Inorganic Chemistry

Article

pubs.acs.org/IC

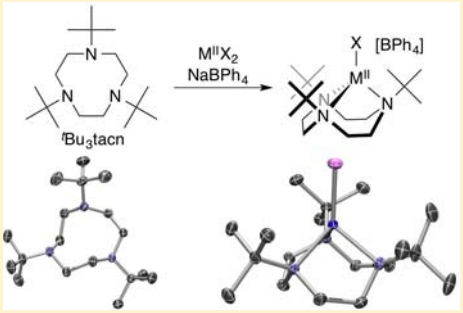
1,4,7-Triazacyclononane Ligands Bearing Tertiary Alkyl Nitrogen Substituents

Arumugam Thangavel, Marika Wieliczko, John Bacsa, and Christopher C. Scarborough*

Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States

Supporting Information

ABSTRACT: The first synthesis of 1,4,7-tri-*tert*-butyl-1,4,7-triazacyclononane (^{t}Bu$_3$tacn) and its adamantyl analog Ad$_3$tacn are described. Cr^{II}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{I} compounds of ^{t}Bu$_3$tacn are reported: the steric properties of this ligand enforce four-coordinate geometries except in the case of five-coordinate Cr^{II}, enabling design of pseudotetrahedral compounds bearing this tridentate redox-inert ancillary ligand.

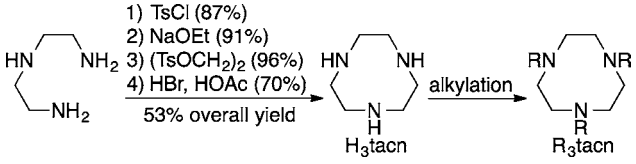


INTRODUCTION

1,4,7-Triazacyclononane (H$_3$tacn) and its N-substituted derivatives (R$_3$tacn) are textbook ligands for transition metals.[1,2] With N−M−N angles near 90°, these facially binding ligands are ideal "caps" for octahedral metal centers. As a saturated, redox-inert, hard σ-only donor ligand, H$_3$tacn can support highly oxidizing metal centers (e.g., Ni^{III} and Mo^{VI}).[3] Although H$_3$tacn supports six-coordinate environments for ions from groups 4−10, the bulkiest R$_3$tacn species reported to date, ^{i}Pr$_3$tacn,[4] typically enforces five-coordinate geometries when bound to these same metals.[5] Remarkably, R$_3$tacn derivatives with tertiary alkyl R groups, which are likely to favor a four-coordinate pseudotetrahedral geometry, have not been reported. Given the success of related bulky tridentate ligands in supporting reactive four-coordinate terminal metal−oxo, −imido, and −nitrido (M(E)) moieties,[6] as well as the rich history of saturated amine macrocycles supporting high-valent M(E) species,[7] ^{t}Bu$_3$tacn is an attractive target for supporting reactive M(E) moieties that are unusually stable to intramolecular decomposition. The absence of ^{t}Bu$_3$tacn in the R$_3$tacn series is an artifact of synthetic routes used to access these ligands.

R$_3$tacn derivatives are generally synthesized by alkylation of H$_3$tacn, either with alkyl halides or by reductive amination. The standard H$_3$tacn synthesis is shown in Scheme 1.[1] This route precludes N-alkylation prior to cyclization, underscoring the need for H$_3$tacn as a precursor to all R$_3$tacn derivatives. Effective methods for tertiary alkylation of secondary nitrogens are unavailable, precluding access to ^{t}Bu$_3$tacn from H$_3$tacn. After more than 40 years of research on R$_3$tacn complexes,[8] ^{t}Bu$_3$tacn has remained inaccessible.

Scheme 1. Standard Route to H$_3$tacn and R$_3$tacn



In this contribution, we describe the first synthesis of ^{t}Bu$_3$tacn, which is carried out in three steps from commercially available reagents and employs crystallization as the sole means of purification. The related ligand, Ad$_3$tacn, is prepared by the same procedure. ^{t}Bu$_3$tacn compounds of Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} are the first four-coordinate R$_3$tacn species of these metals. Five-coordinate [(^{t}Bu$_3$tacn)(MeCN)Cr^{II}(OTf)][OTf] is likewise the lowest-coordinate R$_3$tacn chromium compound to date. [(^{t}Bu$_3$tacn)Cu^{I}(MeCN)][PF$_6$] and [(Ad$_3$tacn)-Cu^{I}(MeCN)][PF$_6$] are described and form the basis for a steric comparison of R$_3$tacn ligands.

EXPERIMENTAL SECTION

General Considerations. All reagents were purchased from either Sigma Aldrich or Strem Chemicals and were used as received unless noted otherwise. All metalation reactions were performed inside an MBRAUN UNIlab 2000 inert-atmosphere glovebox. All anhydrous solvents (acetonitrile, methylene chloride, diethyl ether, pentane, and toluene) were purified and dried by an MBRAUN solvent purification system (SPS). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Varian 300 or 400 MHz NMR spectrometers. IR spectra of neat compounds were recorded using a Nicolet 380 FT-IR (Thermo Electron Corporation). UV−vis/NIR absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Mass spectra were obtained from the Mass Spectrometry Center at Emory University. Elemental Analyses were obtained from Atlantic Microlab Inc., Norcross, Georgia. Solution-phase magnetic moments were

Received: October 17, 2013
Published: November 4, 2013

   dx.doi.org/10.1021/ic402626p | *Inorg. Chem.* 2013, 52, 13282−13287

measured by the Evans method.[9] Cyclic voltammetry (CV) data were recorded on a Princeton Applied Research VersaSTAT 4 potentiostat.

