

## Synthesis and Structure of 6-Aminofulvene-2-aldimine Complexes

Alexander M. Willcocks,<sup>†</sup> Alexander Gilbank,<sup>†</sup> Stephen P. Richards,<sup>†</sup> Simon K. Brayshaw,<sup>†</sup> Andrew J. Kingsley,<sup>‡</sup> Raj Odedra,<sup>‡</sup> and Andrew L. Johnson<sup>\*†</sup>

<sup>†</sup>Department of Chemistry, University of Bath, Bath, BA2 7AY, United Kingdom, and

<sup>‡</sup>SAFC-Hitech, Power Road, Bromborough, Wirral, CH62 3QF, United Kingdom

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We report here a synthetic route to *bis*(*N,N'*-aryl)-6-aminofulvene-2-aldimine (AFA) ligand systems, specifically Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH. The synthesis and structural characterization of a series of Cu(I) complexes [(Ph<sub>2</sub>-AFA)-Cu(CNPh)<sub>2</sub>] (**2**), [(Ph<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)] (**3**), and [(Dip<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)] (**4**), from the reaction of the corresponding lithiated AFA systems with Cu–Cl derivatives are reported; notably in the case of [(Ph<sub>2</sub>-AFA)Cu(CNPh)<sub>2</sub>] studies have revealed the existence of two structural isomers (**2a** and **2b**), both of which can be isolated and structurally characterized. Density functional theory (DFT) calculations suggest that the two crystal forms are comparatively close in energy, and geometry optimization reveals a convergence of these two forms to a geometry that more closely resembles the solid-state structure of isomer **2b**, having a CH···π interaction. The reactions of the AFA compounds Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH with ZnMe<sub>2</sub> and AlMe<sub>3</sub> have also been investigated, and the results of these reactions are described here.

### Introduction

The synthesis and development of ligand systems is of particular importance in the development of organometallic chemistry, as specific ligand-sets impart a dominant influence over both the physical and electronic properties of the metal centers within subsequent complexes. To this end, considerable effort has been directed toward the synthesis monoanionic ligand systems, as replacements (or alternatives) to the ubiqui-

tous cyclopentadienyl ligands. Of particular interest have been ligand systems such as β-diketimate (**A**),<sup>1</sup> amino-troponimate (**B**),<sup>2</sup> anilido-imate ligands (**C**),<sup>3</sup> and 1,2-cyclopentadienyl diimine ligands<sup>4</sup> (**D** and **E**), as represented in Figure 1, all of which are mono anionic ligands with similar ligand architectures. In all cases, these ligands can be tuned electronically and sterically by varying their alkyl or aryl substituents. Subsequently, many main group element, transition metal, and lanthanide metal complexes containing these ligands have been prepared, and their chemistries studied.

In this context, 6-aminofulvene-2-aldimine (AFA) systems (**E**), which have features in common with β-diketimate, amino-troponimate, anilido-imate ligands, and 1,2-cyclopentadienyl diimine ligands (**D**), have been known since 1963.<sup>5</sup> Despite this, it is only recently that AFA-systems have attracted interest as ligands because of their potential to bind to metal atoms via one of two possible bonding modes; either through the diimine donor groups (**E**), or the cyclopentadienyl unit (**E'**).<sup>4c–f</sup> To-date, AFA-complexes of very few metals have been described in the literature [Mg, Zn, Fe, Ru, and

\*To whom correspondence should be addressed. Phone: 44 (0)1225 384467. Fax: 44 (0)1225 386231. E-mail: a.l.johnson@bath.ac.uk.

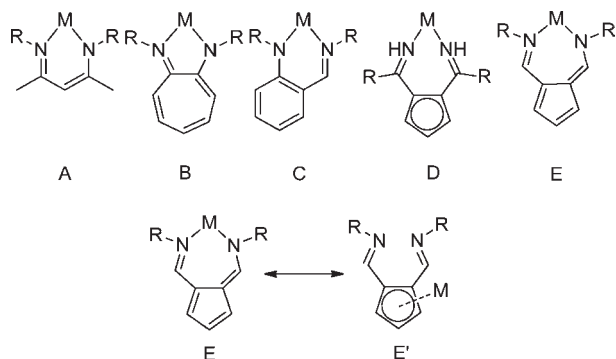
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**Figure 1.** Monoanionic imine based ligands (A–D) with a structural relationship to the AFA system (E), and the two known tautomeric coordination modes of the AFA ligand (E and E').

Pd].<sup>4c–e</sup> More recently we have reported AFA-complexes containing copper.<sup>4f</sup> Here we describe an improved general synthesis for AFA ligand systems and describe the synthesis of selected copper, aluminum, and zinc complexes.

## Experimental Section

**General Data.** All preparations were performed under an atmosphere of dry, O<sub>2</sub>-free argon, employing standard vacuum and Schlenk line techniques. Solvents were reagent grade, distilled under an inert argon atmosphere from appropriate drying agents, and degassed using the freeze–pump–thaw method prior to use. All organic reagents were purified by conventional methods. [(PhNC)<sub>2</sub>Cu(μ<sup>2</sup>-Cl)]<sub>2</sub>,<sup>4f</sup> [(<sup>i</sup>PrNC)Cu(μ<sup>3</sup>-Cl)]<sub>4</sub>,<sup>6</sup> and 6-dimethylamino fulvene<sup>7</sup> were prepared according to literature procedures. Phenyl-isocyanide and isopropyl-isocyanide were prepared using modified literature procedures.<sup>8</sup> The organometallic reagents, ZnMe<sub>2</sub> and AlMe<sub>3</sub> were provided by SAFC-Hitech as neat liquids and made into 2 M stock solutions in toluene. All other materials, unless otherwise stated, were purchased from commercial sources. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker Avance 300 MHz spectrometer, using internal references. Coupling constants are given in hertz. Elemental analyses of the ligand systems were performed “in-house” at the Department of Chemistry, University of Bath. Elemental analysis of the complexes 2–6 were performed by Elemental Microanalysis Ltd.

**Synthesis of Ph<sub>2</sub>-AFAH.** In separate dry Schlenk tubes, and under an inert atmosphere of argon, solutions of oxalyl chloride (3.6 mL, 41.32 mmol) in dichloromethane (DCM) (30 mL) and dimethyl formamide (3.18 mL, 41.32 mmol) in DCM (30 mL) were prepared. Both Schlenks were cooled to 0 °C, and the solution of oxalyl chloride was added dropwise to that of dimethyl formamide. This mixture was then allowed to stir for 2 h, and warmed to room temperature. After rapid addition of a solution of 6-(dimethylamino)fulvene (5 g, 41.32 mmol) in DCM (20 mL) to the slurry, the reaction mixture was then left to stir for a further 16 h, after which time the volatiles were removed under reduced pressure. To the resultant solid, an excess of aniline (9.1 mL, 100 mmol) and ethanol (40 mL) was added, and the mixture was refluxed for 16 h. Thin layer chromatography (1:10, ethyl acetate/hexane) confirmed the completion of the reaction, and the volatiles were then removed under reduced pressure. The resultant crude product was purified by column chromatography (hexane) and recrystallization (hexane) to afford Ph<sub>2</sub>-AFAH as bright orange

crystals (8.3 g, 74%). Elemental analysis calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>; C: 83.78, H: 5.93, N: 10.29, Found; C: 83.80, H: 5.90, N: 10.30. <sup>1</sup>H NMR (300.22 MHz, 298 K, CDCl<sub>3</sub>), δ: 6.27 (t, 1H, CH, <sup>3</sup>J = 3.67 Hz), 6.87 (d, 2H, CH, <sup>3</sup>J = 3.67 Hz), 7.08–7.16 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.21–7.24 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.3–7.39 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 8.09 (d, 2H, CH, <sup>3</sup>J = 6.18 Hz), 15.41 (s, 1H, NH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 298 K, CDCl<sub>3</sub>), δ: 119.5, 121.3, 122.5, 125.2, 129.9, 135.1, 145.7, 151.0.

**Synthesis of Dip<sub>2</sub>-AFAH.** Dip<sub>2</sub>-AFAH was made using the procedure described for Ph<sub>2</sub>-AFAH, substituting 2,6-diisopropylaniline (18.9 mL, 100 mmol) for aniline. Bright yellow crystals of Dip<sub>2</sub>-AFAH were obtained (12.4 g, 68%). Elemental analysis calcd for C<sub>31</sub>H<sub>40</sub>N<sub>2</sub>C; C: 84.48, H: 9.16, N: 6.36, Found; C: 84.60, H: 9.20, N: 6.28. <sup>1</sup>H NMR (300.22 MHz, 298 K, CDCl<sub>3</sub>), δ: 1.18 (d, 24H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, <sup>3</sup>J = 6.79 Hz), 3.21 (sept, 4H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, <sup>3</sup>J = 6.79 Hz), 6.51 (t, 1H, CH, <sup>3</sup>J = 3.65 Hz), 7.08 (d, 2H, CH, <sup>3</sup>J = 3.65 Hz), 7.15–7.29 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 7.92 (d, 2H, CH, <sup>3</sup>J = 7.15 Hz), 14.48 (t, 1H, NH, <sup>3</sup>J = 7.15 Hz). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 298 K, CDCl<sub>3</sub>), δ: 24.2, 28.4, 119.7, 121.1, 123.7, 123.7, 133.6, 142.3, 142.4, 157.7.

