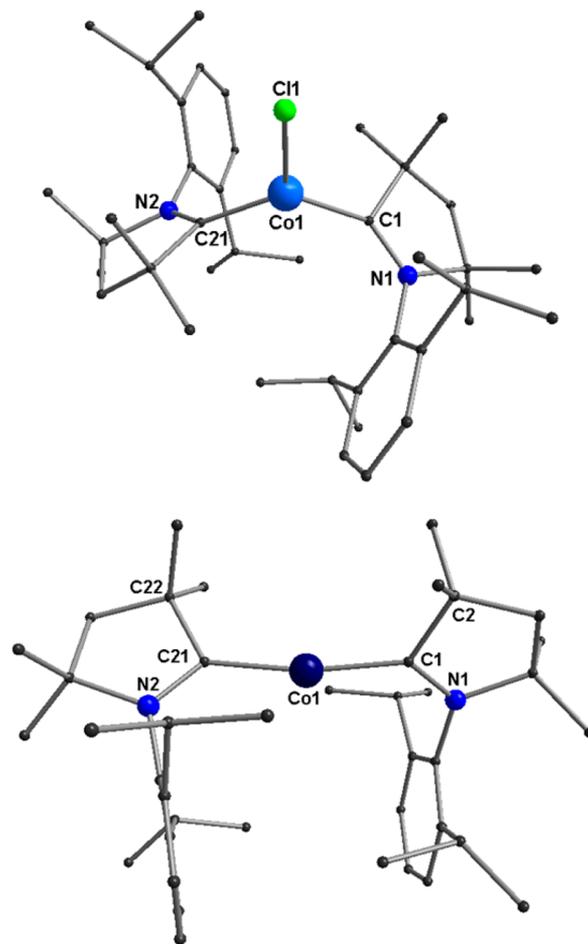


Figure 9. Molecular structures of $(\text{Me}_2\text{-cAAC})_2\text{Co}^{\text{I}}\text{Cl}$ (top) and $(\text{Me}_2\text{-cAAC})_2\text{Co}$ (bottom).

in the range of $120.89(5)^\circ$ – $137.17(6)^\circ$. The C–M bond distances are ranging from 1.920(2) to 2.0931(16) Å [$(^{\text{Mes}}\text{NHC})_2\text{CoCl}$; ^{17}C Co–C 1.953(5) and 1.955(5) Å; $(^{\text{Mes}}\text{NHC})_2\text{Co}^+$; 1.937(2) Å]. It has been found that the carbene-metal bond distances and C–M–C angles gradually increase from cobalt to chromium. The C–N bond distances are in the range of 1.3325(16) to 1.3429(16) Å. The C–N bond distances are slightly longer when compared with the free carbene (~ 1.315 Å),²⁰ suggesting π -back-donation from the metal(I) centers to the carbene carbon atoms ($\text{M}^{\text{I}} \rightarrow \text{C}_{\text{cAAC}}$). The Dipp-groups of $\text{Me}_2\text{-cAAC}$ ligands are oriented in *trans* fashion [NCCN torsion angles ~ 104 – 107° (Co), 108 – 134° (Fe), 106° (Cr)] with respect to the central metal atom (Figures 9 and 11). The NCCN torsion angles are increased when comparatively more bulky carbene ($\text{Et}_2\text{-cAAC}$ instead of $\text{Me}_2\text{-cAAC}$) is employed.^{34–38}

$(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}\text{BR}_4^-$ and $(\text{Me}_2\text{-cAAC})_2\text{Cr}^{\text{I}}\text{BR}_4^-$ possess a center of inversion passing through the cationic metal center (Figure 12).^{37,38} The analogous $\text{Et}_2\text{-cAAC}$ carbene containing complexes do not possess a center of inversion within the molecule (Figure 10).³⁵ The C–M–C bond angles are ~ 165 – 168° . The C–M bond distances are shorter and C–M–C bond angles are wider, respectively, in $(\text{cAAC})_2\text{M}^{\text{I}}\text{BR}_4^-$ when compared to that of $(\text{cAAC})_2\text{M}^{\text{I}}\text{Cl}$. The C–N bond distances are close to those of the free carbene (~ 1.315 Å) suggesting strong σ -donation from the carbene carbon atoms to the metal(I) center ($\text{M}^{\text{I}} \leftarrow \text{C}_{\text{cAAC}}$). The Dipp-groups of cAAC