Representative Ligand Synthesis: ^{t}Bu$_3$tacn. *N,N′-Bis(2-chloroacetyl)-N,N′-di-tert-butylethylenediamine (2).* K_2CO_3 (44.11 g, 0.3191 mol) and methylene chloride (250 mL) were added to an oven-dried 250 mL round-bottom flask. *N,N′*-di-*tert*-butylethylenediamine (31.5 mL, 0.146 mol) was added at room temperature. After the flask was cooled in an ice bath, 2-chloroacetyl chloride (25.37 mL, 0.3191 mol) was added dropwise. As the addition progressed, the colorless solution became light yellow and turbid. The reaction was stirred over an ice bath for 3 h and then heated to 50 °C overnight. After the mixture cooled to room temperature, 50 mL of water was added and the organic layer was separated and washed with water (3 × 250 mL). After the solution was dried over $MgSO_4$ and filtered, the solvent was removed on a rotary evaporator. Crystallization of the crude residue from CH_2Cl_2/hexane afforded pure crystalline **2** in 68.9% yield (32.7 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29 (s, 4H), 3.47 (s, 4H), 1.47 (s, 18H).^{13}C NMR (101 MHz, $CDCl_3$): δ 168.53, 57.24, 45.94, 43.73, 29.91. ESI-MS (m/z): calcd for $\{C_{14}H_{26}N_2O_2Cl_2 + H^+\}$, 325.144 96; found, 325.144 56 (Δ = 1.2 ppm).

1,4,7-Tri-tert-butyl-1,4,7-triazocyclononane-2,6-dione (3). Sodium carbonate (50.0 g, 0.4765 mol) and **2** (62.00 g, 0.1906 mol) were combined in 2 L of anhydrous DMF in a 4 L one-neck round-bottom flask. The reaction mixture was heated at 120 °C for 1h and then brought to room temperature. Neat *tert*-butylamine (22 mL, 0.2096 mol) was added, and the mixture was stirred at room temperature for 30 min and then heated at 120 °C for 3 days. The reaction mixture was brought to room temperature, and ∼85% of the DMF solvent was removed on a rotary evaporator. Water (300 mL) was then added, and the mixture was stirred at room temperature for 1 h. Extraction with Et_2O and DCM, drying the combined organic extracts over $MgSO_4$, filtering, and removal of solvents under reduced pressure afforded the crude product, which was crystallized from ethyl acetate/hexane. This process afforded 41.7 g of pure crystalline **3** (67.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 4H), 3.56 (s, 4H), 1.38 (s, 18H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.75, 63.96, 57.22, 56.39, 46.63, 28.59, 26.09. ESI-MS (m/z): calcd for $\{C_{18}H_{35}N_3O_2 + H^+\}$, 326.280 75; found, 326.280 22 (Δ = 1.6 ppm).

^{t}Bu$_3$tacn. Inside an inert-atmosphere glovebox, commercially available gray-colored $LiAlH_4$ (20.0 g,) was suspended in 500 mL of dry Et_2O. The mixture was stirred overnight and filtered through a preweighed Celite pad. The gray-colored insoluble material (8.03 g) was discarded. (***CAUTION!*** *This material should be quenched very slowly by suspending it in an unreactive solvent (e.g., Et_2O) and slowly adding ^{i}PrOH to avoid ignition.)* The colorless $LiAlH_4$ solution in diethyl ether (11.97 g) was used directly in the next step without isolation. **3** (33.0 g, 0.101 mol) was added portion-wise to the colorless homogeneous $LiAlH_4$ solution. As the addition progressed, the mixture became cloudy. The reaction was stirred at room temperature inside the glovebox overnight. The reaction mixture was then removed from the glovebox and successively quenched with 12, 24, and 36 mL of water, NaOH(aq) (10%), and water, respectively. The insoluble material was removed by filtration and discarded, the colorless solution was dried over $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator. The crude product was purified by crystallization from ethanol, affording 20.92 g of pure ^{t}Bu$_3$tacn (69.7% yield) as colorless, X-ray quality crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.62 (s, 12H), 0.98 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 54.68, 52.85, 26.98. ESI-MS (m/z): calcd for $\{C_{18}H_{39}N_3 + H^+\}$, 298.3222; found, 298.3216 (Δ = 2.0 ppm).

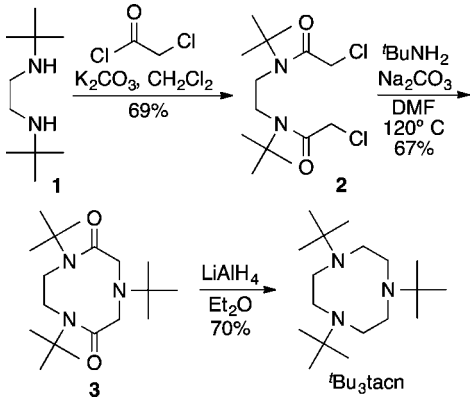
Representative Procedure for the Synthesis of [(^{t}Bu$_3$tacn)-M^{II}X][BPh$_4$]: M^{II}X = Mn^{II}Cl. ^{t}Bu$_3$tacn (4.00 g, 0.1344 mmol), $Mn^{II}Cl_2$ (1.68 g, 0.1344 mmol), and sodium tetraphenylborate (13.8 g, 0.403 mmol) were combined in a 500 mL Schlenk flask with 300 mL of anhydrous acetonitrile. The heterogeneous suspension was stirred at room temperature, and over time the reaction mixture became pinkish-brown. The reaction was stirred overnight, after which time the solvent was removed in vacuo. The resulting viscous suspension was dissolved in anhydrous methylene chloride and stirred overnight. Filtration through a medium-porosity fritted funnel afforded a light-brown solution. The solvent was removed under vacuum, and the solid residue was washed with pentane and dried under vacuum. Analytically pure material was obtained by layering diethyl ether onto an acetonitrile solution of the product: 7.551 g (96.78%). X-ray quality crystals were grown from CH_2Cl_2/pentane. These crystals could be desolvated by heating under vacuum overnight. IR (neat, cm^{-1}): 543, 570, 611, 707, 732, 751, 812, 845, 877, 927, 998, 1031, 1047, 1080, 1135, 1187, 1229, 1286, 1374, 1404, 1418, 1476, 1577, 2162, 2979, 3053. Magnetic moment (Evans method, CD_3CN, 298 K): μ_{eff} = 5.6 μ_B. Anal. Calcd for $C_{42}H_{59}BN_3ClMn$: C, 71.34; H, 8.41; N, 5.94; Cl, 5.01. Found: C, 71.32; H, 8.35; N, 6.02; Cl, 4.88. ESI-MS (m/z): calcd for $\{C_{18}H_{39}N_3ClMn^+\}$, 387.221 30; found, 387.220 27 (Δ = 2.6 ppm). ESI-MS (m/z): calcd for $\{C_{24}H_{20}B^-\}$, 319.165 81; found, 319.168 89 (Δ = 9.6 ppm).