**Synthesis of [(Ph<sub>2</sub>-AFA)Cu(CNPh)<sub>2</sub>], (2b).** In a dry Schlenk tube, under an inert atmosphere of argon, stoichiometric quantities of lithium hexamethyldisilylamide (2.00 mmol, 0.335 g) and Ph<sub>2</sub>-AFAH (2.00 mmol, 0.544 g) were combined in a tetrahydrofuran (THF) solution (20 mL). The reaction mixture was then stirred for 1 h, followed by the addition of [(PhNC)<sub>2</sub>-Cu(μ<sup>2</sup>-Cl)]<sub>2</sub> (0.61 g, 1.00 mmol) in THF (20 mL) and further stirring for 16 h. After which time the volatiles were removed under reduced pressure. Dry hexane (20 mL) was added to the resultant residue, and was left to stir for 15 min. The volatiles were then removed under reduced pressure. This process was repeated three times in total to remove any residual THF. Further hexane (50 mL) was added, and the slurry was filtered through Celite to remove any insoluble materials, and the volatiles removed in vacuo. This resulted in a dark brown crude product that was purified by recrystallization (hexane) to afford **2b** as orange crystals (0.651 g, 81%). Elemental analysis calcd for C<sub>33</sub>H<sub>25</sub>N<sub>4</sub>Cu; C: 73.25, H: 4.66, N: 10.35, Found; C: 73.92, H: 5.04, N: 10.15. <sup>1</sup>H NMR (300 MHz, 296 K, CDCl<sub>3</sub>), δ: 6.32 (triplet, <sup>3</sup>J = 3.57 Hz, 1H, CHCHCH), 6.90 (doublet, <sup>3</sup>J = 3.54 Hz, 2H, CHCHCH), 7.05–7.21 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 7.27–7.44 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 8.28 (s, 2H, PhNCH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.50 MHz, 296 K, CDCl<sub>3</sub>), δ: 115.6, 118.7, 1122.8, 123.9, 126.5, 128.8, 129.6, 129.8, 134.8, 150.3, 156.5, 162.7.

**Synthesis of [(Ph<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)], (3).** In a dry Schlenk tube, under an inert atmosphere of argon, stoichiometric quantities of lithium hexamethyldisilylamide (2.00 mmol, 0.335 g) and Ph<sub>2</sub>-AFAH (2.00 mmol, 0.544 g) were combined in THF (20 mL). The reaction mixture was then stirred for 1 h, followed by the addition of [(<sup>i</sup>PrNC)Cu(μ<sup>3</sup>-Cl)]<sub>4</sub> (0.336 g, 0.50 mmol) in THF (20 mL) with further stirring for 16 h. The volatiles were removed under reduced pressure. Dry hexane (20 mL) was added to the resultant residue, and was left to stir for 15 min. The volatiles were removed under reduced pressure. This process was repeated a total of three times to remove any residual THF. Further hexane (50 mL) was added, and the slurry was filtered through Celite to remove any insoluble materials with subsequent removal of the volatiles in vacuo. This resulted in a dark brown crude product that was purified by recrystallization (hexane) to afford **3** as orange crystals (0.651 g, 81%). Elemental analysis calcd for C<sub>23</sub>H<sub>22</sub>CuN<sub>3</sub>; C: 68.38, H: 5.49, N: 10.40, Found; C: 67.50, H: 5.33, N: 11.14. <sup>1</sup>H NMR (300.22 MHz, 298 K, CDCl<sub>3</sub>), δ: 1.22 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J = 6.70 Hz), 3.66 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J = 6.70 Hz), 6.37 (t, 1H, CH, <sup>3</sup>J = 3.62 Hz), 6.99 (d, 2H, CH, <sup>3</sup>J = 3.62 Hz), 7.02–7.09 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.14–7.20 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.22–7.29 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 8.30 (s, 2H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 298 K, CDCl<sub>3</sub>), δ: 23.0, 47.4, 116.5, 118.5, 122.9, 124.2, 128.9, 135.5, 156.2, 162.8. No resonance for CNCH(CH<sub>3</sub>)<sub>2</sub> was observed.

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Table 1

	Dip <sub>2</sub> -AFAH: Tol	2a	2b	3	4	6
empirical formula	C <sub>38</sub> H <sub>48</sub> N <sub>2</sub>	C <sub>33</sub> H <sub>25</sub> CuN <sub>4</sub>	C <sub>33</sub> H <sub>25</sub> CuN <sub>4</sub>	C <sub>23</sub> H <sub>22</sub> CuN <sub>3</sub>	C <sub>35</sub> H <sub>46</sub> CuN <sub>3</sub>	C <sub>33</sub> H <sub>45</sub> AlN <sub>2</sub>
formula weight	532.78	541.11	541.11	403.98	572.29	496.69
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
crystal system	monoclinic	triclinic	triclinic	orthorhombic	triclinic	orthorhombic
space group	P2 <sub>1</sub> /c	P $\bar{1}$	P $\bar{1}$	P2 <sub>1</sub> 2 <sub>1</sub>	P $\bar{1}$	P2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	10.6560(5)	9.9170(3)	11.1110(8)	8.11400(10)	9.0040(2)	11.4890(2)
b (Å)	20.2830(4)	10.8650(4)	11.5390(7)	11.1000(2)	9.7290(2)	14.4270(2)
c (Å)	15.3220(7)	14.5300(6)	11.9660(10)	21.9760(4)	19.8460(6)	18.4190(4)
α (deg)		106.4740(10)	66.999(2)		97.1120(10)	
β (deg)	99.118(2)	97.129(2)	76.739(2)		91.9950(10)	
γ (deg)		112.271(2)	72.760(3)		106.002(2)	
V	3269.8(2)	1341.18(8)	1337.44(17)	1979.28(6)	1653.95(7)	3052.98(9)
Z	4	2	2	4	2	4
ρ <sub>calc</sub> mg/m <sup>-3</sup>	1.082	1.340	1.344	1.356	1.149	1.081
μ(Mo-Kα), mm <sup>-1</sup>	0.620	0.843	0.845	1.115	0.686	0.089
F(000)	1160	560	560	840	612	1080
crystal size, mm	0.15 × 0.10 × 0.10	0.20 × 0.13 × 0.10	0.20 × 0.13 × 0.08	0.22 × 0.1 × 0.08	0.15 × 0.13 × 0.10	0.10 × 0.10 × 0.08
θ range (deg)	8.53 to 30.53	3.53 to 27.48	8.53 to 23.26	3.11 to 24.71	3.25 to 24.71	4.00 to 27.06
reflections collected	30682	23329	11011	22140	15385	56503
independent reflections [R(int)]	8791 [0.1103]	6046 [0.0432]	3649 [0.1555]	3369 [0.0675]	5632 [0.0314]	6684 [0.1243]
reflections observed [I > 2σ(I)]	5211	4863	2213	2294	4918	4600
max., min transmission	0.9938, 0.9908	0.9204, 0.8495	0.9354, 0.8491	0.9161, 0.7915	0.9346, 0.9041	0.9934, 0.9912
goodness-of-fit	1.017	1.039	0.972	1.059	1.050	0.975
final R1 (wR <sub>2</sub> ) [I > 2σ(I)]	0.0613 (0.1238)	0.0393 (0.0842)	0.0562 (0.1051)	0.0314 (0.0755)	0.0327 (0.0782)	0.0435 (0.0844)
final R1 (wR <sub>2</sub> ) (all data)	0.1240 (0.1551)	0.0572 (0.0934)	0.1163 (0.1270)	0.0435 (0.0814)	0.0410 (0.0831)	0.0882 (0.0960)
absolute structure parameter				-0.020(16)		0.01(14)
largest diff. peak and hole, e Å <sup>-3</sup>	0.214 and -0.191	0.337 and -0.544	0.327 and -0.499	0.420 and -0.587	0.310 and -0.246	0.182 and -0.182

**Synthesis [(Dip<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)], (4).** In a dry Schlenk tube, under an inert atmosphere of argon, stoichiometric quantities of lithium hexamethyldisilylamide (2.00 mmol, 0.335 g) and Dip<sub>2</sub>-AFAH (0.881 g, 2.00 mmol) were combined in THF (20 mL). The reaction mixture was then stirred for 1 h, followed by the addition of [(<sup>i</sup>PrNC)Cu( $\mu^3$ -Cl)]<sub>4</sub> (0.336 g, 0.50 mmol) with further stirring for 16 h. The volatiles were removed under reduced pressure. Dry hexane (50 mL) was added to the resultant residue, and this was left to stir for 15 min. The volatiles were removed under reduced pressure. This process was repeated a total of three times to remove any residual THF. Further hexane (20 mL) was added, and the slurry was filtered through Celite to remove any insoluble materials with subsequent removal of the volatiles in vacuo. This resulted in a dark brown crude product that was purified by crystallization (hexane) to afford **4** as orange crystals (0.732 g, 64%). Elemental analysis calcd for C<sub>35</sub>H<sub>46</sub>CuN<sub>3</sub>; C: 73.45, H: 8.10, N: 7.34, Found; C: 73.06, H: 8.15, N: 7.36. <sup>1</sup>H NMR (300.22 MHz, 300 K, CDCl<sub>3</sub>), δ: 0.96 (d, 6H, CNCH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J = 6.59 Hz), 1.18 (d, 12H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, <sup>3</sup>J = 6.84 Hz), 1.21 (d, 12H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, <sup>3</sup>J = 6.84 Hz), 3.34–3.50 (m, 5H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> and CNCH(CH<sub>3</sub>)<sub>2</sub>), 6.36 (t, 1H, CH, <sup>3</sup>J = 3.55 Hz), 6.94 (d, 2H, CH, <sup>3</sup>J = 3.55 Hz), 7.10–7.18 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 8.03 (s, 2H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 298 K, CDCl<sub>3</sub>), δ: 22.7, 23.5, 24.4, 28.1, 47.1, 115.2, 117.9, 123.4, 124.7, 134.1, 140.8, 151.3, 164.5. No resonances for CNCH(CH<sub>3</sub>)<sub>2</sub> observed.