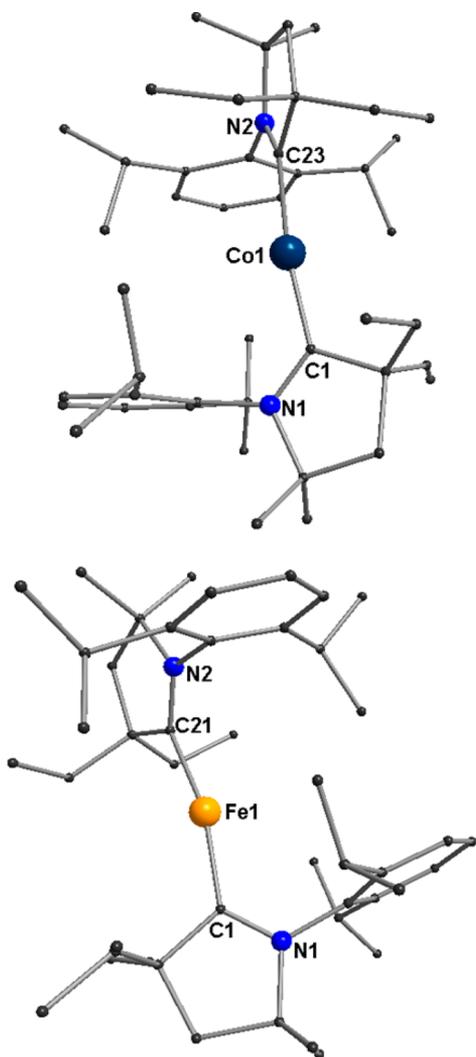
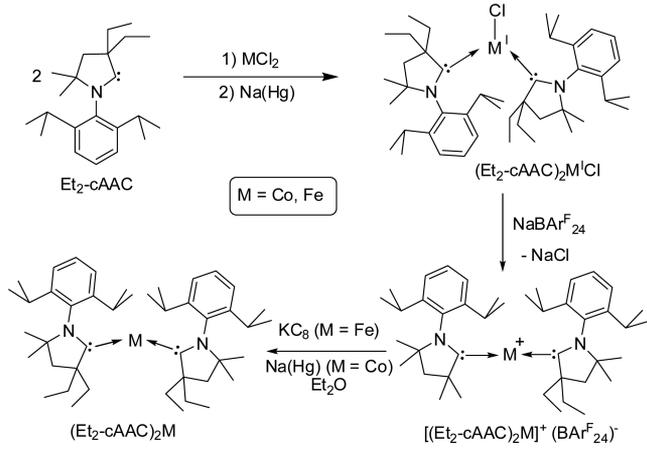


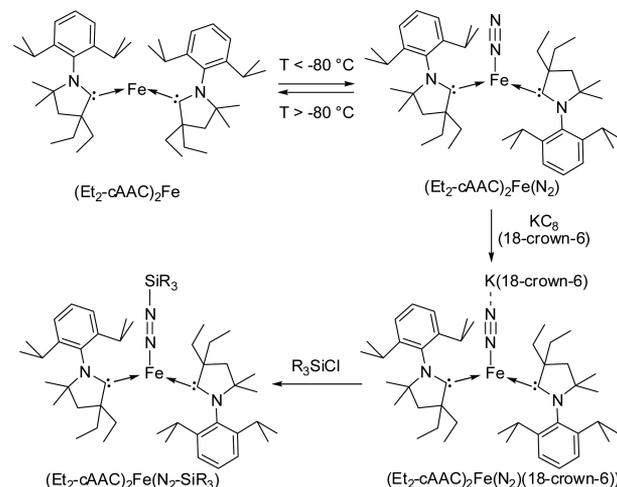
Figure 10. Molecular structures of $[(\text{Et}_2\text{-cAAC})_2\text{Co}]^+$ (top) and $[(\text{Et}_2\text{-cAAC})_2\text{Fe}]^+$ (bottom).

Scheme 10. Synthesis of $(\text{cAAC})_2\text{M}$ ($\text{M} = \text{Co}, \text{Fe}$); $\text{BAR}^{\text{F}}_{24} = \text{Tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl})\text{borate}$

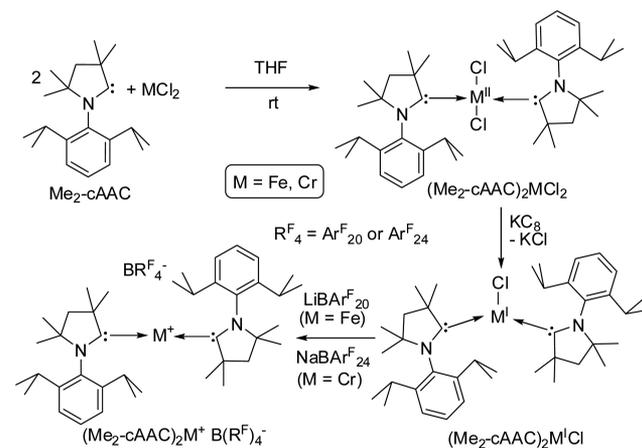


ligands are oriented in *trans* fashion in $(\text{Et}_2\text{-cAAC})_2\text{Fe}^+/\text{Co}^+$ (Figure 10), while nearly orthogonal in $(\text{Me}_2\text{-cAAC})_2\text{Fe}^+/\text{Cr}^+$.^{37,38} The NCCN torsion angle is 71° in $(\text{Et}_2\text{-cAAC})_2\text{Fe}^+$, 70° in $(\text{Et}_2\text{-cAAC})_2\text{Co}^+$ and 180° in $(\text{Me}_2\text{-cAAC})_2\text{Fe}^+/\text{Cr}^+$, respectively (Figure 9).³⁵ The C–Cu–C bond angle is 180° in