Representative Synthesis of [(R_3tacn)Cu^I(MeCN)][PF$_6$]: R = ^{t}Bu. ^{t}Bu$_3$tacn (1.0 g, 3.36 mmol) was suspended in 50 mL of anhydrous acetonitrile in a 100 mL Schlenk flask. $[Cu(NCCH_3)_4][PF_6]$ (1.250 g, 3.36 mmol) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was passed through a small pad of Celite, and the solvent was removed from the filtrate under vacuum. The residue was redissolved in methylene chloride and layered with pentane, providing 1.622 g of colorless X-ray quality crystals (88.6% yield). ^{1}H NMR (CD_3CN, 1.94 ppm): 2.975 (m, 6H), 2.49 (m, 6H), 2.30 (s, 3H), 1.26 (s, 27H). IR (neat, cm^{-1}): 551, 685, 729, 831, 877, 932, 1056, 1091, 1146, 1196, 1226, 1295, 1371, 1402, 1481, 2886, 2971. Anal. Calcd for $C_{20}H_{42}N_4F_6PCu$: C, 43.91; H, 7.74; N, 10.24; F, 20.84. Found: C, 43.89; H, 7.77; N, 10.13; F, 20.55. ESI-MS (m/z): calcd for $\{C_{20}H_{42}N_4Cu^+\}$, 401.270 55; found, 401.270 48 (Δ = 0.2 ppm).

RESULTS AND DISCUSSION

We reasoned that synthesizing ^{t}Bu$_3$tacn should proceed by preinstallation of *tert*-butyl groups on the nitrogens prior to cyclization because effective methods for alkylation of secondary nitrogens with tertiary alkyl groups are unavailable. Intrigued by reported methods for the synthesis of aza-crown compounds[10] that were later applied to access the unsymmetrically substituted R_2R'tacn derivatives Me_2Rtacn (R = norbornenylmethyl)[11] and Me_2Bntacn,[12] we explored the synthesis of ^{t}Bu$_3$tacn from commercially available *N,N′*-di-*tert*-butylethylenediamine (**1**), chloroacetyl chloride, and ^{t}BuNH$_2$ (Scheme 2). Diacylation of **1** with chloroacetyl chloride furnished intermediate **2** in 69% yield after crystallization from CH_2Cl_2/hexane. When combined with ^{t}BuNH$_2$ and Na_2CO_3 in DMF, **2** cyclized to diamide **3** in 67% isolated yield after crystallization from EtOAc/hexane. We encountered difficulties in the reduction of **3** due to low conversion or ring-opening. However, Et_2O-soluble $LiAlH_4$ cleanly reduced **3**

Scheme 2. Synthesis of ^{t}Bu$_3$tacn



dx.doi.org/10.1021/ic402626p | Inorg. Chem. 2013, 52, 13282−13287

to $^{t}Bu_3$tacn, which was crystallized from EtOH in 70% yield (32% over three steps). The X-ray crystal structure of $^{t}Bu_3$tacn is shown in Figure 1. Although the yield of each step is modest,

