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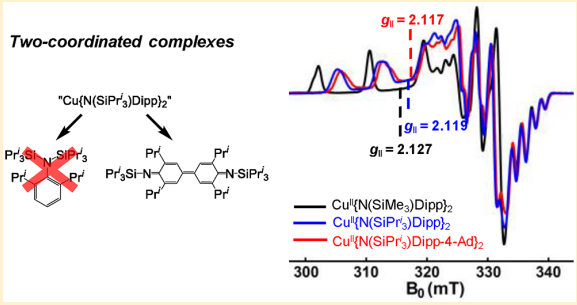
Two-Coordinate, Late First-Row Transition Metal Amido Derivatives of the Bulky Ligand -N(SiPr$^i_3$)Dipp (Dipp = 2,6-diisopropylphenyl): Effects of the Ligand on the Stability of Two-Coordinate Copper(II) Complexes

Clifton L. Wagner, Lizhi Tao, James C. Fettinger, R. David Britt, and Philip P. Power*

Chemistry Department, University of California, Davis, One Shields Avenue, Davis, California 95616, United States

Supporting Information

ABSTRACT: The synthesis and spectroscopic, structural, and magnetic characterization of the quasi-linear metal(II) bis(amides) M{N(SiPr$^i_3$)Dipp}$_2$ [Dipp = C$_6$H$_3$-2,6-Pr$^i_3$; M = Fe (**1**), Co (**2**), or Zn (**3**)] are described. The magnetic data demonstrate the impact of metal ligand π-interactions on the magnetic properties of these two-coordinate transition metal amides. Disproportionation of the copper(I) amide species featuring the ligand -N(SiPr$^i_3$)Dipp resulted in the decomposition product [(Pr$^i_3$Si)N(*c*-C$_6$H$_2$-2,6-Pr$^i_2$)]$_2$ (**4**). The electron paramagnetic resonance spectrum of the unstable two-coordinate Cu{N(SiPr$^i_3$)Dipp}$_2$ displays significantly less Cu−N bond covalency than the stable two-coordinate copper(II) species Cu{N(SiMe$_3$)Dipp}$_2$. The testing of -N(SiPr$^i_3$)Dipp and a range of other, related bulky amide ligands with their copper derivatives highlights the peculiar combination of steric and electronic properties of the Wigley ligand -N(SiMe$_3$)Dipp that enable it to stabilize the unique two-coordinate copper(II) complex Cu{N(SiMe$_3$)Dipp}$_2$.



INTRODUCTION

Our current understanding of the behavior and electronic properties of transition metal complexes highlights the importance of the ligand environment in determining the coordination number of the metal.[1] Open-shell (d^1−d^9), two-coordinate complexes remain, with rare exception,[2] poorly explored due to their relative scarcity. Nonetheless, two-coordinate transition metal complexes are attracting an increased level of interest due to their relatively open, extremely reactive metal centers as well as their unique magnetic and electronic properties.[2a,b,3]

Recent developments in the field of open-shell two-coordinate transition metal complexes have resulted in the synthesis of a range of such derivatives using alkyl, amido, oxo, aryl, and carbene ligands.[4] The currently available data (ca. 160 complexes) demonstrate that only the use of the most sterically hindered of ligands can stabilize two-coordinate geometry. Exploration of different ligand sets has shown the dramatic effects of not only the first but also the second ligand sphere on the electronic properties of the two-coordinate species.[2g] For example, two stable bisamides of nickel, the purple Ni{N(SiMe$_3$)Dipp}$_2$[5] and the green Ni{N(H)Ar$^{Pr^i_6}$}$_2$[4d] (Dipp = 2,6-diisopropylphenyl, and Ar$^{Pr^i_6}$ = 2,6-bis(2,4,6-triisopropylphenyl)phenyl), both feature linear two-coordinate metals; however, the former has a d−d absorption at 508 nm (19700 cm^{-1}), while the latter has a d−d absorption at 778 nm (12900 cm^{-1}), a difference of 6800 cm^{-1} (19.4 kcal mol^{-1}). This highlights the importance of the ligand composition for the electronic properties of two-coordinate transition metal complexes.