**Synthesis of [(Ph<sub>2</sub>-AFA)AlMe<sub>2</sub>], (5).** In a dry Schlenk tube, under an inert atmosphere of argon, THF (20 mL) was added to Ph<sub>2</sub>-AFAH (0.544 g, 2.00 mmol). To this solution trimethyl aluminum (2 M in toluene) (2.00 mmol, 1 mL) was added, and the reaction mixture was allowed to stir for 16 h, after which time any insoluble material was separated by filtration and the solution concentrated by removal of the volatiles in vacuo. This was followed by storage of the solution at -28 °C to afford **5** as yellow crystals (0.322 g, 49%). Elemental analysis; calcd for C<sub>21</sub>H<sub>21</sub>Al<sub>1</sub>N<sub>2</sub>; C: 76.81, H: 6.45, N: 8.53, Found; C: 76.63, H: 6.62, N: 8.39. <sup>1</sup>H NMR (300.22 MHz, 298 K, CDCl<sub>3</sub>), δ: -0.91 (s, 6H, Al(CH<sub>3</sub>)<sub>2</sub>), 6.46 (t, 1H, CH, <sup>3</sup>J = 3.65 Hz), 7.10 (d, 2H, CH, <sup>3</sup>J = 3.65 Hz), 7.10–7.16 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.20–7.25 (m, 2H,

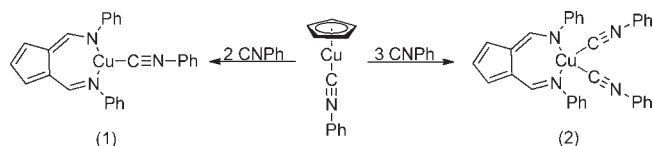
C<sub>6</sub>H<sub>5</sub>), 7.28–7.35 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 8.06 (s, 2H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 238 K, CDCl<sub>3</sub>), δ: -9.1, 117.7, 120.2, 124.2, 126.5, 129.1, 140.6, 148.7, 163.5.

**Synthesis of [(Dip<sub>2</sub>-AFA)AlMe<sub>2</sub>], (6).** In a dry Schlenk tube, under an inert atmosphere of argon, THF (20 mL) was added to Dip<sub>2</sub>-AFAH (0.881 g, 2.00 mmol). To this solution trimethyl aluminum (2 M in toluene) (2.00 mmol, 1 mL) was added and the reaction mixture was allowed to stir for 16 h, after which time any insoluble material was separated by filtration and the solution concentrated by removal of the volatiles in vacuo. This was followed by storage of the solution at -28 °C to afford yellow crystals of **6** (0.360 g, 36%). Elemental analysis calcd for C<sub>34</sub>H<sub>49</sub>Al<sub>1</sub>N<sub>2</sub>; C: 79.80, H: 9.13, N: 5.64, Found; C: 79.18, H: 9.77, N: 5.60. <sup>1</sup>H NMR (300.22 MHz, 300 K, CDCl<sub>3</sub>), δ: -1.01 (s, 6H, Al(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, 6H, PhCH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J = 6.86 Hz), 1.28 (d, 6H, PhCH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J = 6.86 Hz), 3.28 (sept, 6H, Ph(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, <sup>3</sup>J = 6.86 Hz), 6.48 (t, 1H, CH, <sup>3</sup>J = 3.68 Hz), 7.06 (d, 2H, CH, <sup>3</sup>J = 3.68 Hz), 7.19–7.30 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 7.93 (s, 2H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 298 K, CDCl<sub>3</sub>), δ: -10.8, 23.4, 25.8, 28.8, 118.5, 120.2, 124.3, 127.5, 140.6, 143.9, 144.49, 166.6.

**Synthesis of [(Ph<sub>2</sub>-AFA)<sub>2</sub>Zn], (7).** In a dry Schlenk and under an inert atmosphere of argon THF (20 mL) was added to Ph<sub>2</sub>-AFAH (0.544 g, 2.00 mmol). To this solution, dimethyl zinc (1 M in Toluene) (2.00 mmol, 2 mL) was added, and the reaction mixture was allowed to stir for 16 h, after which time any insoluble material was separated by filtration, and the solution concentrated by removal of the volatiles in vacuo. This was followed by storage of the solution at -28 °C to afford **7** as yellow crystals (0.322 g, 49%). Elemental analysis calcd for C<sub>38</sub>H<sub>30</sub>N<sub>4</sub>Zn<sub>1</sub>; C: 75.06, H: 4.97, N: 9.21, Found; C: 74.98, H: 5.01, N: 9.23. <sup>1</sup>H NMR (300.22 MHz, 298 K, CDCl<sub>3</sub>), δ: 6.39 (t, 2H, CH, <sup>3</sup>J = 3.65 Hz), 6.80–6.86 (m, 8H, *m*-C<sub>6</sub>H<sub>5</sub>), 6.94–7.07 (m, 16H, {12H *o/p*-C<sub>6</sub>H<sub>5</sub>, 4H, CH}), 8.06 (s, 4H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (75.49 MHz, 238 K, CDCl<sub>3</sub>), δ: 118.2, 118.9, 122.2, 125.2, 129.1, 140.0, 151.9, 163.1.

**Crystallography.** Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table 1. For all structures, data were collected on a Nonius Kappa CCD

**Scheme 1.** Synthesis of the AFA Complexes [(Ph<sub>2</sub>-AFA)Cu(CNPh)] (1) and [(Ph<sub>2</sub>-AFA)Cu(CNPh)<sub>2</sub>] (2) Formed from [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cu(CNPh)]<sup>4f</sup>



diffractometer at 150(2) K using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Structure solution and refinements were performed using SHELX86<sup>9</sup> and SHELX97<sup>10</sup> software, respectively. Corrections for absorption were made in all cases. All hydrogens attached to carbon atoms were included at calculated positions and refined using the riding model. In the case of the ligand system, [(Dip)<sub>2</sub>-AFAH]:Tol, the N-H hydrogen atom was found in the difference Fourier map and was freely refined.

The asymmetric unit of [(Ph<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)], **3**, consists of one full molecule of the copper complex. The coordinated CN<sup>i</sup>Pr ligand is disordered with respect to the central core, and has been refined and modeled over two positions, in a 62% to 38% occupancy ratio. To obtain a stable convergence, refinement of both the major and the minor component of disorder were refined with isotropic displacement parameters. Disorder is also present in complex **4**, [(Dip)<sub>2</sub>-AFA)Cu(CN<sup>i</sup>Pr)], in which one of the four isopropyl groups of the {Dip<sub>2</sub>-AFA} ligand is disordered over two positions, in a 53% to 47% occupancy ratio. As with **3**, to obtain a stable convergence, refinement of both the major and the minor component of disorder in **4** were refined with isotropic displacement parameters.

**Computational Methods.** Density functional calculations were performed using the B3LYP<sup>11</sup> hybrid density functional under the Gaussian09 package.<sup>12</sup> The SDD pseudopotential and associated basis set<sup>13</sup> were used for copper, and the 6-31G(d)<sup>14</sup> basis set was used for all other atoms. To give corrected “experimental” geometries, the hydrogen atoms were optimized with the PM6 functional, with the non-hydrogen atoms kept fixed (X-ray geometries systematically underestimate X-H distances). Subsequent full geometry optimizations were performed with B3LYP/6-31G(d) and frequency calculations were used to confirm the stationary points were true minima. For the compound **2b**, there were problems with the initial internal coordinates, and hence a preliminary optimization in Cartesian coordinates was performed, prior to a final optimization using internal coordinates.

## Results and Discussion

We have recently reported the formation of the AFA complexes [(Ph<sub>2</sub>-AFA)Cu(CNPh)] (**1**) and [(Ph<sub>2</sub>-AFA)Cu(CNPh)<sub>2</sub>] (**2**) via the double migratory insertion of phenyl isocyanide, Ph-NC, into two vicinal sp<sup>2</sup> C-H bonds of the  $\eta^5$ -coordinated cyclopentadienyl group in the complex [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cu(CNPh)] (Scheme 1).

Motivated by these results, we have sought a higher yielding route to AFA ligand systems to further explore their

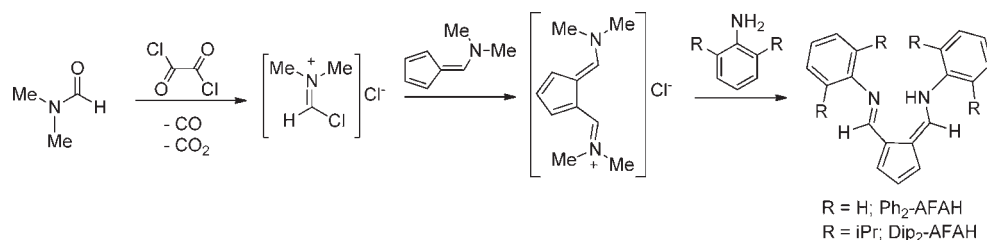
coordination chemistry, which could prove to be extensive given the rich chemistry of the related dicarbonyl substituted cyclopentadienide complexes.<sup>15</sup>

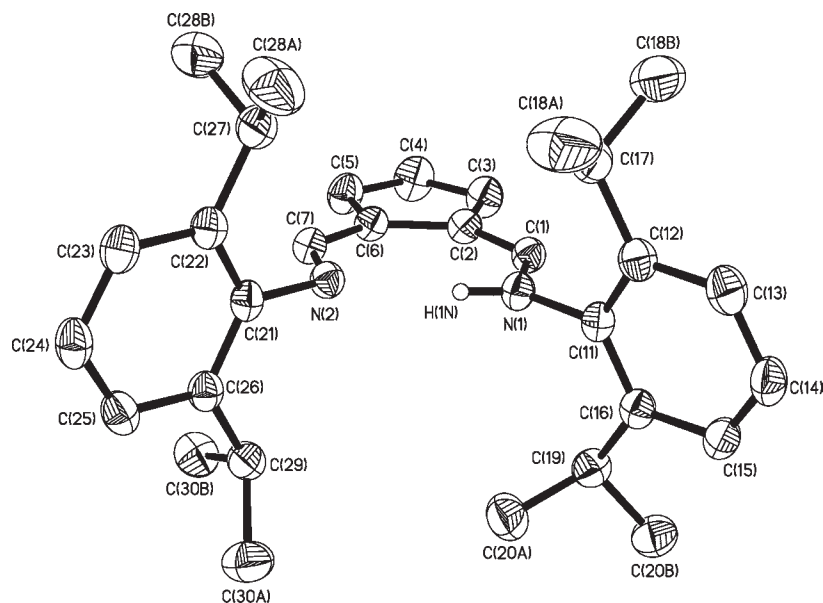
Inspired by the previously published multistep procedure for the synthesis of AFA ligand systems reported by Sanz and co-workers,<sup>16</sup> which is itself based upon earlier work by Muller-Westerhoff,<sup>17</sup> we have developed a modified procedure that is capable of providing a much wider range of N-substituted AFA ligands, than described here, in moderate to high yields. The first step consists of the selective monosubstitution of 6-dimethylamino-fulvene by the Vilsmeier-Haack reagent, [Me<sub>2</sub>N=C(H)Cl]Cl, formed in situ by the reaction of dimethyl formamide and oxalyl chloride.<sup>18</sup> Reaction of these two reagents is complete after several hours forming the intermediate [C<sub>5</sub>H<sub>3</sub>{C(H)NMe<sub>2</sub>}]Cl. In the second step, removal of solvent under vacuum followed by addition of an ethanolic solution containing an excess (> 2 equiv) of the desired primary amine, or aniline, results in the formation of the corresponding *N,N'*-disubstituted AFA ligand system (Scheme 2), which can be purified by column chromatography.