Scheme 11. Reduction of $[(\text{Et}_2\text{-cAAC})_2\text{Fe}(\text{N}_2)]$ and Subsequent Trapping with Silylating Reagents



Scheme 12. Synthesis of $(\text{cAAC})_2\text{M}^+$ ($\text{M} = \text{Fe}, \text{Cr}$); $\text{BAR}^{\text{F}}_{20} = \text{Tetrakis}(\text{pentafluorophenyl})\text{borate}$



$(\text{Me}_2\text{-cAAC})_2\text{Cu}^+\text{OTf}^-$, while $(\text{Et}_2\text{-cAAC})_2\text{Cu}^+\text{I}^-$ possesses two types of molecules with C–Cu–C bond angles ranging from 168° to 180° .²⁸

Reduction of $(\text{Me}_2\text{-cAAC})_2\text{Co}_2\text{Cl}_4$ with four and three equiv of KC_8 led to the isolation of the neutral and the cationic bis-carbenedicobalt complexes $(\text{Me}_2\text{-cAAC})_2\text{Co}_2$ (top) and $(\text{Me}_2\text{-cAAC})_2\text{Co}_2^+\text{OTf}^-$, respectively (Figure 13) with eight coordinate cobalt atoms.³³

Neutral complex $(\text{Me}_2\text{-cAAC})_2\text{M}$ possesses a center of inversion passing through the central metal atom [$\text{M} = \text{Zn},^{27\text{a}}$ $\text{Mn},^{27\text{b}}$ $\text{Cu},^{28}$ Au^{30}] which is coordinated by two C_{cAAC} molecules (Figures 3 and 6). The C–M–C bond angle is 180° with C–M bond distances in the range of 1.8850(17)–1.991(2) Å. The C–N bond distances range from 1.3510(13) to 1.376(2) Å which are slightly longer than those of the free carbene (~ 1.31 Å),²⁰ suggesting accumulation of electron densities on the C_{cAAC} . The Dipp-groups of $\text{Me}_2\text{-cAAC}$ ligands are oriented in *trans* fashion with respect to the central metal atom.

$(\text{Me}_2\text{-cAAC})_2\text{M}$ [$\text{M} = \text{Ni},^{31}$ $\text{Pd},^{32}$ Pt^{32}] does not have a center of inversion passing within the molecule (Figure 7). The central metal atom is coordinated by two carbene carbon atoms like those in Zn/Mn/Cu/Au complexes [torsion angle 180°] (Figures 3 and 6). The Dipp-groups of $\text{Me}_2\text{-cAAC}$ ligands are

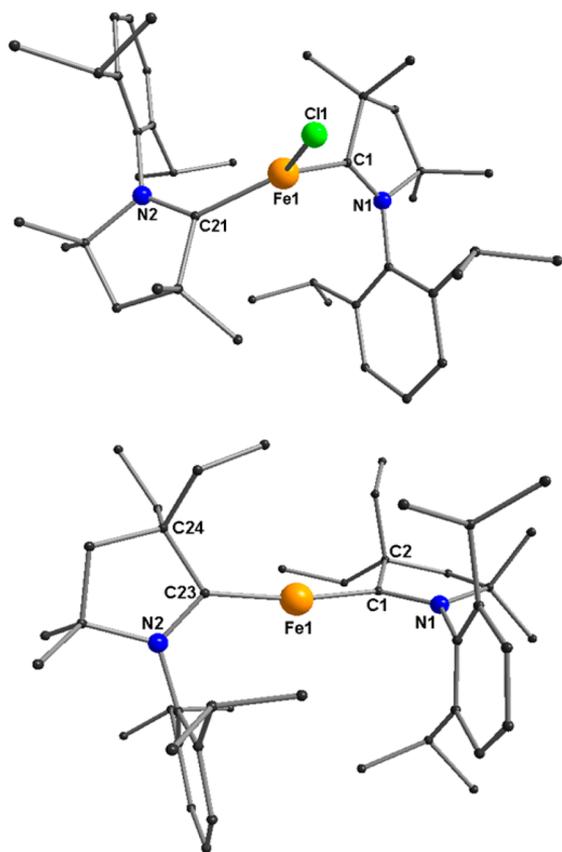


Figure 11. Molecular structures of $(\text{Me}_2\text{-cAAC})_2\text{Fe}^1\text{Cl}$ (top) and $(\text{Et}_2\text{-cAAC})_2\text{Fe}$ (bottom).