Another challenge in the chemistry of two-coordinate complexes is that the achievement of strictly linear coordination that can have a large effect on magnetic properties, for example, in the linear complexes M{C(SiMe$_3$)$_3$}$_2$ (M = Mn or Fe),[4a,b] M{N(H)Ar$^{Pr^i_6}$}$_2$ (M = Fe, Co, or Ni),[4c,d] and M{N(SiMe$_3$)Dipp}$_2$ (M = Mn, Fe, Co, or Ni)[5,6] whose orbital magnetic moments are mostly unquenched and where London dispersion forces (LDF) may play a role in setting the geometries.[7]

The latter series is particularly noteworthy because it includes the only currently known, stable two-coordinate copper(II) complex where it is believed London dispersion forces are key to its stability.[6c] We therefore turned to a bulkier version of the so-called Wigley ligand -N(SiMe$_3$)Dipp in which the -SiMe$_3$ substituent is replaced by the bulkier -SiPr$^i_3$ group to afford the -N(SiPr$^i_3$)Dipp ligand that was first reported by Luo and co-workers.[8] Several other ligands [-N(SiMe$_3$)$_2$,

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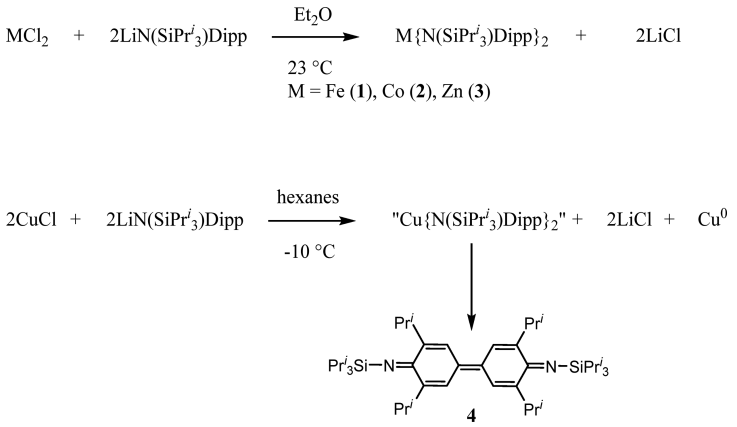
Scheme 1. Synthesis of Compounds 1−4



-N(SiPh$_2$Me)$_2$, -C(SiMe$_3$)$_3$, -OAr^{Ad_2Me}, -N(H)Ar$^{Pr^i_4}$, -N(3,5-Xyl)Ad, and -N(SiMe$_3$)Ad] (Ad = adamantyl; Ar^{Ad_2Me} = 2,6-diadamantyl-4-methylphenyl) were also tested with copper, but only -N(SiPr$^i_3$)Dipp and -N(SiPr$^i_3$)Dipp-4-Ad afforded signals consistent with the formation of their two-coordinate copper(II) complexes in solution.

Herein, we report the isolation and characterization of the quasi-linear two-coordinate compounds Fe{N(SiPr$^i_3$)Dipp}$_2$ (**1**), Co{N(SiPr$^i_3$)Dipp}$_2$ (**2**), and Zn{N(SiPr$^i_3$)Dipp}$_2$ (**3**). We also report the electron paramagnetic resonance (EPR) characterization of the transient two-coordinate copper(II) species of the homoleptic species Cu{N(SiPr$^i_3$)Dipp}$_2$ and Cu{N(SiPr$^i_3$)Dipp-4-Ad}$_2$ (Dipp-4-Ad = 2,6-diisopropyl-4-adamantylphenyl).

RESULTS AND DISCUSSION

Complexes **1**−**3** were synthesized by the addition of a solution of the lithium salt LiN(SiPr$^i_3$)Dipp[8] in diethyl ether to the corresponding anhydrous metal dichloride (Scheme 1). The reaction mixtures for the formation of **1** and **3** were filtered, and the volume was decreased to ca. 15 mL. The reaction flasks were stored in a −30 °C freezer overnight to afford red and colorless crystals for Fe and Zn, respectively. The reaction mixture to form **2** did not crystallize with diethyl ether, hexanes, or pentane as the solvent. However, extraction of the reaction mixture with toluene, decreasing the solvent volume, and subsequent storage in an approximately −30 °C freezer for 1 week yielded **2** as dark brown crystals.