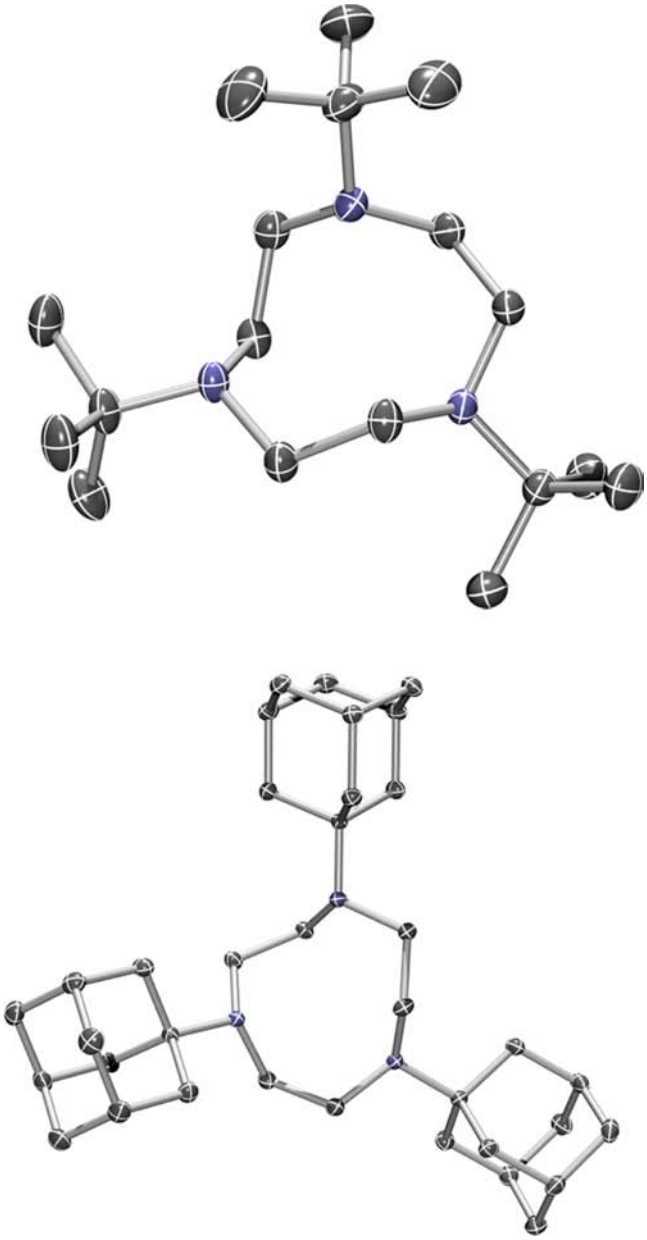


Figure 1. Solid-state molecular structures of $^{t}Bu_3$tacn (top) and Ad_3tacn (bottom). Hydrogen atoms are omitted for clarity.

the route has been scaled to afford 21g of $^{t}Bu_3$tacn in a single batch. By comparison, Me_3tacn is synthesized in five linear steps in 27% overall yield. Despite decades of synthetic inaccessibility, it appears that $^{t}Bu_3$tacn is among the most easily accessed N-substituted derivatives of H_3tacn owing to its three-step synthesis.

The route in Scheme 2 is amenable to the synthesis of Ad_3tacn, although each step is lower yielding (39%, 40%, and 57%, respectively); the crystal structure of this ligand is shown in Figure 1.[13] Both $^{t}Bu_3$tacn and Ad_3tacn crystallize in an orientation where two nitrogen lone pairs project into the opposite face of the nine-membered ring than the lone pair of the third nitrogen, revealing that nitrogen inversion is a prerequisite for coordination. The same orientation was observed in crystalline samples of Ts_3tacn[14] and certain R_3tacn derivatives,[15] and as with these ligands, the solid-state orientation does not inhibit the coordination of $^{t}Bu_3$tacn or Ad_3tacn to transition metals.

All known first-row transition-metal complexes of H_3tacn and R_3tacn in the Cambridge Structural Database,[16] except those of copper and zinc, have crystallized in five-coordinate or higher geometries. A series revealing the steric influence of R in R_3tacn compounds on coordination number is depicted in Figure 2a.[1,5a,b,d,17] Progressing in size of R results in a systematic

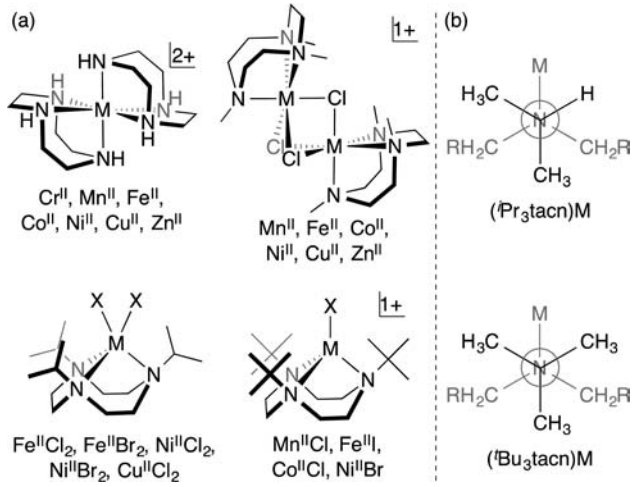


Figure 2. (a) Effect of R in R_3tacn on coordination environment of first-row transition metals as revealed by X-ray crystallography. (b) Newman projections along the R–N bond of the (R_3tacn)M unit demonstrating the solid-state orientation of the R groups in $^{i}Pr_3$tacn and $^{t}Bu_3$tacn.

change in observed coordination environment, with $^{i}Pr_3$tacn providing sufficient steric bulk to exclude a sixth ligand from the coordination sphere. In the solid-state geometry of five-coordinate $^{i}Pr_3$tacn complexes, the ^{i}Pr groups project the H and one methyl of the tertiary carbon into the metal coordination sphere in a staggered conformation (Figure 2b). Replacement of ^{i}Pr with ^{t}Bu should result in substantial crowding by projecting two methyls per ^{t}Bu group into the coordination sphere. Indeed, $^{t}Bu_3$tacn complexes of Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} are isolated as the first four-coordinate compounds of these metals bearing R_3tacn ligands, underscoring the pronounced size difference of ^{i}Pr and ^{t}Bu groups in these ligands.

The cations $[(^{t}Bu_3tacn)M^{II}X]^{+}$ were isolated as $[BPh_4]^{-}$ salts by combining $^{t}Bu_3$tacn, MX_2, and $NaBPh_4$ in acetonitrile (Figure 3a). The solid-state molecular structure of the cation in $[(^{t}Bu_3tacn)Co^{II}Cl][BPh_4]$ is shown in Figure 3b; the structures of the remaining $[(^{t}Bu_3tacn)M^{II}X]^{+}$ salts are included in the Supporting Information. The average X–M–N and N–M–N angles for each species are shown in Figure 3c and reveal that the ligand is geometrically suited for facially capping an octahedron but sterically enforces a coordination number of four.