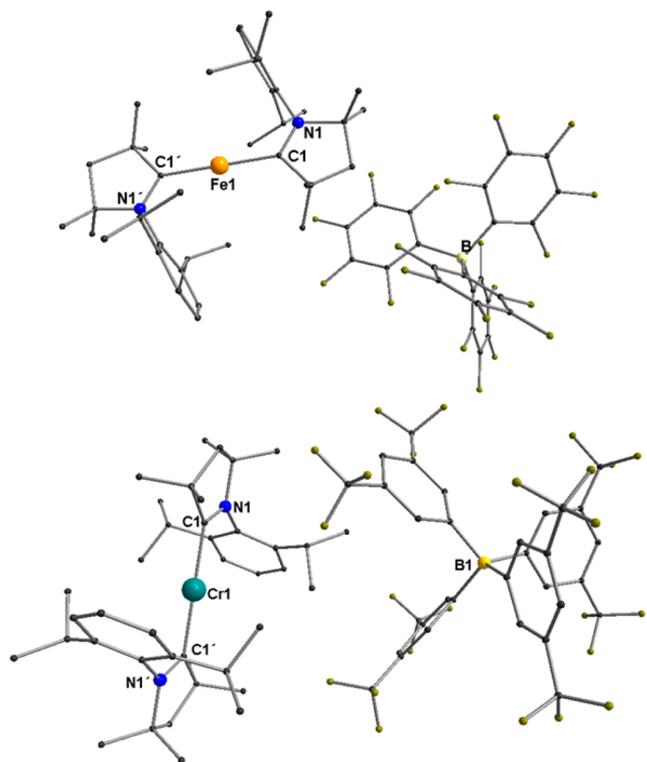


Figure 12. Molecular structures of complexes $(\text{Me}_2\text{-cAAC})_2\text{Fe}^+\text{BARF}_5^-$ (top) and $(\text{Me}_2\text{-cAAC})_2\text{Cr}^+\text{BARF}_{24}^-$ (bottom).

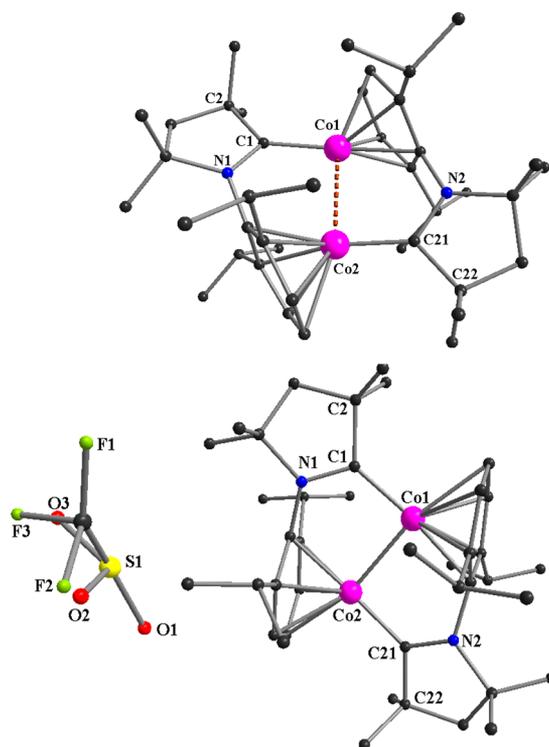


Figure 13. Molecular structures of $(\text{Me}_2\text{-cAAC})_2\text{Co}_2$ (top) and $(\text{Me}_2\text{-cAAC})_2\text{Co}_2^+\text{OTf}^-$ (bottom).

nearly oriented in *cis* fashion [NCCN torsion angles $\sim 78^\circ$ (Ni), 70° (Pd), 73° (Pt)] with respect to the central metal atom. The C–M–C bond angles are sharper ($\sim 165\text{--}172^\circ$) nearly by $10^\circ\text{--}15^\circ$ when compared with that of $(\text{Me}_2\text{-cAAC})_2\text{M}$ [180° ; M = Zn/Mn/Cu/Au] with C–M bond distances in the range of 1.8419(13) Å in $(\text{Me}_2\text{-cAAC})_2\text{Ni}^0$ to 2.0054(13) Å in $(\text{Me}_2\text{-cAAC})_2\text{Pd}^0$ [(MesNHC) $_2\text{M}$, Ni–C 1.827(6)–1.830(6) Å; Pt–C 1.959(8)–1.942(8) Å; [(AdNHC) $_2\text{Pd}$ Pd–C 2.076(5)–2.084(5) Å].^{10,11} $(\text{Me}_2\text{-cAAC})_2\text{Co}^0$ and $(\text{Et}_2\text{-cAAC})_2\text{Fe}^0$ complexes^{34,35} (Figures 9 and 11) are isostructural with those of Ni/Pd/Pt analogues.^{31,32}

■ MAGNETIC PROPERTY

$(\text{Me}_2\text{-cAAC})_2\text{Cr}^1\text{Cl}$ and $[(\text{Me}_2\text{-cAAC})_2\text{Cr}]^+(\text{BARF}_{24})^-$ have $S = 5/2$ spin ground state.³⁸ The magnetic moment of $(\text{Me}_2\text{-cAAC})_2\text{Cr}^1\text{Cl}$ is $6.20 \mu_B$ at 210 K. It exhibits slow relaxation of magnetization under an applied dc magnetic field of 500 Oe (Figure 14), suggesting single ion magnet (SIM) behavior.³⁸ The magnetic moments of $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ and $(\text{Me}_2\text{-cAAC})_2\text{Mn}$ are 4.15 and $5.82 \mu_B$ at rt, suggesting $S = 3/2$ and $5/2$ spin ground states, respectively.^{27b} Both complexes do not display slow magnetic relaxation due to the lack of magnetic anisotropy.