Similarly, the preparation of the Ni(II) variants of **1**−**3** via the reaction of 2 equiv of LiN(SiPr$^i_3$)Dipp with NiCl$_2$ or NiBr$_2$ afforded elimination of the lithium halide salt and a purple-colored solution (cf. refs 2d and 5). However, workup in the usual way and attempted recrystallization from the solvents hexane, toluene, diethyl ether, tetrahydrofuran (THF), dimethyl sulfide, and hexamethyl disiloxane did not afford a crystalline product.

The addition of a solution of the lithium salt LiN(SiPr$^i_3$)-Dipp in hexanes to CuCl was carried out with cooling in a CaCl$_2$/ice bath at ca. −10 °C. After 2 h at ca. −10 °C, copper metal precipitated from the reaction mixture and it became blue in color. This behavior is broadly similar to that seen for the two-coordinate copper(II) complex Cu{N(SiMe$_3$)Dipp}$_2$ that was sufficiently stable to isolate.[6c]

The X-ray data show that **1** has a two-coordinate quasi-linear geometry at the metal with a N−Fe−N angle of 175.86(6)° (see Figure 1). This is in contrast to the closely related bulky

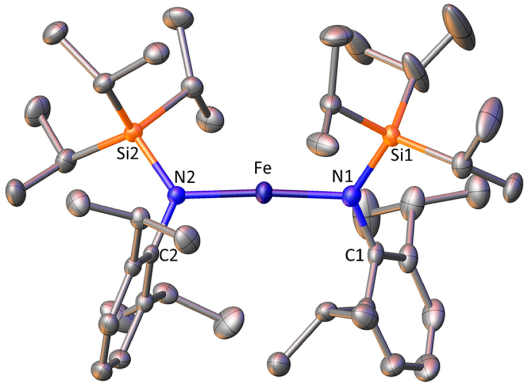


Figure 1. Molecular structure of Fe{N(SiPr$^i_3$)Dipp}$_2$ (**1**). H atoms are not shown. The thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (angstroms) and angles (degrees): Fe−N1, 1.8854(14); Fe−N2, 1.8911(15); N1−Si1, 1.7411(16); N2−Si2, 1.7466(15); N1−Fe−N2, 175.86(6); C1−N1−Si1, 127.54(11); C2−N2−Si2, 124.46(11).

silylamido Fe(II) species Fe{N(SiMe$_3$)Dipp}$_2$[5] that has a rigorously linear N−Fe−N angle of 180.0°. The triisopropylsilyl substituent of the ligands in complex **1** adds additional steric crowding that likely prevents the eclipsed arrangement of the ligands found in Fe{N(SiMe$_3$)Dipp}$_2$.[5] Instead of the eclipsed ligand orientation, complex **1** possesses a torsion angle of 44.090(3)° between the N1 and N2 coordination planes of the ligands. Calculations for the electronic structure of the two-coordinate transition metal complexes with the ligand -N(SiMe$_3$)Dipp indicate a significant contribution from the M−N π-bonding state[2d] as well as the N−Si π-antibonding hyperconjugative interaction with the metal.[6c] This deviation from the eclipsed arrangement with a high-potential steric clash significantly disrupts M−N multiple bonding and hyperconjugation to the N−Si bond. Fe{N(SiMe$_3$)Dipp}$_2$ has an M−N bond length (1.8532(13) Å) shorter than that in **1**, which has an average M−N bond length of 1.889(2) Å,

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possibly as a result of the diminished M−N multiple-bond character.

Complex **2** also has a two-coordinate quasi-linear geometry at the metal atom with an N−M−N angle of 175.21(10)° (see Figure 2). The structure of **2**, like that of **1**, has a large ligand

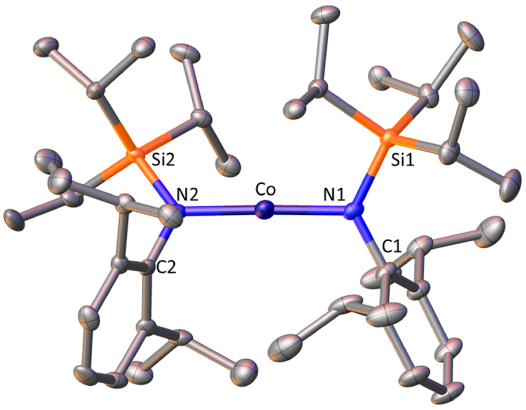

Figure 2. Molecular structure of Co{N(SiPr$^i_3$)Dipp}$_2$ (**2**). The thermal ellipsoids are shown at the 30% probability level. Only one of the two molecules in the asymmetric unit is shown. Selected bond lengths (angstroms) and angles (degrees): Co−N1, 1.859(2); Co−N2, 1.836(2); N1−Si1, 1.746(2); N2−Si2, 1.748(2); N1−Co−N2, 175.21(10); C1−N1−Si1, 123.3(2); C2−N2−Si2, 122.6(2).

