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Comparison of the Structure and Stability of New α-Diimine Complexes of Copper(I) and Silver(I): Density Functional Theory versus Experimental

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New compounds of the general formulas [M(Ar-BIAN)$_2$]BF$_4$ and [M(Ar-BIAN)(NCMe)$_2$]BF$_4$, where M = Cu^{I} or Ag^{I} and Ar-BIAN = bis(aryl)acenaphthenequinonediimine, were synthesized by the direct reaction of [Cu(NCMe)$_4$]BF$_4$ or [Ag(NCMe)$_4$]BF$_4$ with the corresponding Ar-BIAN ligand in dried CH$_2$Cl$_2$. The synthesized compounds are [M(*o,o*′,*p*-Me$_3$C$_6$H$_2$-BIAN)$_2$]BF$_4$ where M = Cu^{I} (**1**) and Ag^{I} (**2**), [M(*o,o*′-*i*Pr$_2$C$_6$H$_3$-BIAN)(NCMe)$_2$]BF$_4$ where M = Cu^{I} (**3**) and Ag^{I} (**4**), and [Ag(*o,o*′-*i*Pr$_2$C$_6$H$_3$-BIAN)$_2$]BF$_4$ (**5**). The crystal structures of compounds **1**−**3** and **5** were solved by single-crystal X-ray diffraction. In all cases copper(I) or silver(I) are in a distorted tetrahedron that is constructed from the four nitrogen atoms of the two α-diimine ligands or, in **3**, from one α-diimine ligand and two acetonitrile molecules. All compounds were characterized by elemental analyses, matrix-assisted laser desorption−ionization time-of-flight mass spectrometry, and IR, UV−vis, and ^{1}H NMR spectroscopy. The analysis of the molecular geometry and the energetic changes for the formation reactions of the complexes, in a CH$_2$Cl$_2$ solution, were evaluated by density functional theory calculations and compared with the experimental results.

Introduction

Copper(I) and silver(I) compounds have many applications as catalysts in homogeneous catalysis.[1] In particular, copper(I) was recently found[2] to be an efficient catalyst for the 1,3-dipolar cycloaddition of azides and alkynes, becoming the best “click reaction” to date.[3] Copper is also an essential transition metal to all organisms because of its use as catalytic and structural element in enzymes and other molecules.[4] The antimicrobial efficacy of silver is also well documented.[5] On the other hand, α-diimine ligands have been known for a long time[6,7] and are well-known to stabilize organometallic complexes.[8] More recently, Elsevier et al.[9] described the synthesis and full characterization of rigidly chelating bidentate nitrogen ligands [Ar-BIAN = bis(aryl)acenaphthenequinonediimine] by condensation of the rigid acenaphthenquinone with a proper amine. Complexes with these types of ligands and a great variety of transition metals have been synthesized, and many

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catalytic applications were found.[10-12] The reactivity of these ligands with main-group metals calcium and magnesium and metalloid germanium has also been studied.[13] Despite the large number of metallic complexes bearing these types of ligands, few reports on copper(I) were found,[14] including copper(I) complexes obtained from the reduction of the corresponding copper(II) complexes. So far, no reports on silver(I) complexes have been found. In this paper, we present the synthesis and structure of new copper(I) and silver(I) complexes bearing Ar-BIAN ligands and make a comparative study between copper(I) and silver(I) complexes. Theoretical calculations of the molecular geometries and the thermodynamical feasibility of the synthesis of these complexes in solution were performed, in order to evaluate and compare them with experimental results.

Experimental Section

General Procedures and Materials. All reactions and manipulations of solutions were performed under an argon atmosphere using Schlenk-line techniques. Solvents were reagent-grade and were dried according to literature methods. Ligands were prepared according to the literature.[9] Elemental analyses were performed at the Analytical Services of the Laboratory of REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, on a Thermo Finnigan CE Flash-EA 1112-CHNS instrument. IR spectra were recorded as Nujol mulls on NaCl plates using a Bruker Tensor 27 FTIR spectrometer. NMR spectra were recorded using a Bruker AVANCE II 400 and program *TOPSPIN 2.0* (Bruker).