$(\text{Et}_2\text{-cAAC})_2\text{Fe}^0$ possesses $S = 1$ spin ground state with high spin d^8 (Fe^0) electronic configuration (magnetic moment $4.3 \mu_B$ in solution).³⁵ The magnetic moment of $[(\text{Et}_2\text{-cAAC})_2\text{Fe}(\text{N}_2)][\text{K}(18\text{-crown-6})]$ in C_6D_6 solution is $1.9 \mu_B$ (d^9 , Fe^-) at rt. It has a $S = 1/2$ spin ground state.³⁶ The $(\text{Et}_2\text{-cAAC})_2\text{Co}^1\text{Cl}$ has a magnetic moment of $2.9 \mu_B$ in solution as expected ($S = 1$).³⁵ Two-coordinate $[(\text{Et}_2\text{-cAAC})_2\text{Co}]^+(\text{BARF}_{24})^-$ exhibits a magnetic momentum of $3.2 \mu_B$ which is slightly higher than its three-coordinate precursor. This might be due to the change in the coordination number. The $(\text{cAAC})_2\text{M}$ [M = Zn, Ni, Pd, Pt] complex is diamagnetic ($S = 0$) and hence it was characterized

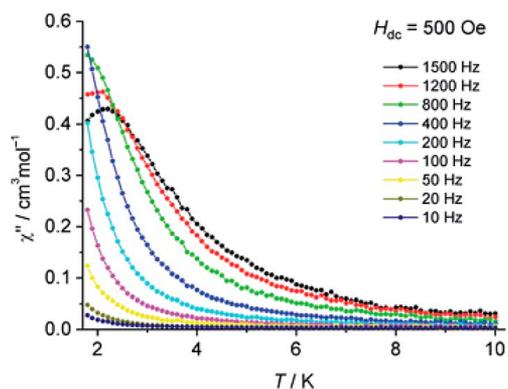


Figure 14. Plots of χ'' vs T of $(\text{Me}_2\text{-cAAC})_2\text{Cr}^{\text{I}}$ at indicated frequencies under applied magnetic field ($H_{\text{dc}} = 500$ Oe).

by NMR.^{31,32} A two-coordinate cationic nickel(I) ion stabilized by bulky NHCs acts as a SIM below 9 K ($U_{\text{eff}}/k_{\text{B}} = 11.8$ cm^{-1}).¹⁵ Complex $(\text{cAAC})_2\text{M}^0$ [$\text{M} = \text{Co}, \text{Au}$]^{30,34} is a one electron paramagnetic complex, which has been confirmed by EPR. The magnetic moment of $(\text{cAAC})_2\text{Cu}$ (d^{10} , Cu^+ , one cAAC· radical) is $1.74 \mu_{\text{B}}$ at 155 K which is in good agreement with one unpaired electron.²⁸

The magnetic anisotropy of a metal ion often can be enhanced by lowering the coordination number. The dc magnetic susceptibility measurements (magnetic moment $4.84 \mu_{\text{B}}$) showed that $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}$ has $S = 3/2$ spin ground state as expected for the Fe^{I} ion ($3d^7$) with coordination number three.³⁷ $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}$ does not show detectable out-of-phase (χ'') signal in the absence of the dc field. However, $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}$ exhibits slow relaxation of magnetization under the application of the dc field of 500 Oe (Figure 15, top). This suggests fast quantum tunneling of magnetization (QTM) under zero applied field which is suppressed when a dc field of 500 Oe is applied. Additionally, slow relaxation of magnetization is thermally accessible at higher temperatures of the Arrhenius plot (Figure 15, bottom). A linear fit using $\tau = \tau_0 \exp(U_{\text{eff}}/k_{\text{B}}T)$ produces an energy barrier of $U_{\text{eff}}/k_{\text{B}} = 22.4$ cm^{-1} with $\tau_0 = 7.0 \times 10^{-8}$ s which suggests that $(\text{Me}_2\text{-cAAC})_2\text{Fe}^{\text{I}}$ is a single ion magnet (SIM).³⁷ $[(\text{Me}_2\text{-cAAC})_2\text{Fe}]^+(\text{Ph}_4\text{B})^-$ with two-coordinate Fe^{I} also exhibits a detectable out-of-phase signal suggesting that it might be a single ion magnet ($U_{\text{eff}} < 20$ cm^{-1}).³⁷