The ligands systems reported here, Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH, were obtained in isolated yields of 74% and 68%, respectively, which in comparison to previously reported synthetic procedures represents a significant improvement.<sup>16,17</sup> In the case of both ligand systems, the isolated materials are yellow air stable systems with a notable tendency to crystallize, an advantageous feature in terms of their purification and characterization. During the course of these investigations crystals suitable for single crystal X-ray diffraction studies of both Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH were isolated and shown to be identical to the previously reported systems.<sup>4e,19</sup> Recrystallization of the Dip<sub>2</sub>-AFAH ligand system from toluene yielded crystals of the toluene solvate system Dip<sub>2</sub>-AFAH:Tol, the molecular structure of which is shown in Figure 2. Table 2 shows selected bond lengths and angles.

A comparison with the non-solvated Dip<sub>2</sub>-AFAH recently reported by Bailey et al.<sup>4e</sup> shows little, if any, difference between the two crystal systems. In both cases, the molecular structures contain a planar {C<sub>5</sub>(CN)<sub>2</sub>} backbone (the mean deviation from planarity for the atoms N(1), C(1)–C(7), N(2) is 0.0203(11) Å) with the pendant 2,6-diisopropylphenyl units approaching a perpendicular orientation to the {C<sub>5</sub>(CN)<sub>2</sub>} plane [C(11)–C(16)/N(1),C(1)–C(7),N(2) = 80.11(5) °; C(21)–C(26)/N(1),C(1)–C(7),N(2) = 89.02(4) °], an observation which is in contrast to the Ph<sub>2</sub>-AFAH system, in which the phenyl rings are closer to coplanarity with the {C<sub>5</sub>(CN)<sub>2</sub>} backbone [{C<sub>5</sub>(CN)<sub>2</sub>/phenyl angles of 19.0 and 6.7°].<sup>19</sup> Despite the obvious steric differences between the Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH ligands, the N···N distances in both systems are comparable [2.781(2) Å in Dip<sub>2</sub>-AFAH cf. 2.51 Å in Ph<sub>2</sub>-AFAH],<sup>19</sup> which is presumably a result of the intermolecular hydrogen bond present in both systems. A cursory

**Scheme 2.** Modular “one-pot” Synthesis of AFA Ligand System Precursors





**Figure 2.** Molecular structure of the solvated ligand system Dip<sub>2</sub>-AFAH in the solvated complex Dip<sub>2</sub>-AFAH·Tol. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been removed for clarity.

comparison of the bond lengths around the {C<sub>5</sub>(CN)<sub>2</sub>} backbone indicates that while the C–C and C–N bonds are midway between single and double bonds in character there is some localization of electron density resulting in an alternating pattern of “single/long” and “double/short” bonds around the molecule (Figure 2).

Initial attempts to form copper complexes of the {Ph<sub>2</sub>-AFA} and {Dip<sub>2</sub>-AFA} ligand systems focused on the reaction of [Cu(Mes)<sub>5</sub>] (Mes = 2,4,6-trimethylphenyl) with stoichiometric amounts of the ligands Ph<sub>2</sub>-AFAH and Dip<sub>2</sub>-AFAH in tetrahydrofuran (THF). In both cases, only unreacted ligand was isolated from the reaction mixtures. The kinetic stability of organo-copper systems such as mesityl-copper has been previously attributed to the high degree of aggregation encountered in Cu(I)-aryl systems and strong three-center two-electron

**Table 2.** Selected Bond Lengths and Angles for Dip<sub>2</sub>-AFAH·Tol

Selected Bond Lengths (Å)			
N(1)–C(1)	1.324(2)	C(4)–C(5)	1.414(3)
C(1)–C(2)	1.379(2)	C(5)–C(6)	1.394(2)
C(2)–C(3)	1.436(2)	C(6)–C(7)	1.428(2)
C(3)–C(4)	1.375(3)	C(7)–N(2)	1.289(2)
C(6)–C(2)	1.459(2)		
N(1)···N(2)	2.781(2)	H(1N)···N(2)	1.974(3)
N(1)–H(1N)	0.88(3)		
Selected Bond Angles (deg)			
N(1)–C(1)–C(2)	127.04(4)	C(1)–N(1)–C(11)	121.13(13)
N(2)–C(7)–C(6)	126.63(4)	C(7)–N(2)–C(21)	116.54(13)
N(1)–H(1N)–N(2)	159 (2)		

(3c-2e<sup>-</sup>) bonding found in these systems.<sup>20</sup> These features, coupled with the sterically restricted access of the organo-copper reagent to the acidic N–H group of the AFA ligand, presumably render the reactants kinetically inert toward each other.

Treatment of Ph<sub>2</sub>-AFAH with lithium bis(trimethylsilyl)amide (or *n*-butyl lithium) in THF, followed by reaction with [(PhNC)<sub>2</sub>Cu(μ<sup>2</sup>-Cl)]<sub>2</sub>, provides the complex [(Ph<sub>2</sub>-AFA)Cu(CNPh)<sub>2</sub>] (**2**), and represents an alternative pathway for the production of complex **2** (Scheme 3), which has previously been synthesized by the insertion of phenylisocyanide into the C–H bonds of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Cu(CNPh)].<sup>4f</sup> After workup and recrystallization from hexane at –40 °C, crystals were isolated in 81% yield. Both the <sup>1</sup>H NMR spectrum of **2**, which shows resonances at δ 6.40 (t), 7.01 (d), and 8.35 ppm (s) associated with the AFA ligand and a multiplet between δ 7.12–7.42 ppm corresponding to the 20 H of the aromatic groups, and also the elemental analysis of the complexes made by both routes are the same (within experimental error). However, isolation of the product from the salt-metathesis route followed by recrystallization from hexane at –40 °C yielded crystals with very different asymmetric unit cell dimensions (Table 1) to those previously isolated from the insertion reaction.<sup>4f</sup>

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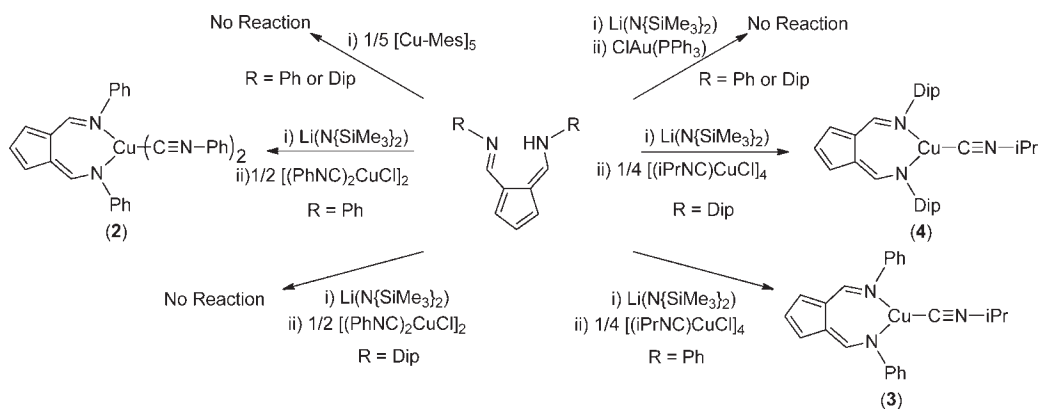
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Scheme 3. Synthesis and Attempted Synthesis of Group 11 Metal-AFA Complexes



A closer inspection of the crystals using single crystal X-ray diffraction revealed a new structural isomer of **2** (i.e., **2b**); For comparison, the molecular structure of the original isomer (**2a**) is shown in Figure 3, and the molecular structure of the newly isolated structural isomer (**2b**) is shown in Figure 4. Selected bond lengths and angles for **2a** and **2b** are shown in Table 3.

Although the copper centers in both **2a** and **2b** are four-coordinate, with the two nitrogen atoms of the AFA ligand and the divalent carbon atoms of two phenyl isocyanide ligands coordinated to the metal centers, only complex **2a** has angles about the Cu center that are close to an ideal tetrahedral (see table 3). In direct contrast, complex **2b** has a highly distorted geometry, with two angles, N(2)–Cu(1)–C(41) and C(31)–Cu(1)–C(41), which are greater than  $120^\circ$  [ $123.62(19)^\circ$  and  $123.2(2)^\circ$  respectively]. Figure 5 shows a least-squares overlay of the two complexes (**2a** in green; **2b** in red). While the imine substituents on the AFA ligands are, not unsurprisingly, orientated differently in both complexes, the core {Cu–C<sub>5</sub>(CN)<sub>2</sub>} fragments, in both complexes shows good correlation, with an error of displacement of 0.0844 Å,

serving to highlight the considerable differences in Cu–CNPh bonding environments in the two complexes.

Both complexes possess AFA backbones, {C<sub>5</sub>(CN)<sub>2</sub>}, that are near planar; the mean deviation from planarity for the atoms N(1), C(1)–C(7), N(2) is 0.0776(20) Å in **2a** and 0.0538(41) Å in **2b**. The Cu–N distances in **2a** and **2b** are very similar [**2a**; Cu(1)–N(1), 2.0530(18) Å and Cu(1)–N(2), 2.0366(17) Å; **2b**; Cu(1)–N(1) 2.0366(17) Å and Cu(1)–N(2) 2.069(4) Å] (in the two adducts). As with previously reported systems,<sup>4a,b,d,e</sup> **2a** and **2b** display a distortion such that the metal center is displaced out of the plane of the AFA ligand by 0.36 Å and 0.72 Å, respectively, a direct consequence of the dihedral angles between the N(1)–Cu(1)–N(2) plane and the N(1)–C(1)–C(7)–N(2) plane [**2a**,  $17.71(11)^\circ$ ; **2b**,  $35.19(23)^\circ$ ] in the two complexes.