torsion angle of 41.4(8)° between the nitrogen coordination planes. Co{N(SiPr$^i_3$)Dipp}$_2$ is isostructural to the iron analogue and has structural details similar to those previously mentioned for iron complex **1**. While the M−N distance (average of 1.844(5) Å) in **2** is significantly longer than that of Co{N(SiMe$_3$)Dipp}$_2$ (1.8179(14) Å) it is similar to those of Co{N(H)Ar$^{Pr^i_6}$}$_2$ (1.8645(19) Å), although the ligands in both compounds possess an eclipsed arrangement of their ligand coordination planes (see Table 3).

The M−N bond lengths for the zinc species **3** (average of 1.834(3) Å) fall within the known range of Zn(II)−N bond lengths in two-coordinate zinc amides (see Figure 3).[2i] The near linearity in the N−Zn−N bond angle resembles the linearity or near linearity generally observed in two-coordinate zinc amides (cf. Table 1). The long N−Si distances (average of 1.746(2) Å) are likely due to the steric repulsion within the ligand.

The electronic spectra of **1** and **2** are very similar to those of Fe{N(SiMe$_3$)Dipp}$_2$ and Co{N(SiMe$_3$)Dipp}$_2$ respectively. The iron amide electronic spectrum in hexanes has absorptions at 360 and 480 nm, while the cobalt amide has absorptions at 440 nm with a shoulder near 580 nm. While their electronic spectra may not distinguish **1** and **2** from Fe{N(SiMe$_3$)Dipp}$_2$ (360 nm) and Co{N(SiMe$_3$)Dipp}$_2$ (430 nm), the magnetic data are diagnostic.

The magnetic susceptibilities of **1** and **2** from 2 to 300 K were collected using a SQUID magnetometer (see the Supporting Information). The air and water sensitivity of the samples required that they be sealed in quartz tubes under vacuum. Due to the poor thermal conductivity of the sample containers, extremely long delays were necessary to reach thermal equilibrium during the initial cooling to 2 K (6 h) and at low temperatures (<10 K, 2 h).

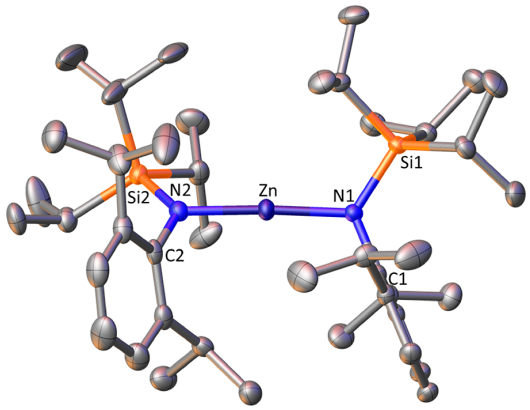

Figure 3. Molecular structure of Zn{N(SiPr$^i_3$)Dipp}$_2$ (**3**). The thermal ellipsoids are shown at the 30% probability level. Only one of the two molecules in the asymmetric unit is shown. Selected bond lengths (angstroms) and angles (degrees): Zn−N1, 1.8275(14); Zn−N2, 1.8289(14); N1−Si1, 1.7415(15); N2−Si2, 1.7459(15); N1−Zn−N2, 178.04(6); C1−N1−Si1, 124.69(15); C2−N2−Si2, 123.29(14).

The magnetic data for **1** are in agreement with those for most two-coordinate iron(II) complexes (see Table 2).[2g,15] There is a large orbital contribution to the magnetic moment (cf. 5.59 μ_B at 110 K, which is larger than the spin only value of 4.90 μ_B).[1a] However, it is not as high as the magnetic moment in the rigorously linear iron bis(amide) (6.04 μ_B[5] for Fe{N(SiMe$_3$)Dipp}$_2$) or 6.6 μ_B[16] for the bis(alkyl) Fe{C(SiMe$_3$)$_3$}$_2$].