ELECTRONIC STRUCTURES

The correct electronic structures (Scheme 13) of $(\text{cAAC})_2\text{M}$ complexes are studied by EPR, magnetic susceptibility measurements (see above) and were correlated with theoretical calculations. Neutral complexes with two-coordinate Zn/Mn/Cu/Au possess metal atoms in nonzero oxidation states with delocalized radical electrons spanning over two carbene carbon atoms. Diamagnetic $(\text{cAAC})_2\text{Zn}^{\text{II}}$ prefers a carbene centered 1,3-singlet diradical spin ground state rather than a $(\text{cAAC})_2\text{Zn}^0$. The $(\text{cAAC})_2\text{Mn}$ complex has two electronic conformers with $S = 3/2$ spin ground state confirmed by EPR and magnetic susceptibility measurements. The conformer $(\text{cAAC})_2\text{Mn}^{\text{II}}$ which is analogous to $(\text{cAAC})_2\text{Zn}^{\text{II}}$ has been theoretically predicted to be the minor conformer, while its electronic isomer $(\text{cAAC})\text{Mn}^{\text{I}}(\text{cAAC})$ is the major conformer. One-electron paramagnetic complexes $(\text{cAAC})_2\text{Cu}$ and $(\text{cAAC})_2\text{Au}$ possess similar electronic structures like $(\text{cAAC})\text{Mn}^{\text{I}}(\text{cAAC})/(\text{cAAC})\text{Mn}^{\text{I}}(\text{cAAC})$ which was confirmed by

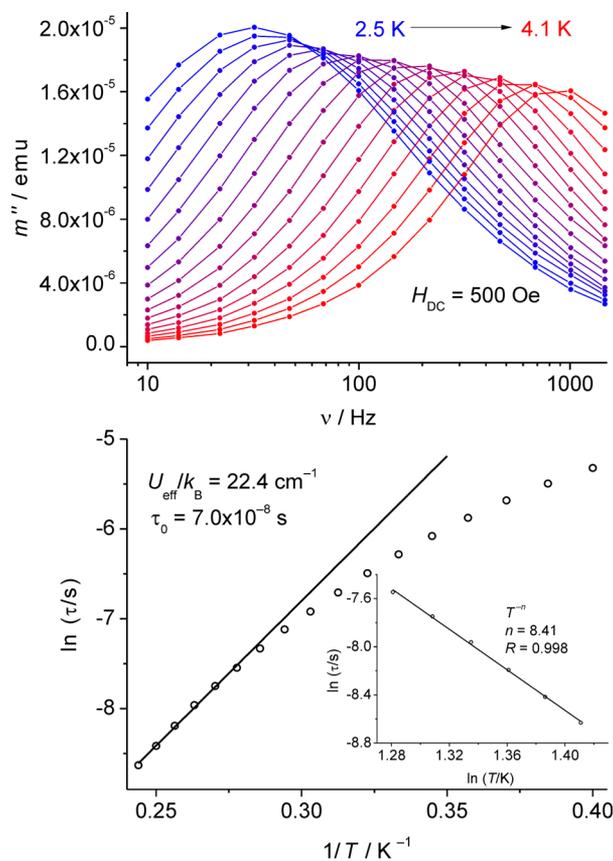
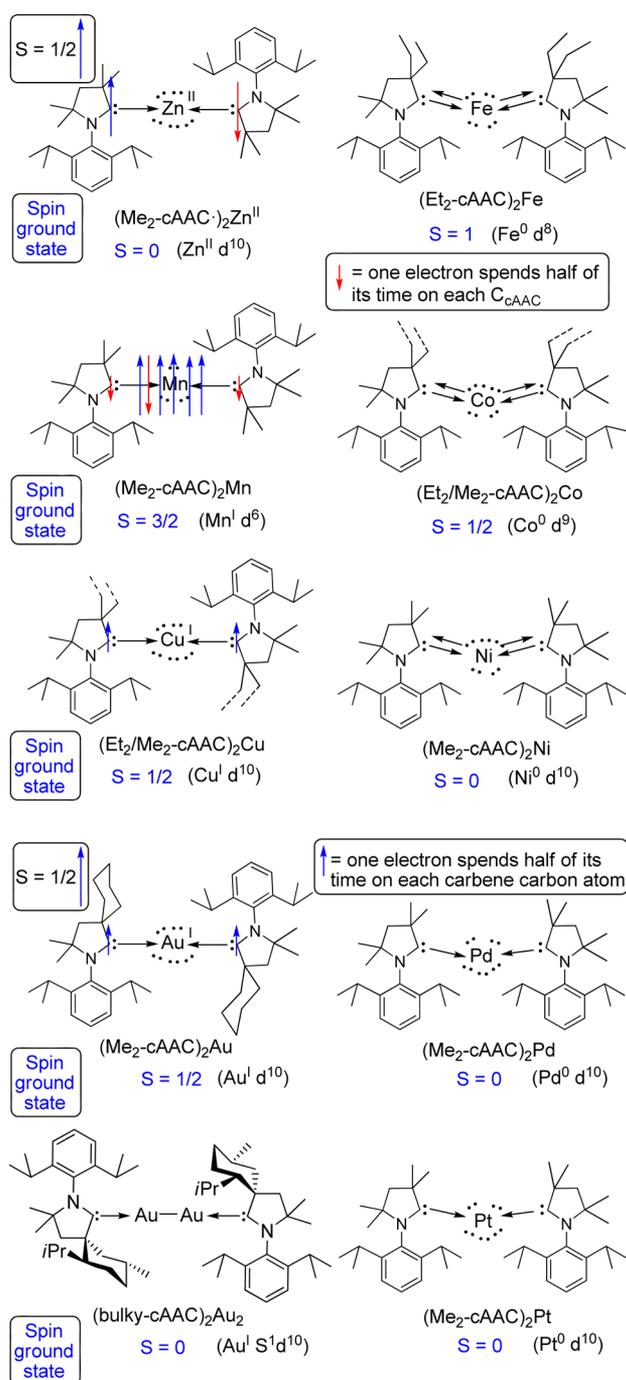


Figure 15. Plots of χ'' vs ν (top) and Arrhenius plot (bottom). The black straight line describes a thermally activated relaxation.