The coordination environment about the copper center in **2b** is possibly best described as distorted trigonal pyramidal, with the nitrogen atoms of the {Ph<sub>2</sub>-AFA} ligand [N(1) and N(2)] and one of the two phenyl isocyanide carbon atoms [C(41)] occupying the basal positions, with the copper center displaced out of the plane [N(1)–N(2)–C(41)] by 0.569 Å.

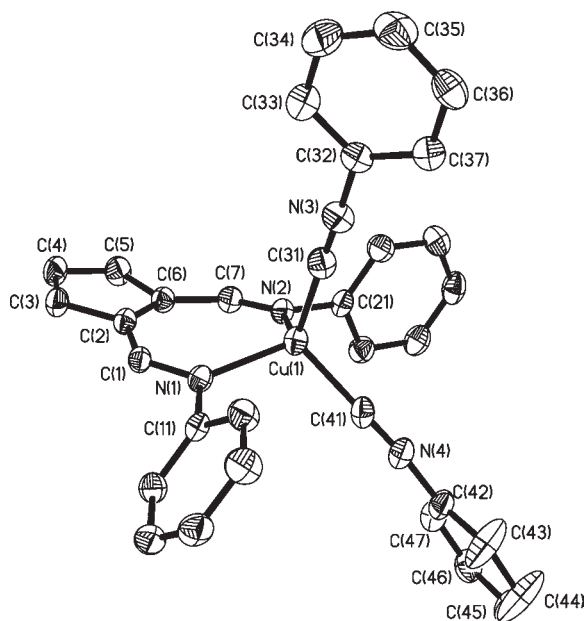


Figure 3. Molecular structure of complex **2a**. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been removed for clarity.

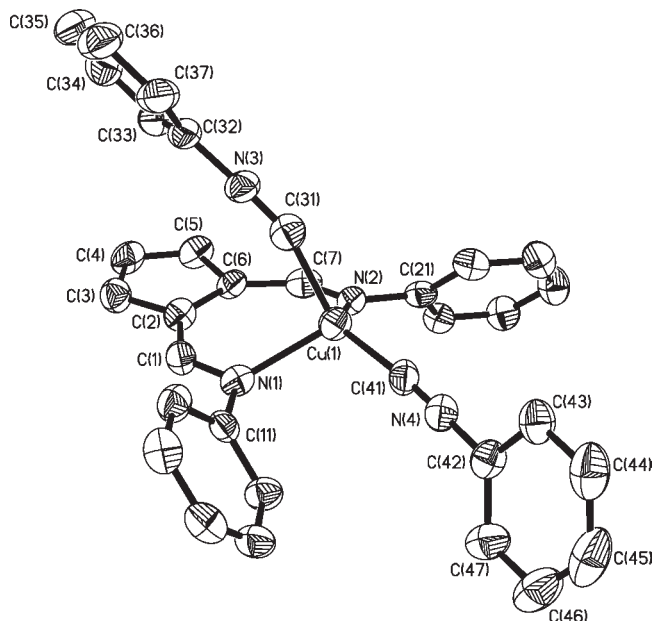
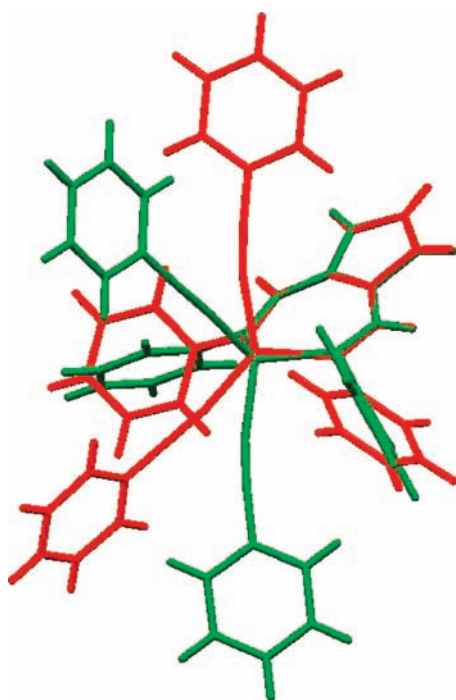


Figure 4. Molecular structure of complex **2b**. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been removed for clarity.

**Table 3.** Selected Bond Lengths and Angles for the Structural Isomers, Complexes **2a** and **2b**

	selected bond lengths (Å)		selected bond angles (deg)	
	<b>2a</b>	<b>2b</b>	<b>2a</b>	<b>2b</b>
Cu(1)–N(1)	2.0530(18)	2.024(5)		
Cu(1)–N(2)	2.0366(17)	2.069(4)	N(1)–Cu(1)–N(2)	105.87(7)
Cu(1)–C(31)	1.907(2)	1.943(6)	N(1)–Cu(1)–C(31)	108.15(8)
Cu(1)–C(41)	1.917(2)	1.877(6)	N(1)–Cu(1)–C(41)	112.54(8)
N(1)–C(1)	1.308(3)	1.299(7)	N(2)–Cu(1)–C(31)	112.01(8)
C(1)–C(2)	1.415(3)	1.416(8)	N(2)–Cu(1)–C(41)	100.67(8)
C(2)–C(3)	1.421(3)	1.411(7)	C(31)–Cu(1)–C(41)	116.96(10)
C(3)–C(4)	1.384(3)	1.400(8)		
C(4)–C(5)	1.391(3)	1.381(7)	Cu(1)–C(31)–N(3)	174.7(2)
C(5)–C(6)	1.414(3)	1.381(7)	C(31)–N(3)–C(32)	178.2(2)
C(6)–C(7)	1.426(3)	1.421(7)	Cu(1)–C(41)–N(4)	171.24(19)
C(2)–C(6)	1.447(3)	1.457(7)	C(41)–N(4)–C(42)	173.6(2)
C(7)–N(2)	1.294(3)	1.315(7)		
C(31)–N(3)	1.164(3)	1.158(6)	Cu(1)–N(1)–C(1)	127.28(15)
C(41)–N(4)	1.164(3)	1.164(7)	Cu(1)–N(2)–C(7)	130.80(15)
N(1)–C(11)	1.429(3)	1.437(7)		
N(2)–N(22)	1.437(3)	1.439(6)		

**Figure 5.** Least-squares overlay of the two complexes **2a** (green) and **2b** (red), demonstrating the significant structural differences in the phenyl isocyanide coordination to the copper centers.

The apical position is occupied by the carbon atom of the second phenyl isocyanide group [C(31)], although the coordination environment of this group is further distorted from ideal, such that the ligand is orientated toward the  $\{C_5(NC)_2\}$  core of the AFA ligand; the angle between the N(1)–Cu(1)–N(2) plane and the vector described by the bond Cu(1)–C(31) being  $100.13(5)^\circ$ . The apical isocyanide ligand is further distorted with a nonlinear angle at C(31) [Cu(1)–C(31)–N(3) =  $156(5)^\circ$ ], which directs the phenyl group toward the  $\{C_5\}$ -ring of the AFA ligand. This orientation preference of the apical phenyl isocyanide group is rationalized by the presence of a weak C–H $\cdots\pi$  interaction between a C–H group [C(33)–H(33)] on the phenyl isocyanide and the electron rich  $\{C_5\}$ -ring of the AFA ligand [C(33)– $\{C_5\}_{CT}$  = 3.750(4) Å; H(33)– $\{C_5\}_{CT}$  = 2.958 Å;

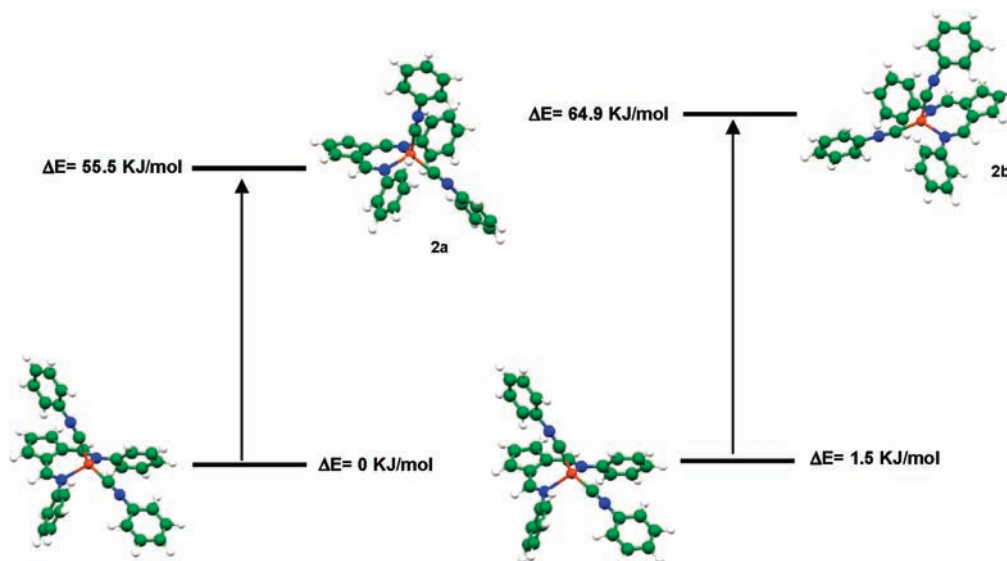
C(33)–H(33) $\cdots\{C_5\}_{CT}$  =  $141.66^\circ$ ].<sup>21</sup> This molecular geometry is in stark contrast to the *pseudo* tetrahedral geometry encountered in complex **2a**.