When $^{t}Bu_3$tacn and $[Cr^{II}(OTf)_2{\cdot}(MeCN)_2]$[18] are combined in CH_2Cl_2, the pseudomonovacant octahedral species $[(^{t}Bu_3tacn)(MeCN)Cr^{II}(OTf)][OTf]$ is isolated as blue-green crystals (Figure 4). This five-coordinate species is the lowest-coordinate crystallographically characterized R_3tacn chromium complex to date, highlighting again the unique steric environ-

dx.doi.org/10.1021/ic402626p | Inorg. Chem. 2013, 52, 13282–13287

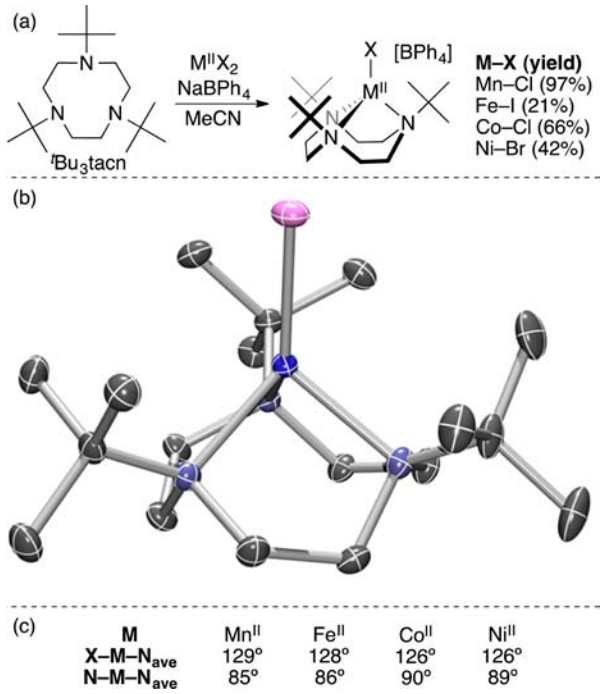


Figure 3. (a) Synthetic route to $[(^tBu_3tacn)M^{II}X][BPh_4]$ compounds, with yields of isolated crystalline material given in parentheses. (b) Solid-state molecular structure of $[(^tBu_3tacn)Co^{II}X][BPh_4]$. The counterion and H atoms are omitted for clarity. (c) Average X–M–N and N–M–N angles of each compound.

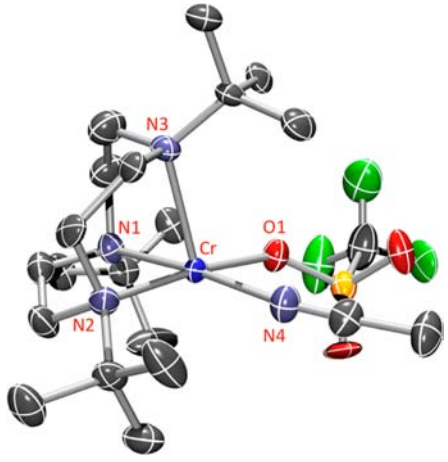


Figure 4. Solid-state molecular structure of the cation in $[(^tBu_3tacn)(MeCN)Cr^{II}(OTf)][OTf]$. Counterion and H atoms are omitted for clarity. Selected bond lengths revealing axial elongation: Cr–N1 2.199(5) Å, Cr–N2 2.182(5) Å, Cr–N3 2.360(5) Å, Cr–N4 2.092(5) Å, and Cr–O1 2.062(4) Å.

ment imposed by $^tBu_3$tacn among the R_3tacn ligands. The ability of this species to adopt a five-coordinate geometry stems from the electronic structure of high-spin Cr^{II}, which in a four-coordinate C_{3v} geometry is unstable to a first-order Jahn–Teller distortion by elongation of one Cr–N bond. Such an elongation opens the coordination sphere of the Cr^{II} ion enough to enable coordination of an acetonitrile ligand. The axial Cr–N_{tacn} bond (2.36 Å) is much longer than the equatorial Cr–N_{tacn} bonds (2.18 Å and 2.20 Å, Figure 4) as expected for a high-spin Cr^{II} species in this geometry. The ^tBu groups on the equatorial $^tBu_3$tacn nitrogens project into the empty axial coordination site, blocking access to a sixth ligand.

To quantify the steric environment imposed by R_3tacn ligands, we sought a transition metal that favors a four-coordinate geometry regardless of the identity of R. The four-coordinate cations $[(R_3tacn)(MeCN)Cu^I]^+$ (R = Me[19] and ^{i}Pr[20]) have been crystallographically characterized. $[(^tBu_3tacn)(MeCN)Cu^I][PF_6]$ and $[(Ad_3tacn)(MeCN)Cu^I][PF_6]$ were obtained by combining each ligand with $[(MeCN)_4Cu^I][PF_6]$ in MeCN as crystalline material in 89% and 78% yield. The X-ray crystal structures of the cations in these species are shown