EPR and magnetic susceptibility measurements and supported by theoretical calculations. Complexes $(\text{cAAC})_2\text{Co}^0$ and $(\text{cAAC})_2\text{Fe}^0$ are paramagnetic having $S = 1/2$ and 1, which match with their magnetic momentum. Theoretical calculations suggest that cAAC significantly accepts π -backdonation ($\text{C}_{\text{cAAC}} \leftarrow \text{M}$) from the electron rich metal center. Diamagnetic complexes $(\text{cAAC})_2\text{Ni}^0$, $(\text{cAAC})_2\text{Pd}^0$, and $(\text{cAAC})_2\text{Pt}^0$ are 14e systems with each metal atom contributing d^{10} electrons. $(\text{cAAC})_2\text{M}^0$ [$\text{M} = \text{Co}, \text{Au}$] has been theoretically investigated to have a singlet ground state with a M–M bond. The shape of Laplacian distribution of $(\text{Me}_2\text{-cAAC})_2\text{Co}_2$ shows a small area of charge concentration at the bond critical point of the Co–Co bond.¹¹ The other two orbital contributions $\Delta E_{\text{orb}}(3) = -44.0$ kcal/mol and $\Delta E_{\text{orb}}(4) = -40.4$ kcal/mol are attributed to the components of the $\text{cAAC} \leftarrow \text{CoCo} \rightarrow \text{cAAC}$ π -backdonation. Both $(\text{cAAC})_2\text{Co}_2$ and $(\text{cAAC})_2\text{Co}_2^+$ were found to have a Co–Co bond.³³ However, the Au–Au bond of $(\text{bulky-cAAC})_2\text{Au}_2$ is formed via the coupling of unpaired electrons in the valence AOs of each gold ($d^{10}s^1p^0$) atom which is sd-hybridized.³⁰

CATALYSIS

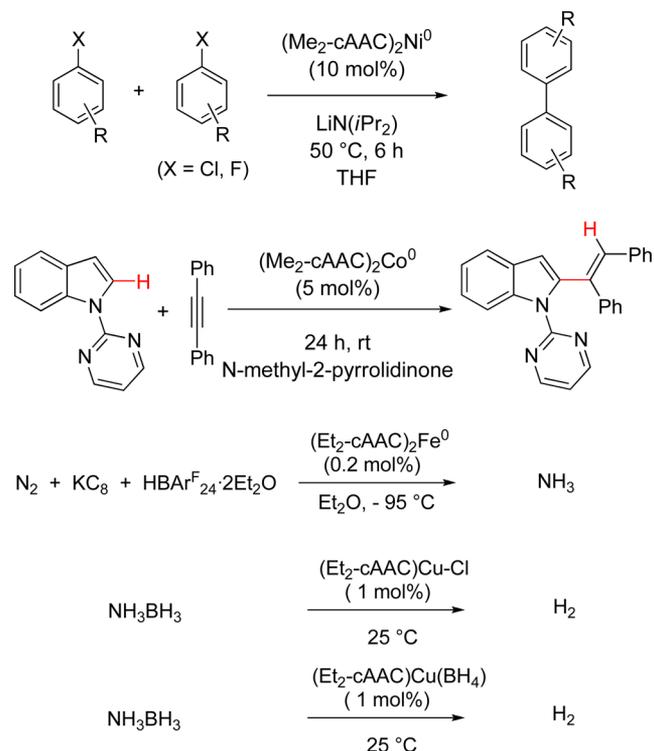
The homocoupling of aryl halides is one of the most powerful methods to form C–C bonds to produce biaryls. The use of readily available and inexpensive aryl chlorides is still scarce probably due to the high energy cleavage of the C–Cl bond. Catalytic activation of unactivated C–F bonds is even more challenging. $(\text{Me}_2\text{-cAAC})_2\text{Ni}^0$ was used as a catalyst (10 mol %) for the homocoupling of *para*-chlorotoluene, chlorobenzene, and fluorobenzene, respectively in the presence of $\text{LiN}(i\text{Pr})_2$ as

Scheme 13. Electronic Configurations of Neutral Complexes (cAAC)₂M (M = Mn–Zn, Au, Pd, Pt)⁴⁴

⁴⁴Spin ground state of (cAAC)₂M is designated by S.

the reducing agent at 50 °C (Scheme 14).³¹ The biaryls (Ar–Ar) were isolated in ~80% yield after 6 h.