The magnetic data for the cobalt species **2** show that it has a room-temperature value of ∼4.8 μ_B, which is significantly greater than the calculated spin only value of 3.87 μ_B. However, the μ_{eff} value is markedly lower than the value of 5.93 μ_B in the rigorously linear complex Co{N(SiMe$_3$)Dipp}$_2$ (cf. the free Co^{2+} ion value of 6.63 μ_B).[1a] It is closer to the μ_{eff} values seen in the more strongly bent Co{N(SiMePh$_2$)$_2$}$_2$[4g] or Co{N(H)Ar$^{Me}_6$}$_2$[4d] (see Table 3). Thus, the value for **2** is a notable reduction in the magnetic moment where both the first ligand sphere and the second ligand sphere are similar but the L−M−L bond angle deviates from linearity by <5°. Previous isolobal ligand systems for two-coordinate structures have seen significant decreases in the magnetic moment with bending of the L−M−L angle.[4d] Gao and co-workers reported an apparent relationship between the ligand torsion angle and magnetic susceptibility in a series of two-coordinate iron and cobalt compounds with a heteroleptic (amide and carbene) ligand environment.[17] The interligand torsion angle for **2** is 41.4(8)°, whereas the other linear coordinated amides of cobalt have no torsion angles between ligand planes (see Table 3). Similarly, for **1**, the interligand torsion angle is 44.090(3)° and most of the other linear metal amides feature no ligand torsion angles between the ligand coordination (see Table 2). However, the quasi-linear Fe{N(SiMePh$_2$)$_2$}$_2$ has a ligand torsion angle of 76.64(6)° and a corresponding magnetic moment of 5.07 μ_B.[4g] These examples suggest that torsion angles between the ligands and the resulting π-overlap[2d,5,17,18] have a correlation with the orbital enhancement of the magnetic moment.

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Table 1. Comparison of the Structures of Two-Coordinate Zinc Silylamides

metal complex	average M−N (Å)	average N−Si (Å)	average N−C (Å)	∠N−M−N (deg)	∠L−L (deg)
3	1.8282(14)	1.7437(15)	1.443(2)	178.04(6)	43.0(5)
$Zn\{N(SiMe_3)Dipp\}_2$[6d]	1.8209(13)	1.7281(14)	1.434(2)	180	0
$Zn\{N(SiMe_3)$-2,6-Xyl$\}_2$[6d]	1.817(2)	1.722(3)	1.424(4)	180	19.65(11)
$Zn\{N(SiMe_3)$-C_6H_3-2,5-$Bu^t\}_2$[6d]	1.838(3)	1.731(3)	1.443(4)	179.58(17)	16.67(19)
$Zn\{N(SiMe_3)_2\}_2$	1.824(14),[a] 1.833(11)[b]	1.729(7)[b]		180,[a] 175.2(4)[b]	75.43(9)[b]

[a]Structure determined by gas electron diffraction.[9] [b]Structure determined by single-crystal X-ray diffraction.[10]

Table 2. Comparison of M−N Distances, N−Fe−N Bond Angles, and μ_{eff} Values for Two-Coordinate Fe(II) Amides

	M−N (Å)	∠M−N−M (deg)	μ_{eff} (μ_B)
1	1.89106(11)	175.864(10)	5.59
$Fe\{N(SiMe_3)Dipp\}_2$[5]	1.8532(13)	180	5.89
$Fe\{N(SiMePh_2)_2\}_2$[11]	1.901(3)	169.0(1)	5.07
$Fe\{N(H)Ar^{Pr^i_6}\}_2$[2g]	1.9018(17)	180	5.80
Fe{1,8-Ph_2-3,6-$Me_2C_{12}H_4N\}_2$[12]	1.9715(18)	177.92(9)	4.73
$Fe\{N(CH_2Bu^t)Dipp\}_2$[13]	1.842(2)	168.8(2)	5.21
$Fe\{NBu^t_2\}_2$[14]	1.880(2)	179.45(8)	5.55

Table 3. Comparison of M−N Distances, N−Co−N Bond Angles, and μ_{eff} Values for Two-Coordinate Co(II) Amides