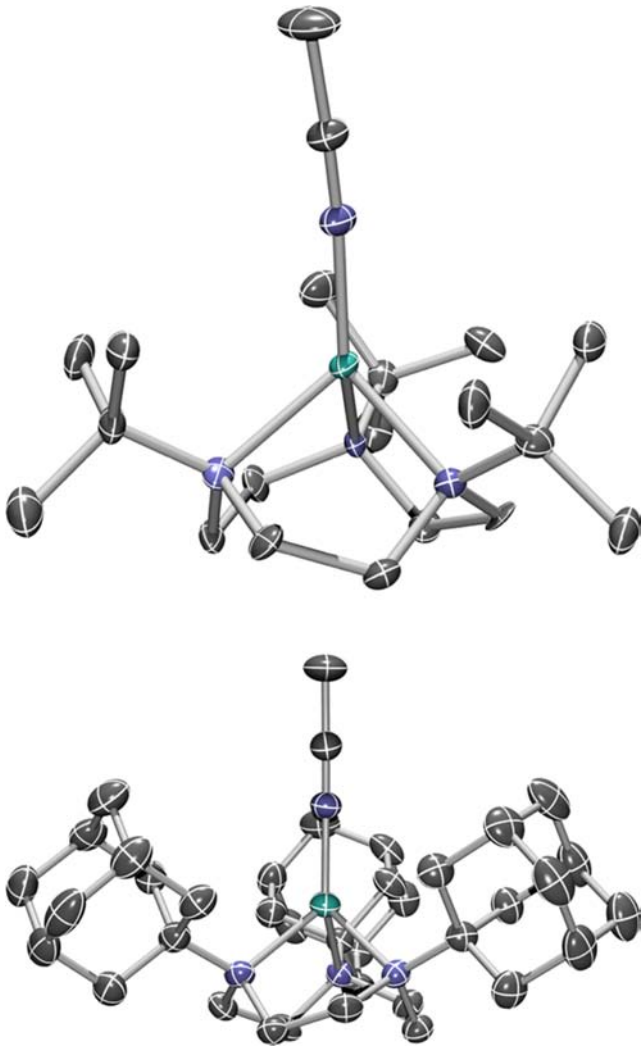


Figure 5. Solid-state molecular structures of the cations in $[(^tBu_3tacn)(MeCN)Cu^I][PF_6]$ (top) and $[(Ad_3tacn)(MeCN)Cu^I][PF_6]$ (bottom). H atoms and $[PF_6]^-$ counterions are omitted for clarity.

in Figure 5. The steric environments imposed by Me_3tacn, $^iPr_3$tacn, $^tBu_3$tacn, and Ad_3tacn in the solid-state structures of $[(R_3tacn)(MeCN)Cu^I]^+$ were quantified using the percent buried volume ($\%V_B$)[21] method employed extensively as a steric probe of *N*-heterocyclic carbene ligands.[22] This method calculates the percentage of the volume of a metal-centered sphere of defined radius that is occupied by a ligand. To focus the analysis on the nitrogen substituents, we have only included the nitrogen atoms and their substituents in the $\%V_B$

dx.doi.org/10.1021/ic402626p | *Inorg. Chem.* 2013, 52, 13282–13287

calculations. $\%V_B$ is shown in Figure 6 as a function of the radius of the copper-centered sphere. The $\%V_B$ is dominated by

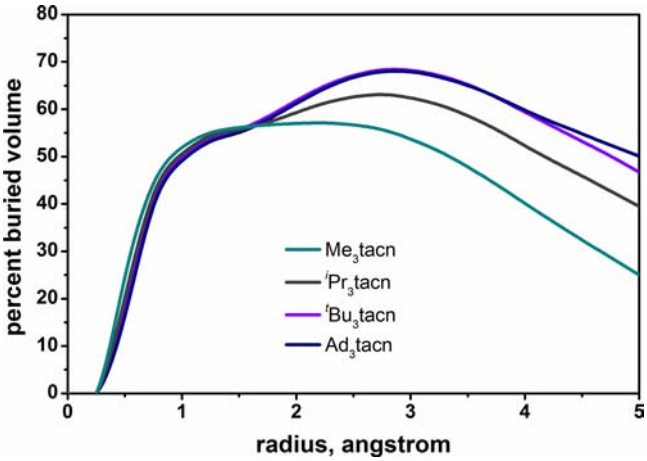


Figure 6. $\%V_B$ as a function of radius of a Cu^I-centered sphere in X-ray crystal structures of $[(R_3tacn)(MeCN)Cu^I]^+$ species. Acetonitrile ligand, copper, counterion, and R_3tacn ethylene bridges are omitted in the calculated values.

the bound nitrogen atoms up to 1.5 Å, below which all ligands appear nearly isosteric. At larger radii, the nitrogen substituents begin to dominate the $\%V_B$ and reveal a notable increase in size from Me to ^{i}Pr to ^{t}Bu/Ad in these ligands. $[(^iPr_3tacn)(MeCN)Cu^I]^+$ crystallizes in an orientation in which one ^{i}Pr group has both methyl groups gauche to the Cu−N bond (cf. Figure 2b), whereas the other two ^{i}Pr groups have one methyl anti to the N−M bond.[20] This seems to be an artifact of the alleviated steric interactions associated with four-coordinate compounds of this type, as all five-coordinate $^iPr_3tacnM$ compounds have all three ^{i}Pr groups in the orientation shown in the top of Figure 2b.[5] In the solid state, $^tBu_3tacn$ and Ad_3tacn are clearly the bulkiest R_3tacn species to date based on both $\%V_B$ and the four-coordinate geometry enforced by $^tBu_3tacn$ (Figure 3). $^tBu_3tacn$ and Ad_3tacn are essentially isosteric within 4 Å of the copper center.