A comparison of the two Cu–C bond distances in **2a** [Cu(1)–C(31), 1.907(2) Å and Cu(1)–C(41), 1.917(2) Å] shows that the two bonds are similar to each other, whereas the comparable distances in **2b** [Cu(1)–C(31), 1.943 Å; Cu(1)–C(41), 1.877(6) Å] reveal a difference in the Cu–C bonding in the two metal ligand interactions with the ‘*basal*’ isocyanide group displaying a significantly shorter bond distance to the copper center, than the ‘*apical*’ group. This short Cu–C bond distance is, in fact, comparable to the Cu–C bond distance found in the three coordinate system [(Ph<sub>2</sub>-AFA)Cu(CNPh)] (**1**).<sup>4f</sup>

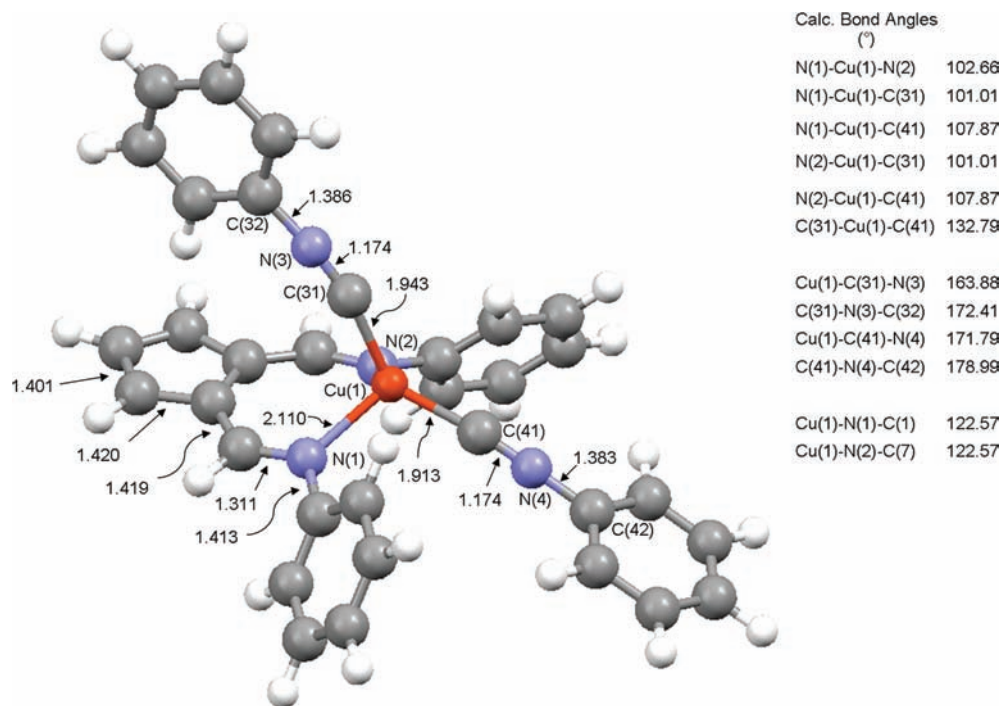
To shed light upon the reasons for the two different isomeric forms for compound **2**, gas phase Density Functional Theory (DFT) calculations were performed. A comparison of the energies of the two forms based upon the experimental determined geometries (solid state) reveals that of the isomers crystallographically characterized, complex **2a** was the lowest energy conformation ( $\Delta E$  = 9.4 kJ/mol) (Figure 6). Upon geometry optimization (gas phase), both forms give similar geometries, differing only in the orientation of the peripheral phenyl rings of the diimine ligand. The associated energy changes of 55.5 and 63.4 kJ/mol respectively are not unsurprising given the difference between solid state DFT systems and gas-phase systems.

These two DFT optimized, gas-phase forms, have similar energies, with the form derived from **2b** being slightly more stable ( $\Delta E$  = 1.5 kJ/mol). In both cases, the optimized geometries more closely resembled form **2b**, in which the apical phenyl isocyanide is involved in a CH $\cdots\pi$  interaction between the  $\{C_5\}$ -ring of the AFA ligand and one of the *ortho*-CH groups of the isocyanide ligand. Figure 7 shows the optimized molecular structure of complex **2** derived from the experimentally determined geometries of complex **2a**. Examination of the calculated bond lengths and angles in the optimized complex **2** (Figure 7) reveals a high degree of

(21) (a) Madhavi, N. N. L.; Katz, A. K.; Carrell, H. L.; Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1997**, 2249. (b) Madhavi, N. N. L.; Katz, A. K.; Carrell, H. L.; Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1997**, 1953.



**Figure 6.** Representation of the relative energies of the crystallographically determined structures **2a** and **2b**, and their optimized molecular structures, obtained at the B3LYP/6-31G(d) level.



**Figure 7.** Optimized geometry of  $[(\text{Ph}_2\text{-AFA-Ph})\text{Cu}(\text{CNPh})_2]$  obtained at the B3LYP/6-31G(d) level, showing relevant calculated distances (Å), and calculated bond angles (deg).

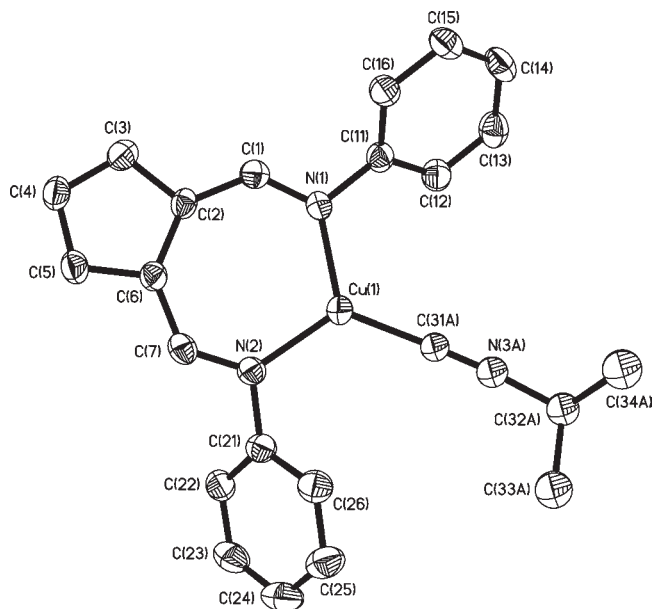
symmetry, such that the molecule possesses a mirror plane defined by {CNC} atoms of the two phenyl isocyanide ligands and the copper center which bisects the molecule. A brief comparison of the solid state structure of complex **2b**, and the geometry optimized system, **2**, reveals that the copper center is displaced further out of the plane of the AFA ligand [0.820 Å] than in **2b**, and consequently possesses greater dihedral angles between the N(1)–Cu(1)–N(2) plane and the N(1)–C(1)–C(7)–N(2) plane [38.47°].

The ‘apical’ isocyanide ligand in the DFT optimized structure of **2** also shows less distortion than that observed in solid-state **2b** with a nonlinear angle at C(31) [Cu(1)–C(31)–N(3) = 163.88°]; as in the solid-state structure of **2b**

the phenyl group is directed toward the {C<sub>5</sub>}–ring of the AFA ligand, revealing an interesting C–H··· $\pi$  interaction between the {C<sub>5</sub>}–ring of the AFA ligand (which is known to carry substantial negative charge)<sup>4c</sup> and a C–H group [C(33)–H(33)] on the phenyl isocyanide [C(33)–{C<sub>5</sub>}<sub>CT</sub> = 3.87 Å; H(33)–{C<sub>5</sub>}<sub>CT</sub> = 2.79 Å; C(33)–H(33)···{C<sub>5</sub>}<sub>CT</sub> = 171.92°], which presumably contributes to the stability of this isomeric form, and that of **2b**.

While computational studies show that there is a moderate change in the relative energies of complexes **2a** and **2b** upon geometry optimization (gas-phase), what is more significant is the observation that there is only a small energy difference ( $\Delta E$  = 9.4 kJ/mol) between the two molecular structures **2a**





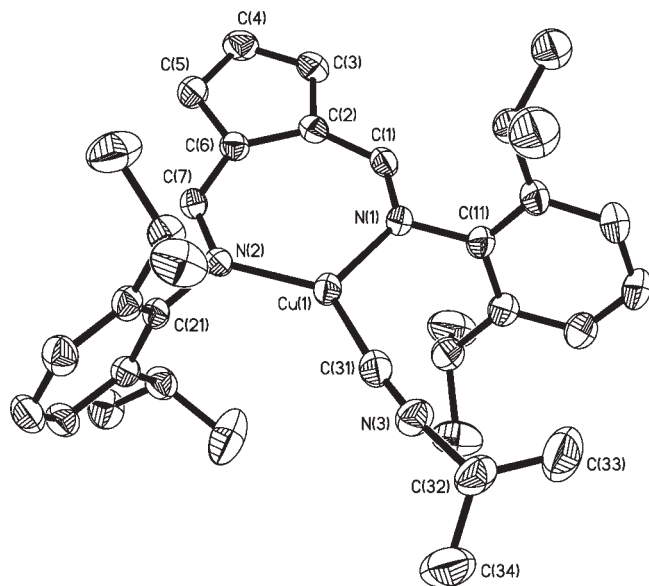
**Figure 8.** Molecular structure of complex **3**. Disorder in the isopropyl isocyanide ligand has been omitted for clarity, and the major component of the disorder [C(31)-N(3A)-C(32A)-C(33A)-C(34A) with 63% occupancy] is shown as isotropic. All anisotropic atoms are shown with thermal ellipsoids at 50% probability.

and **2b** derived from the solid-state geometries. The similar energies, and the absence of significant differences in geometries, strongly suggest that the existence of two forms in the solid state is a consequence of different packing effects, arising from the differences in crystallization conditions.

As part of the study we have attempted to control the crystallization conditions in an effort to selectively isolate either of the two isomeric forms of **2**. Despite multiple attempts, we have been unsuccessful in determining the precise conditions that would selectively allow isolation of one isomer over another, and given the relatively small energy differences and the large number of potential variables in terms of factors such as temperature, rate of cooling, and concentration, this is not surprising. Similarly, attempts to interconvert between isomeric forms have also been fraught with difficulties.