	M−N (Å)	∠N−M−N (deg)	μ_{eff} (μ_B)
2	1.844(5)	175.21(10)	4.8
$Co\{N(SiMe_3)Dipp\}_2$[5]	1.8179(14)	180	5.93
$Co\{N(SiMePh_2)_2\}_2$[11]	1.901(3)	147.0	4.42
$Co\{N(H)Ar^{Pr^i_6}\}_2$[19]	1.8645(19)	180	6.2
$Co\{N(H)Ar^{Me}_6\}_2$[19]	1.836(8)	144.1(4)	4.65
$Co\{N(BMes_2)Mes\}_2$[4e]	1.910(3)	168.4(1)	4.36
$Co\{N(BMes_2)Ph\}_2$[4e]	1.909(5)	127.1(2)	4.11

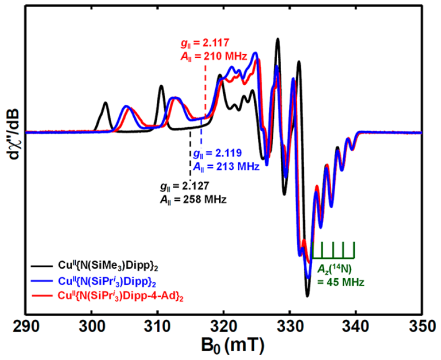

Figure 4. X-Band CW EPR spectra of a frozen solution of $Cu\{N(SiMe_3)Dipp\}_2$ (black trace), $Cu\{N(SiPr^i_3)_2Dipp\}_2$ (blue trace), and $Cu\{N(SiPr^i_3)Dipp\text{-}4\text{-}Ad\}_2$ (red trace) in hexanes (~2 mM) acquired at 30 K using a 0.063 mW power (no saturation), with the corresponding g tensors determined to be **g** = [2.1270, 2.0425, 2.0076], **g** = [2.1190, 2.0463, 2.0065], and **g** = [2.1170, 2.0463, 2.0065], respectively. The other spectrometer settings are a microwave frequency of 9.38 GHz, a conversion time of 40 ms, a modulation amplitude of 0.3 mT, and a modulation frequency of 100 kHz.

COPPER

Many research groups have found that sterically hindered ligands promote reduction of copper(II) species to copper(I) species due, it is thought,[20] to the sterically crowded metal center preventing square-planar coordination that stabilizes copper(II) species. Therefore, the reported synthesis of a stable two-coordinate Cu(II) complex, $Cu\{N(SiMe_3)Dipp\}_2$, via copper(I) chloride was surprising, particularly due to the general stability of two-coordinate copper(I) compounds. However, this compound can be readily decomposed, in the presence of electron-rich solvents, to copper metal as well as DippNNDipp and $N(SiMe_3)_2Dipp$, the latter involving a silyl group transfer.[6c] To hinder this decomposition, the ligand -$N(SiPr^i_3)Dipp$ was chosen with the assumption that the greater steric congestion in the $N(SiPr^i_3)_2Dipp$ moiety might hinder this process and enhance the stability of the metal complex. Attempts to synthesize the copper(II) analogues of **1**−**3** via our previously reported[6c] route were unsuccessful in isolating $Cu\{N(SiPr^i_3)_2Dipp\}_2$, although $Cu\{N(SiPr^i_3)_2Dipp\}_2$ was formed as indicated by the observation of a characteristic blue color as well as an EPR spectrum (see Figure 4). It decomposes in a hexanes/pentane solution to copper metal and **4** (Scheme 1) at approximately −10 °C. Although this reactivity contrasts that of $V\{N(SiPr^i_3)Dipp\}_2$,[21] which undergoes methyl C−H activation, it resembles that of $Cu\{N(SiMe_3)_2Dipp\}_2$ in that it appears to be accelerated by the presence of electron-rich solvents (toluene, benzene, diethyl ether, and tetrahydrofuran). A similar reactivity was encountered earlier in copper arylnitrene chemistry[22] and has been utilized in organic synthesis.[23] We have observed the same product **4** from the reaction of the lithium salt $LiN(SiPr^i_3)Dipp$ with either PdI_2 or AgCl. However, in the case of copper, the transient metal species was stable enough for EPR analysis. Additionally, reactions with the ligands $LiN(SiMe_3)_2$, $LiN(SiMePh_2)_2$, and $[(THF)_4Li][Li\{C(SiMe_3)_3\}_2]$ were also attempted under the same reaction conditions but resulted only in their known copper(I) products.[20g,24]