Sterically enforcing four-coordinate geometries can have a pronounced effect on compound redox properties and, by extension, stability of the accessible oxidation states. The relative redox potentials of $[(H_3tacn)_2M^{II}]^{2+}$ and $[(^tBu_3tacn)M^{II}X]^+$ for cobalt and nickel provide information about the effect of coordination number on metal redox activity. To avoid complicating redox noninnocence of $[Ph_4B]^-$, we prepared $[(^tBu_3tacn)M^{II}X][PF_6]$ ($M^{II}X$ = $Co^{II}Cl$ and $Ni^{II}Br$). These four-coordinate complexes are oxidized in electrochemically irreversible events at +1.03 and +1.07 V vs Fc/Fc^+, respectively (Figure S3, Supporting Information), revealing that they are significantly more difficult to oxidize than the respective six-coordinate $[(H_3tacn)_2M^{II}]^{2+}$ species ($E_{1/2}$ = −0.81 and +0.55 V).[3a,23] These $^tBu_3tacn$ species are also robust with respect to reduction: electrochemical reduction occurs at −1.81 and −1.60 V (Figure 7), demonstrating a wide potential window where the divalent oxidation state is favored. This contrasts a structurally related triphosphine $Co^{II}I$ complex,[24] with reversible Co^I/Co^{II} and Co^{II}/Co^{III} couples at $E_{1/2}$ = −0.92 and +0.01 V vs Fc/Fc^+. We are currently exploring whether the redox stability endowed by $^tBu_3tacn$ on divalent transition-metal ions will enable isolation of M(E) species in unusually low oxidation states.[25]

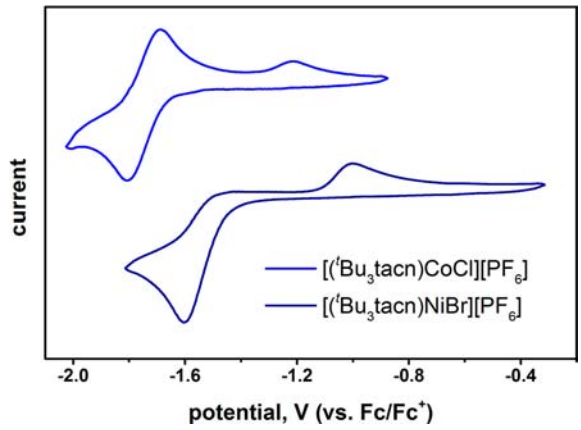


Figure 7. Cyclic voltammograms showing reductive events associated with $[(^tBu_3tacn)Co^{II}Cl][PF_6]$ (top) and $[(^tBu_3tacn)Ni^{II}Br][PF_6]$ (bottom). Conditions: 0.1 M $[N(nBu)_4][PF_6]$ in CH_3CN at 22 °C, 100 mV/s scan rate. Potentials are referenced to an internal ferrocene standard. Full potential sweeps are shown in Figure S3 (Supporting Information).

A description of the d-orbital splitting in $[(^tBu_3tacn)M^{II}X]^+$ cations for metals from groups 6−11, derived from the angular overlap model, molecular orbital theory, and DFT calculations is provided in the Supporting Information. The conclusions from this analysis are summarized as follows:

(1) The N−M−X angles (Figure 3c) are near the "magic angle" where the nitrogen lone pairs have no net overlap with the metal d_{z^2} orbital, suggesting that the M−X bond is a pure two-center bond.
(2) The d-orbital splitting is a 2-1-2 pattern for local C_{3v} symmetry, with the degenerate d_{xz}/d_{yz} orbitals most destabilized followed by d_{z^2}.
(3) These compounds are unstable to a large first-order Jahn−Teller distortion for Cr^{II} and Cu^{II}, and in each case the distorted geometry is intermediate between C_{3v} and a cis-divacant octahedron.

As discussed above, the structure of $[(^tBu_3tacn)(MeCN)Cr^{II}(OTf)]^+$ can be viewed as derivied from this Jahn−Teller distortion. The Fe^{II} species in local C_{3v} symmetry is also unstable to a Jahn−Teller distortion, but the unequally occupied degenerate orbitals in this case are approximately nonbonding, resulting in a very mild calculated distortion that is in good agreement with the crystal structure of $[(^tBu_3tacn)Fe^{II}I][BPh_4]$ in which this species adopts a nearly ideal local C_{3v} geometry. High-spin d^4 and d^9 metal ions in local C_{3v} symmetry are unstable to a large Jahn−Teller distortion analogous to the same electron counts in octahedral symmetry characterized by a pronounced "static" Jahn−Teller distortion; high-spin $d^6[(^tBu_3tacn)Fe^{II}I]^+$ is analogous to high-spin d^6 in octahedral symmetry that is characterized by a weak "dynamic" Jahn−Teller distortion. The DFT calculations are in good agreement with our crystallographic results and qualitative orbital descriptions, and these calculations provide the theoretical foundation that will guide our ongoing exploration of the coordination properties of $^tBu_3tacn$.

■ CONCLUSIONS

We have described the first synthesis of $^tBu_3tacn$ and its Cr^{II}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^I coordination compounds. Except for Cu, all species crystallize in the lowest-coordinate

environments to date for R_3tacn compounds of these metals due to the steric influence of this bulky ligand. Both $^tBu_3$tacn and Ad_3tacn are significantly bulkier than the previously bulkiest R_3tacn derivative, $^iPr_3$tacn, and are essentially isosteric within a 4 Å coordination sphere. The low coordination number and hard nature of the nitrogen donors has a pronounced effect on the electrochemical properties of cobalt and nickel compounds of $^tBu_3$tacn, as revealed by a much larger potential window wherein the divalent oxidation state is preferred compared to related compounds bearing a triphosphine ligand or two H_3tacn ligands. Our efforts have now turned to applying these redox-inert $^tBu_3$tacn and Ad_3tacn ligands to studies of reactive M(E) units.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Remaining synthetic procedures and characterization data, details of crystallographic data collection and refinement, crystallographic information files in CIF format, remaining cyclic voltammograms, details of percent buried volume calculations, details of DFT calculations, theoretical treatment of $[(^tBu_3tacn)M^{II}Cl]^+$ cations, and raw characterization data of organic and transition-metal compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*C. C. Scarborough. E-mail: scarborough@emory.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

C.S. gratefully acknowledges Emory University for providing the startup funds that supported this work. Dr. Fred Strobel is thanked for assistance with mass spectrometry.