Treatment of the sterically more demanding AFA ligand, Dip<sub>2</sub>-AFAH, with lithium bis(trimethylsilyl)amide (or *n*-butyl lithium) in THF followed by reaction with [(PhNC)<sub>2</sub>Cu( $\mu^2$ -Cl)]<sub>2</sub> failed to provide the 2,6-diisopropylphenyl derivatized analogues of **2a** or **2b**. Only unreacted ligand was isolated from the reaction mixture, suggesting that the steric bulk of {Dip<sub>2</sub>-AFA} precludes complex formation.

In contrast, reaction of Li[Ph<sub>2</sub>-AFA] and Li[Dip<sub>2</sub>-AFA], formed in situ, with stoichiometric amounts of [(<sup>*i*</sup>PrNC)-Cu( $\mu^3$ -Cl)]<sub>4</sub> results in the formation and isolation of the complexes [(Ph<sub>2</sub>-AFA)Cu(CN<sup>*i*</sup>Pr)] (**3**) and [(Dip<sub>2</sub>-AFA)Cu(CN<sup>*i*</sup>Pr)] (**4**), respectively. The <sup>1</sup>H NMR spectra of both **3** and **4** show the coordination of both CN<sup>*i*</sup>Pr and AFA ligands to the copper metal center. Upon coordination, the doublet associated with the imine {H-C=N} group changes to become sharp singlet resonances [ $\delta$  = 8.30 ppm (**3**);  $\delta$  = 8.03 ppm (**4**)], which is accompanied by the shifting of several peaks. In the case of the {Dip<sub>2</sub>-AFA} ligand, coordination to the copper center results in an inequivalence of the methyl groups of the 2,6-diisopropyl phenyl substituent, with the <sup>1</sup>H NMR spectrum of **4** showing the presence of two doublets at



**Figure 9.** Molecular structure of complex **4**. Disorder in one of the isopropyl groups of the 2,6-diisopropylphenyl substituent [C(11)] ligand has been omitted for clarity and the major component of the disorder [C(17A)-C(18A)-C(18B) with 53% occupancy] is shown as isotropic. All anisotropic atoms are shown with thermal ellipsoids at 50% probability.

$\delta$  = 1.18 and 1.21 ppm, both accounting for 12H each. The observed inequivalence is a result of restricted rotation about the N-aryl bond, resulting in two distinct methyl environments: within the “bite” of the ligand, and outside the “bite” of the ligand.

Recrystallization of complexes **3** and **4** (separately) from hexane, yields crystals of the corresponding compound of suitable quality for single crystal X-ray diffraction studies. The molecular structures of both complexes are shown in Figures 8 and 9, respectively, and selected bond lengths and angles are shown in Table 4. Both complexes feature three coordinate trigonal planar metal centers, with the nitrogen atoms of the AFA ligands and divalent carbon of the isocyanide ligand occupying the three-coordination sites. The Cu–N distances [**3**: Cu–N = 1.962(2) and 1.961(2) Å; **4**: Cu–N = 1.975(16) and 1.934(15) Å] and Cu–C distances [**3**: Cu–C = 1.866(11) Å; **4**: Cu–C = 1.858(2) Å] in complexes **3** and **4** are comparatively shorter than the corresponding distances observed in complexes **2a** and **2b**.

While the sum of the angles about each copper center indicates near perfect planar geometry [ $\sum_{\text{Cu}} = 359.94^\circ$  (**3**) and  $360^\circ$  (**4**)] (the copper atom in both systems resides fractionally above the plane of the three atoms, N(1), N(2), and C(31) by 0.0287 Å in **3** and 0.0028 Å in **4**) a closer inspection of the geometry about the copper centers reveals asymmetric coordination environments; with the AFA-Cu bite angle (N–Cu–N) of both complexes being the smallest angle [N(1)–Cu(1)–N(2); 113.43(10) $^\circ$  (**3**), and 110.79(7) $^\circ$  (**4**)] and the largest angle being that subtended between N(2)–Cu(1)–C(31) [124.06(18) $^\circ$  (**3**), 132.86(8) $^\circ$  (**4**)].

Despite this asymmetry, there is very little difference in the core bonding features of the {Cu-AFA} coordination which would explain the significant differences in bond angles between the two systems; average Cu–N bond lengths are comparable [1.961 Å (**3**) vs 1.955 Å (**4**)], although there is a difference between the two Cu–N bonds in complex **4** [Cu(1)–N(1) 1.9758(16) Å; Cu(1)–N(2) 1.9341(15) Å]. The relative

**Table 4.** Selected Bond Lengths and Angles for [(Ph<sub>2</sub>-AFA)Cu(CN<sup>t</sup>Pr)] (**3**) and [(Dip<sub>2</sub>-AFA)Cu(CN<sup>t</sup>Pr)] (**4**)

	<b>3</b>	<b>4</b>		<b>3</b>	<b>4</b>
Selected Bond Lengths (Å)					
Cu(1)–N(1)	1.962(2)	1.9758(16)	Cu(1)–(C31) <sup>a</sup>	1.867(5)	1.858(2)
Cu(1)–N(2)	1.961(2)	1.9341(15)	C(31)–N(3) <sup>a</sup>	1.145(6)	1.151(3)
N(1)–C(1)	1.314(4)	1.301(2)			
C(1)–C(2)	1.404(4)	1.418(3)	C(4)–C(5)	1.387(4)	1.388(3)
C(2)–C(3)	1.419(4)	1.410(3)	C(5)–C(6)	1.416(4)	1.413(3)
C(3)–C(4)	1.390(4)	1.392(3)	C(6)–C(7)	1.414(4)	1.413(3)
C(6)–C(2)	1.457(4)	1.455(3)	C(7)–N(2)	1.314(4)	1.306(2)
Selected Bond Angles (deg)					
N(1)–Cu(1)–N(2)	113.43(10)	110.79(7)	Cu(1)–C(31)–N(3) <sup>a</sup>	177.6(5)	173.35(19)
N(1)–Cu(1)–C(31) <sup>a</sup>	122.45(18)	116.35(8)	Cu(1)–N(1)–C(11)	178.5(9)	113.42(12)
	123.9(3)			115.4(2)	
N(2)–Cu(1)–C(31) <sup>a</sup>	124.06(18)	132.86(8)	Cu(1)–N(2)–C(21)	117.17(18)	116.28(11)
	120.2(3)				

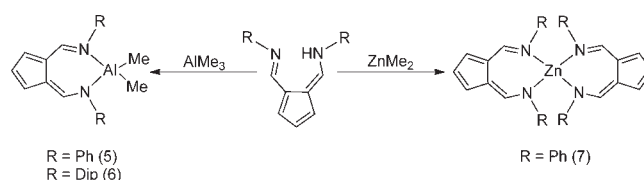
<sup>a</sup> Disorder in the isopropyl isocyanide groups modeled over two positions [C(31A)–N(3A)–C(32A)–C(33A)–C(34A)] (63% occupancy) and [C(31B)–N(3B)–C(32B)–C(33B)–C(34B)] (37% occupancy).

orientation of the AFA aryl substituents in the two complexes is different, which is apparent from Figures 8 and 9, with the angles subtended between the phenyl ring substituents on {Ph<sub>2</sub>-AFA} and the plane defined by the {C<sub>5</sub>(CN)<sub>2</sub>} plane, in complex **3** [45.11(7)° and 48.06(7)°] closer to coplanar than those in the {Dip<sub>2</sub>-AFA} system, [72.72° and 82.57°]. Assuming the orientation of the AFA substituents to be a factor in the solid-state deformation, it may be expected that the {Dip<sub>2</sub>-AFA} complex [(Dip<sub>2</sub>-AFA)Cu(CN<sup>t</sup>Pr)] (**4**) would be the most symmetric of these complexes, as the approximate coplanarity of the aryl substituents provides a less sterically restricted environment for {CuCN<sup>t</sup>Pr} coordination; however, this is not found to be the case.

The large N(2)–Cu(1)–C(31) angle in complex **4** results in a pronounced distortion of the isopropyl isocyanide coordination such that the ligand is displaced toward one side of the ligand's maw (specifically toward the aryl substituent C(11)–C(16)). This distortion is further amplified by a nonlinear coordination, of the isopropyl isocyanide at the Cu atom [Cu(1)–C(31)–N(3) = 173.35(19)°] compared to near the more linear coordination observed in complex **3** [Cu(1)–C(31)–N(3) = 177.35(19)°].

Attempts to synthesize gold(I) AFA complexes by the reaction of lithiated AFA ligands with [ClAu(PPh<sub>3</sub>)] and [ClAu(THT)] in THF resulted in the initial formation of a dark orange solution which rapidly darkened and turned black, depositing gold metal on the walls of the reaction vessel. Successive attempts to isolate stable complexes from these reactions have, to-date, been unsuccessful. In contrast, related reactions between metalated β-diketiminato ligands and [ClAu(THT)], or metalated aminotroponiminato ligands with [ClAu(PPh<sub>3</sub>)], have been shown to yield complexes containing Au(I).<sup>22</sup>

Reaction of either Dip<sub>2</sub>-AFAH or Ph<sub>2</sub>-AFAH with AlMe<sub>3</sub> in THF affords the dimethyl derivatives, [(Ph<sub>2</sub>-AFA)AlMe<sub>2</sub>] (**5**) and [(Dip<sub>2</sub>-AFA)AlMe<sub>2</sub>] (**6**), respectively (Scheme 4). The yellow complexes could be isolated in high yields, direct from the reaction mixture, but recrystallization from suitable solvents (THF and toluene) resulted in reduced overall yields (36–

**Scheme 4.** Synthesis of Aluminum and Zinc AFA Complexes

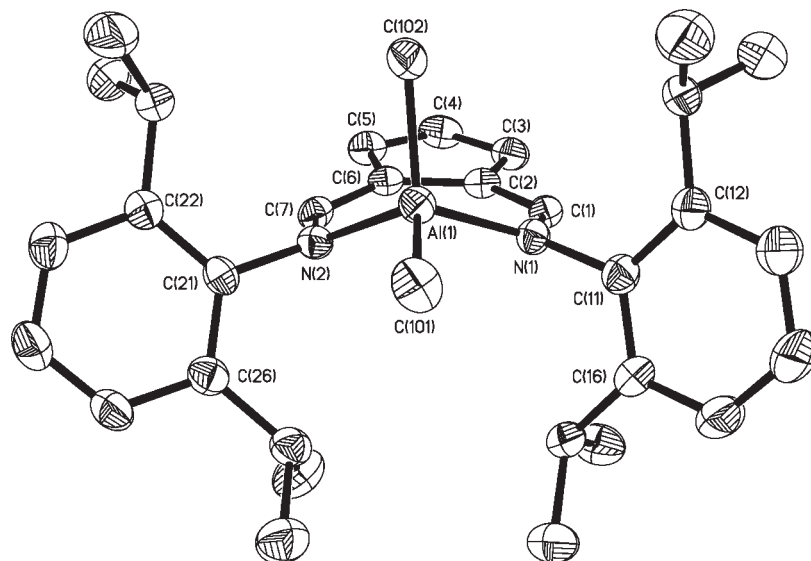
49%). Nevertheless, what appeared to be single crystals of [(Ph<sub>2</sub>-AFA)AlMe<sub>2</sub>], however, have been obtained. Unfortunately the crystals and subsequent X-ray diffraction data were not of satisfactory quality to refine the molecular structure. In the case of [(Dip<sub>2</sub>-AFA)AlMe<sub>2</sub>] crystals suitable for single crystal X-ray analysis experiments were isolated. The molecular structure of the complex **6** is shown in Figure 10, and selected bond lengths and angles are shown in Table 5.