The C2-alkenylation of *N*-pyrimidylindole with diphenylacetylene and cyclotrimerization of diphenylacetylene proceeded smoothly at rt in the presence of (Me₂-cAAC)₂Co⁰ as catalyst (5 mol %) in *N*-methyl-2-pyrrolidone (NMP) (Scheme 14).³⁴ The yield is 70%. The use of THF and toluene led to the cyclotrimerization of diphenylacetylene to produce hexaphenyl benzene in ~80% yield. Yoshikai et al. have shown that alkenylation of *N*-methylpyrrolidinone is catalyzed by CoBr₂ as a metal source and pyphos (pyphos = Ph₂P(CH₂)₂–C₅H₄N) as

Scheme 14. Catalysis of (cAAC)₂M⁰ (M = Ni, Co, Fe)

a ligand in the presence of 60 mol % of Grignard reagent (*t*BuCH₂MgBr) at rt. The Grignard reagents (RMgBr) often reduce the metal ion to its lower oxidation state under elimination of R–R. The actual intermediate species was not isolated. The well characterized (Me₂-cAAC)₂Co⁰ catalyzes the similar process without any additional Grignard reagent.³⁴

(Et₂-cAAC)₂Fe⁰ effectively catalyzes the formation of N(SiMe₃)₃ reacting N₂ with Me₃SiCl in the presence of equiv amounts of KC₈. (Et₂-cAAC)₂Fe⁰ reversibly binds to dinitrogen at around -80 °C (Scheme 11) to produce (Et₂-cAAC)₂Fe⁰(N₂) which undergoes a one electron reduction by KC₈ to yield (Et₂-cAAC)₂Fe⁰(N₂)⁻. These species are spectroscopically as well as structurally characterized. The turnover number (TON) was calculated to be ~19.5.³⁶ A comparable reaction was also catalyzed by [(Et₂-cAAC)₂Fe]⁺BAR^F₂₄⁻ with slightly lower TONs. Similarly, hydrogenation of dinitrogen proceeds via binding of dinitrogen to the Fe⁰-complex below -95 °C and then subsequently reacts with hydrogen gas (H₂) to produce ammonia. Very small amount of (Et₂-cAAC)₂Fe⁰ (0.2 mol %) is required for the reduction of dinitrogen to ammonia (Scheme 14).³⁶

(Et₂-cAAC)Cu–Cl reacts with NaBH₄ and NH₃BH₃ to produce (Et₂-cAAC)Cu(BH₄) (Scheme 3).³⁹ Both (Et₂-cAAC)Cu–Cl and (Et₂-cAAC)Cu(BH₄) complexes are air-stable and promote the catalytic hydrolytic dehydrogenation of ammonia borane (NH₃BH₃) (Scheme 14). The turnover frequency (TOF) is 3100 per mol_{H₂}⁻¹ mol_{cat}⁻¹ h⁻¹ when (Et₂-cAAC)Cu–Cl is used as a catalyst. It is 500 times higher than that of (Ph₃P)₂CuCl. The catalytic activity decreases when Et₂-cAAC is replaced by a comparatively bulky cAAC ligand. The TOF is increased to 3360 when a 1:1 molar mixture of (Et₂-cAAC)Cu–Cl:potassium tetrakis(pentafluorophenyl)borate is employed. Further studies showed that (Et₂-cAAC)Cu(BH₄) is a better catalyst with the TOF of 8400 mol_{H₂}⁻¹ mol_{cat}⁻¹ h⁻¹ at 25 °C.

reflects that $(cAAC)_2Fe^I Cl$ acts as a single ion magnet. Moreover, it shows that the two coordinate metal(0) complexes of Ni, Co, Fe, and Au act as promising catalysts for various organic transformations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hroesky@gwdg.de

Notes

The authors declare no competing financial interest.

Biographies

Sudipta Roy received her Ph.D in 2012 from the University of Regensburg under the supervision of Professor Oliver Reiser. Afterward, she worked as a postdoctoral fellow at the Institute of Organic and Biomolecular Chemistry, University of Göttingen on transition metal catalyzed C–H bond activation. Since July, 2014, she has been working as a postdoctoral fellow with Professor Herbert W. Roesky. Her research interests include the synthesis of cyclic alkyl(amino) carbene stabilized highly air and moisture sensitive Si–P compounds and transition metal complexes with their application in catalysis.

Kartik Chandra Mondal received his Ph.D in 2011 from Karlsruhe Institute of Technology under the supervision of Professor Annie K. Powell. He moved to University of Göttingen in October 2011. Since then he has been working with Professor Herbert W. Roesky as a postdoctoral fellow. His research interest mainly focuses on the stabilization of low valent low coordinate group 14 elements and transition metal complexes.

Herbert W. Roesky obtained his doctorate from University of Göttingen. After working at Du Pont in the United States, he returned to Göttingen and finished his habilitation. Then he became a professor at the Johann-Wolfgang-Goethe-Universität, Frankfurt am Main in 1971. He moved to University of Göttingen in 1980 and was the director of the Institute for Inorganic Chemistry until 2004. He is primarily known for his pioneering work on fluorides of both transition and main group elements. His current research interest is focused on the synthesis and reactivity of compounds with heavier group 13 and 14 elements.

ACKNOWLEDGMENTS

H.W.R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/64-I) for financial support. Dedicated to Professor Anton Meller on the occasion of his 84th birthday.

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