The corresponding X-band (9.38 GHz) continuous-wave (CW) EPR spectrum of a frozen solution of $Cu\{N(SiPr^i_3)_2Dipp\}_2$ in hexanes (~2 mM) is shown in Figure 4 (blue trace), which resembles our previously reported spectrum of $Cu\{N(SiMe_3)Dipp\}_2$ (Figure 4, black trace) by showing a rhombic **g** tensor and a similar superhyperfine coupling pattern from two equivalent ^{14}N nuclei (I = 1).[6c] However, we observed that the g_x ($g_\parallel$) value of 2.119 and the ^{63}Cu hyperfine value of 213 MHz for $Cu\{N(SiPr^i_3)_2Dipp\}_2$ are somewhat smaller than the corresponding values for $Cu\{N(SiMe_3)Dipp\}_2$ [$g_\parallel$ = 2.127, and $A_\parallel$ (^{63}Cu) = 258 MHz], suggesting that less spin density resides on the metal Cu^{II} center for $Cu\{N(SiPr^i_3)_2Dipp\}_2$ that could result from a lower $Cu^{II}-^{14}N$ bond covalency.

The observation of reductive coupling through the *para* position of the aryl rings within the ligand suggested that steric hindrance of the *para* position could prevent decomposition of the transient species. Therefore, the ligand salt $LiN(SiPr^i_3)$-

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Dipp-4-Ad (Dipp-4-Ad = 2,6-diisopropyl-4-adamantylphenyl) was also synthesized[2e,25] (see the Supporting Information) and reacted with CuCl. Although the disproportionation of the Cu(I) species occurred at a slightly elevated temperature (40 °C), the disproportionation produced Cu(II){N(SiPr$^i_3$)Dipp-4-Ad}$_2$, which could not be isolated as a crystalline solid. However, as in the previous case, its EPR spectrum was observable, as shown in Figure 4 (red trace), which resembles the spectrum of Cu{N(SiPr$^i_3$)$_2$Dipp}$_2$. The slightly smaller $g_\parallel$ value of 2.117 and the ^{63}Cu hyperfine value of 210 MHz, in comparison to the parameters of Cu{N(SiPr$^i_3$)$_2$Dipp}$_2$, suggest that the Cu^{II} center of Cu{N(SiPr$^i_3$)Dipp-4-Ad}$_2$ has a spin density comparable to but slightly lower than that of Cu^{II} in Cu{N(SiPr$^i_3$)$_2$Dipp}$_2$.

CONCLUSIONS

The synthesis and magnetic properties for the quasi-linear compounds Fe{N(SiPr$^i_3$)Dipp}$_2$ (**1**) and Co{N(SiPr$^i_3$)Dipp}$_2$ (**2**) with use of the Luo ligand -N(SiPr$^i_3$)Dipp demonstrate that, in addition to a quasi-linear geometry and the ligand coordination sphere, the potential π-overlap for metal amido complexes can affect their magnetic properties. The use of this more crowded ligand in the preparation of a copper(II) amide demonstrates a new decomposition pathway for the copper(II) amide. However, neither the N(SiPr$^i_3$)Dipp ligand nor the N(SiPr$^i_3$)Dipp-4-Ad ligand provides the required environment to stabilize the copper(II) amide. The EPR spectrum of Cu{N(SiPr$^i_3$)Dipp}$_2$ suggests lower Cu−N bond covalency in this complex in comparison to that of Cu{N(SiMe$_3$)Dipp}$_2$.

EXPERIMENTAL SECTION

All manipulations were performed with the use of modified Schlenk techniques or in a Vacuum Atmospheres OMNI-Lab drybox. All solvents were dried over an alumina column, followed by storage over a potassium mirror, and were degassed (freeze−pump−thaw method) prior to use. FeCl$_2$, CoCl$_2$, and ZnCl$_2$ were freshly dried under vacuum while being heated to 300 °C for 8 h. LiN(SiPr$^i_3$)Dipp[2e] was synthesized according to literature procedures. Ultraviolet−visible spectra were recorded for samples as dilute hexane solutions in a 3.5 mL quartz cuvette with an Olis spectrophotometer. Melting points were measured in glass capillaries sealed under N$_2$ by using a Mel-Temp II apparatus and are uncorrected.