As with the copper complexes **1–4**, the AFA ligand in **6** binds to the metal center via the imine nitrogen atoms. Two methyl groups around the aluminum center complete the metals pseudo tetrahedral coordination sphere. The Al–N bond lengths [Al(1)–N(1) = 1.9426(17) Å; Al(1)–N(2) = 1.9487(14) Å] are fractionally longer than those observed in both the comparable 2,6-diisopropylphenyl substituted diketiminato complex [{HC(CMeN(C<sub>6</sub>H<sub>3</sub><sup>t</sup>Pr<sub>2</sub>))}AlMe<sub>2</sub>], [1.928(2) Å],<sup>23</sup> and the related 1,2-cyclopentadienyl diimine complex described by Stephan and co-workers [1.853(9) Å],<sup>4a</sup> and are probably a consequence of the larger N–Al–N bite angle observed for **6** [N(1)–Al(1)–N(2) = 104.32(9)° (cf. 96.18(9)°<sup>23</sup> and 99.72(7)°,<sup>4a</sup> respectively)]. In contrast, the Al–C distances in **6** [Al(1)–C(101) = 1.950(2) Å; Al(1)–C(102) = 1.963(2) Å] are directly comparable to similar bonds in the two previously mentioned related complexes [cf. 1.964(3) Å and 1.953(2) Å, respectively].<sup>4a,23</sup>

As with complexes **1–4**, the AFA backbone in complex **6** is very close to planar, with the mean deviation from planarity for the atoms N(1), C(1)–C(7), N(2) being 0.0530(16) Å, but the aluminum center is located 0.87 Å out of this plane. This

(22) (a) Dias, H. V. R.; Flores, J. A. *Inorg. Chem.* **2007**, *46*, 5841. (b) Meiners, J.; Herrmann, J. S.; Roesky, P. W. *Inorg. Chem.* **2007**, *46*, 4599.

(23) Qian, B. X.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070.



**Figure 10.** Molecular structure of complex **6**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been removed for clarity.

**Table 5.** Selected Bond Lengths and Angles for Complex **6**

Selected Bond Lengths (Å)			
Al(1)–N(1)	1.9426(17)	Al(1)–C(101)	1.950(2)
Al(1)–N(2)	1.9487(14)	Al(1)–C(102)	1.963(2)
N(1)–C(1)	1.330(2)		
C(1)–C(2)	1.398(2)	C(4)–C(5)	1.385(3)
C(2)–C(3)	1.412(2)	C(5)–C(6)	1.412(3)
C(3)–C(4)	1.396(3)	C(6)–C(7)	1.406(3)
C(6)–C(2)	1.455(2)	C(7)–N(2)	1.311(2)
N(1)–C(11)	1.465(2)		
N(2)–C(22)	1.455(2)		
Selected Bond Angles (deg)			
C(101)–Al(1)–C(102)	116.78(10)	N(1)–Al(1)–C(102)	109.07(8)
N(1)–Al(1)–N(2)	104.32(7)	N(2)–Al(1)–C(101)	112.38(8)
N(1)–Al(1)–C(101)	108.07(9)	N(2)–Al(1)–C(102)	105.48(8)
N(1)–C(1)–C(2)	128.49(17)	C(1)–N(1)–C(11)	115.44(16)
N(2)–C(7)–C(6)	130.05(16)	C(7)–N(2)–C(21)	114.79(14)

displacement of the metal center out of the plane of the AFA ligand results in an acute angle of  $40.87(16)^\circ$  between the  $\{\text{AlN}_2\}$  plane and the mean plane defined by the two imine, C=N, bonds.

Displacement of the Al center above the plane of the ligand, also allows the steric burden within the maw of ligand to be relieved by a slight twisting of the 2,6-diisopropylphenyl substituents toward the space vacated by the  $\{\text{AlMe}_2\}$  group; such that the angle between the  $\{\text{C}_5(\text{CN})_2\}$  plane of the ligand and each phenyl ring is significantly more acute [ $\{\text{C}_5(\text{CN})_2\}/\text{C}(11)–\text{C}(16) = 73.5^\circ$ ;  $\{\text{C}_5(\text{CN})_2\}/\text{C}(21)–\text{C}(26) = 61.6^\circ$ ] than corresponding angles found in both the free ligand, Dip<sub>2</sub>-AFAH, and complex **4**.

The <sup>1</sup>H NMR spectra of complexes **5** and **6** show the presence of a single resonance for the methyl groups on Al

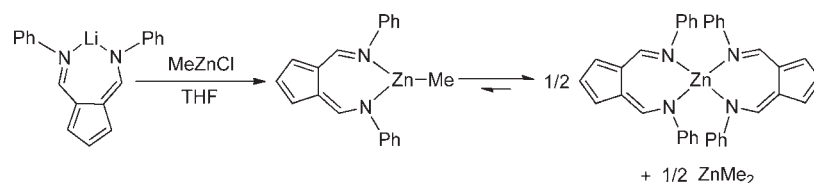
at  $\delta = -0.91$  and  $-1.01$  ppm respectively, suggesting a rapid interchange between the two distinct methyl environments observed in the solid-state structure of **6**.

Treatment of  $\text{ZnMe}_2$  with  $\text{Ph}_2\text{-AFAH}$  in THF affords the *bis*-AFA complex,  $[(\text{Ph}_2\text{-AFA})_2\text{Zn}]$  (**7**) exclusively. While complex **7** has previously been reported by Bailey and co-workers as the product from the reaction of  $\text{ZnCl}_2$  with  $\text{Na}[\text{Ph}_2\text{-AFA}]$ ,<sup>4d</sup> we had hoped controlled reaction of the parent ligand system with dimethyl zinc would afford complexes comparable to the methyl magnesium derivative  $[(\text{Cy}_2\text{-AFA})\text{MgMe}(\text{THF})]$ , also reported by Bailey.<sup>4c</sup> Attempts to react the lithiated ligand  $[(\text{Ph}_2\text{-AFA})\text{Li}]$  with  $\text{MeZnCl}$  also resulted in the isolation of complex **7**, presumably a result of a Schlenk equilibrium, in which complex **7** is a thermodynamic sink (Scheme 5).

Crystals of compound **7**, suitable for single crystal X-ray diffraction, were obtained during the course of this study (Table 1). The molecular structure determined in this study is identical (within experimental error) to that previously determined by Bailey et al.<sup>4d</sup>

In contrast, reaction of  $\text{ZnMe}_2$  (or  $\text{MeZnCl}$ ) with the more sterically demanding ligand system, Dip<sub>2</sub>-AFAH, failed to result in any observable reaction, irrespective of the reaction stoichiometries used, solvent systems, or conditions employed. Similar observations regarding this ligand system have been reported by others; for example, the failure to synthesize the *mono*- or *bis*-Dip<sub>2</sub>-AFA complexes of palladium, and have been attributed to the size of the 2,6-diisopropylphenyl substituents, which in some cases not only prevent initial coordination but precludes complexation completely.<sup>4c</sup>

**Scheme 5.** Proposed Reaction Pathway to Complex **7**



## Conclusions

In summary, we have described a one-pot synthesis for aryl substituted AFA ligands, and reported the subsequent reaction chemistry of these species with selected copper, gold, aluminum, and zinc reagents. It is hoped that with the development of this ligand synthesis we can further expand the known coordination chemistry of these ligand systems.

Reaction of Li[Ph<sub>2</sub>-AFA] with [(PhNC)<sub>2</sub>Cu( $\mu^2$ -Cl)]<sub>2</sub> resulted in the isolation of two independent structural isomers of the complex [{Ph<sub>2</sub>-AFA}Cu(CNPh)<sub>2</sub>]<sub>2</sub>, **2**, both of which can be structurally characterized, suggesting a highly flexible system, both electronically and coordinatively. DFT calculations and geometry optimization of these systems reveal minimal energy differences between these two solid-state forms, consistent with our hypothesis that the observed differences are the consequence of different packing effects arising from the differences in crystallization conditions. The introduction of sterically demanding *N*-substituents,

that is, the bulky 2,6-diisopropylphenyl substituent, has a significant effect on the chemistry of these ligands, and in several cases reaction of the {Dip<sub>2</sub>-AFA} ligand system with metal reagents resulted in no observable reaction, which we attribute to a kinetic rather than thermodynamic effect.

**Acknowledgment.** We acknowledge the financial support of the University of Bath and the EPSRC for the award of a CASE for New Academics (A.M.W.). We thank UMICORE AG & Co. KG for a generous gift of precious metal compounds. A.L.J. thanks Prof. P. R. Raithby (UoB) and Dr. M. S. Hill (UoB) for helpful comments and fruitful discussions.

**Supporting Information Available:** X-ray crystallographic files in CIF format. Further details about the geometry of complexes **2a** and **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.