■ REFERENCES

(1) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

(2) Wainwright, K. P. *Coord. Chem. Rev.* **1997**, *166*, 35.

(3) (a) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Kueppers, H. J. *Inorg. Chem.* **1983**, *22*, 2953. (b) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1938. (c) Wieghardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650. (d) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94. (e) McGowan, P. C.; Podesta, T. J.; Thornton-Pett, M. *Inorg. Chem.* **2001**, *40*, 1445.

(4) Haselhorst, G.; Stoetzel, S.; Strassburger, A.; Walz, W.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1993**, 83.

(5) (a) Kawamura, M.; Sunada, Y.; Kai, H.; Koike, N.; Hamada, A.; Hayakawa, H.; Jin, R.-H.; Nagashima, H. *Adv. Synth. Catal.* **2009**, *351*, 2086. (b) Rebilly, J.-N.; Charron, G.; Rivière, E.; Guillot, R.; Barra, A.-L.; Serrano, M. D.; van Slageren, J.; Mallah, T. *Chem.—Eur. J.* **2008**, *14*, 1169. (c) Han, W.; Li, L.; Liu, Z.-Q.; Yan, S.-P.; Liao, D.-Z.; Jiang, Z.-H.; Shen, P.-W. *Z. Anorg. Allg. Chem.* **2004**, *630*, 591. (d) Higashimura, H.; Kubota, M.; Shiga, A.; Fujisawa, K.; Moro-oka, Y.; Uyama, H.; Kobayashi, S. *Macromolecules* **2000**, *33*, 1986. (e) Halfen, J. A.; Tolman, W. B. *J. Am. Chem. Soc.* **1994**, *116*, 5475. (f) Halfen, J. A.; Hallman, J. K.; Schultz, J. A.; Emerson, J. P. *Organometallics* **1999**, *18*, 5435. (g) Diebold, A.; Elbouadili, A.; Hagen, K. S. *Inorg. Chem.* **2000**, *39*, 3915. (h) Halfen, J. A.; Mahapatra, S.; Wilkinson, E. C.; Gengenbach, A. J.; Young, V. G., Jr.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 763.

(6) Saouma, C. T.; Peters, J. C. *Coord. Chem. Rev.* **2011**, *255*, 920.

(7) (a) McDonald, A. R.; Que, L., Jr. *Coord. Chem. Rev.* **2013**, *257*, 414. (b) Suh, Y.; Seo, M. S.; Kim, K. M.; Kim, Y. S.; Jang, H. G.; Tosha, T.; Kitagawa, T.; Kim, J.; Nam, W. *J. Inorg. Biochem.* **2006**, *100*, 627. (c) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 522. (d) Que, L., Jr. *Acc. Chem. Res.* **2007**, *40*, 493.

(8) Koyama, H.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481.

(9) Evans, D. F.; Jakubovic, D. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2927.

(10) (a) Bradshaw, J. S.; Krakowiak, K. E.; Izatt, R. M. *Tetrahedron Lett.* **1989**, *30*, 803. (b) Bradshaw, J. S.; Krakowiak, K. E.; Izatt, R. M. *J. Heterocycl. Chem.* **1989**, *26*, 1431. (c) Krakowiak, K. E.; Bradshaw, J. S.; Izatt, R. M. *J. Org. Chem.* **1990**, *55*, 3364.

(11) Grenz, A.; Ceccarelli, S.; Bolm, C. *Chem. Commun.* **2001**, 1726.

(12) Belousoff, M. J.; Duriska, M. B.; Graham, B.; Batten, S. R.; Moubaraki, B.; Murray, K. S.; Spiccia, L. *Inorg. Chem.* **2006**, *45*, 3746.

(13) CCDC 944691−944701 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

(14) (a) Gott, A. L.; McGowan, P. C. *Acta Crystallogr.* **2003**, *E59*, o1702. (b) André, V.; Barroso, S.; Martins, A. M.; Duarte, M. T. *Acta Crystallogr.* **2007**, *C63*, o594.

(15) (a) Adam, B.; Bill, E.; Bothe, E.; Goerdt, B.; Haselhorst, G.; Hildenbrand, K.; Sokolowski, A.; Steenken, S.; Weyhermüller, T.; Wieghardt, K. *Chem.—Eur. J.* **1997**, *3*, 308. (b) Moore, D. A.; Fanwick, P. E.; Welch, M. J. *Inorg. Chem.* **1989**, *28*, 1504. (c) Tei, L.; Blake, A. J.; Lippolis, V.; Wilson, C.; Schröder, M. *Dalton Trans.* **2003**, 304.

(16) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

(17) (a) Scarborough, C. C.; Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. *Inorg. Chem.* **2011**, *50*, 12446. (b) Bossek, U.; Nühlen, D.; Bill, E.; Glaser, T.; Krebs, C.; Weyhermüller, T.; Wieghardt, K.; Lengen, M.; Trautwein, A. X. *Inorg. Chem.* **1997**, *36*, 2834. (c) Steed, J. W.; Goeta, A. E.; Lipkowski, J.; Swierczynski, D.; Panteleon, V.; Handa, S. *Chem. Commun.* **2007**, 813.

(18) Hagen, K. S. *Inorg. Chem.* **2000**, *39*, 5867.

(19) Bar-Nahum, I.; Gupta, A. K.; Huber, S. M.; Ertem, M. Z.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2009**, *131*, 2812.

(20) Berreau, L. M.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1998**, *37*, 1091.

(21) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759.

(22) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, 841.

(23) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(24) Jenkins, D. M.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 7148.

(25) MacBeth, C. E.; Thomas, J. C.; Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2004**, *43*, 4645.