Fe{N(SiPr$^i_3$)Dipp}$_2$ (1). LiN(SiPr$^i_3$)Dipp (1.0 g, 3.0 mmol) was dissolved in 40 mL of Et$_2$O and added dropwise to a suspension of freshly dried FeCl$_2$ (0.192 g, 1.5 mmol) in Et$_2$O (10 mL). After the dark brown mixture was stirred for 24 h, it was filtered and concentrated to incipient crystallization. Storage of this mixture at approximately −30 °C overnight afforded large, orange crystals of **1** that were suitable for X-ray crystallography: yield 0.286 g (27%); mp 154 °C; UV−vis (hexane) λ_{max} (ε) 360 nm (1900 cm^{-1} M^{-1}), 465 nm (700 cm^{-1} M^{-1}); IR (nujol) υ 415, 440, 480, 520, 780, 880, 890, 995, 1100, 1170, 1230, 1250, 1370, 1450 cm^{-1}.

Co{N(SiPr$^i_3$)Dipp}$_2$ (2). LiN(SiPr$^i_3$)Dipp (1.0 g, 3.0 mmol) was dissolved in 40 mL of Et$_2$O and added dropwise to a suspension of freshly dried CoCl$_2$ (0.192 g, 1.5 mmol) in Et$_2$O (10 mL). After the dark brown mixture was stirred for 24 h, it was filtered and the volatile materials were removed under vacuum. The residue was extracted with toluene (20 mL), and the brown filtrate was concentrated to ca. 5 mL. Storage of this mixture at ca. −30 °C overnight afforded large, brown crystals of **2** that were suitable for X-ray crystallography: yield 0.420 g (39%); mp 152 °C; UV−vis (hexane) λ_{max} (ε) 430 nm (3100 cm^{-1} M^{-1}); IR (nujol) υ 440, 490, 530, 700, 730, 780, 820, 975, 995, 1010, 1100, 1180, 1235, 1260, 1300, 1380, 1420, 1510 cm^{-1}.

Zn{N(SiPr$^i_3$)Dipp}$_2$ (3). LiN(SiPr$^i_3$)Dipp (1.0 g, 3.0 mmol) was dissolved in 40 mL of Et$_2$O and added dropwise to a suspension of ZnCl$_2$ (0.192 g, 1.5 mmol) in Et$_2$O (10 mL). After the colorless mixture was stirred for 24 h, it was filtered and concentrated to incipient crystallization. Storage of this mixture at −30 °C overnight afforded large, colorless crystals of **3** that were suitable for X-ray crystallography: yield 0.881 g (82%); mp 148 °C; IR (nujol) υ 360, 420, 440, 495, 535, 700, 740, 780, 850, 870, 900, 980, 1040, 1060, 1100, 1175, 1230, 1250, 1300, 1350, 1375, 1420, 1460 cm^{-1}.

EPR Spectroscopy. The frozen solution samples for three copper compounds (~2 mM) were prepared in a nitrogen-filled glovebox by using a deoxygenated and water-free hexane solvent. The X-band (9.38 GHz) CW EPR spectra were recorded on a Bruker (Billerica, MA) Biospin EleXsys E500 spectrometer equipped with a superhigh Q resonator (ER4122SHQE). Cryogenic temperatures were achieved and controlled using an ESR900 liquid helium cryostat in conjunction with a temperature controller (Oxford Instruments ITC503) and gas flow controller. CW EPR data were collected under slow-passage, nonsaturating conditions. The spectrometer settings were as follows: conversion time of 40 ms, modulation amplitude of 0.3 mT, and modulation frequency of 100 kHz.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01159.

Further synthetic details, crystallographic parameters, electronic spectra, and ^{1}H NMR spectra (PDF)

Accession Codes

CCDC 1906096−1906100 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pppower@ucdavis.edu.

ORCID

Lizhi Tao: 0000-0001-9921-2297

James C. Fettinger: 0000-0002-6428-4909

R. David Britt: 0000-0003-0889-8436

Philip P. Power: 0000-0002-6262-3209

Notes

The authors declare no competing financial interest.

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