Spectrophotometric Measurements. Absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. The linearity of absorption versus concentration was checked in the concentration range used ($10^{-4}-10^{-6}$ M). All spectrophotometric titrations were performed as follows: stock solutions of the ligand (ca. 10^{-3} M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with freshly dried CH_2Cl_2 UVA sol. All measurements were performed at 298 K. The titration solutions ($[L] = 10^{-5}$ M) were prepared by the appropriate dilution of the stock solutions. Titrations of the ligand were carried out by the addition of microliter amounts of standard solutions of silver(I) in the form of $[Ag(NCMe)_4]BF_4$ salt and copper(I) as $[Cu(NCMe)_4]BF_4$ salt in freshly dried dichloromethane.

Mass Spectrometry. Matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were obtained in the REQUIMTE MALDI-TOF-MS Service Laboratory and have been performed in a MALDI-TOF-MS voyager DE-PRO Biospectrometry Workstation equipped with a nitrogen laser radiating at 337 nm from Applied Biosystems (Foster City, CA). MALDI-MS spectra were acquired and treated with the *Data Explorer*, version 4, software series. The MALDI-TOF-MS study in dichloromethane was carried out for all of the synthesized compounds. Samples were dissolved in dichloromethane (1 μg/μL), and 1−2 μL of the corresponding solution was spotted on a well of a MALDI-TOF-MS sample plate and allowed to dry. No matrix was added. Measurements were performed in the reflector positive- or negative-ion mode, with a 20 kV accelerating voltage, 80% grid voltage, 0.005% guide wire, and a delay time of 200 ns. Mass spectral analysis for each sample was based on the average of 500 laser shots. Time-of-flight mass spectrometry electron impact and time-of-flight mass spectrometry field desorption spectra were obtained in the REQUIMTE MS Service Laboratory using a Micromass GCT model.

Crystallography. Single crystals of complexes **1**−**3** and **5** were mounted on a Nonius Kappa CCD area detector diffractometer [λ(Mo Kα) = 0.710 73 Å]. The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from the reflections taken from one set of 10 frames (1.0° steps in the ϕ angle), each at 20 s exposure. The structures were solved using direct methods (*SHELXS97*)[15] and refined against F^2 using *SHELXL97* software.[16] The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in *SHELXL97*. In the cases of complexes **1** and **2**, a *SQUEEZE* procedure[17] was used to avoid the disorder refinement of one pentane solvent molecule. Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as CCDC 752678−752681. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

Computational Details. Unrestricted calculations were carried out using the *Gaussian 03* package.[18] The hybrid density functional theory method known as B3LYP was applied.[19] Effective core potentials were used to represent the innermost electrons of the transition-metal atoms, and the basis set of valence double-ζ quality was associated with the pseudopotentials known as LANL2DZ.[20] The basis set for the light elements such as carbon, nitrogen, and hydrogen was 6-31G*.[21] Energies in solution were taken into account by PCM calculations (dichloromethane and acetonitrile, $\varepsilon = 8.93$ and

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36.64, respectively),[22] keeping the geometry optimized for the gas phase (single-point calculations). The structural data were obtained through a systematic search of the Cambridge Structural Database (version 5.30 with one update, Nov 2008).[23]

Synthesis of Copper Complexes. Synthesis of [Cu(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)$_2$]BF_4 (1). A suspension of [Cu(NCMe)$_4$]BF_4 (0.075 g, 0.24 mmol) in CH_2Cl_2 (10 mL) was treated with a red solution of *o*,*o*′,*p*-$Me_3C_6H_2$-BIAN (0.2 g, 0.48 mmol) in CH_2Cl_2 (20 mL). The mixture turned quickly to a red-wine color; it was stirred overnight until everything was dissolved. After filtration of the solution, the solvent was partially removed and petroleum ether was added. The solution was put in a refrigerator. The brown crystals formed were separated by filtration and washed with pentane (2 × 10 mL). A total 0.17 g of **1** was obtained (yield 72%). Crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane in a CH_2Cl_2 solution of **1**.

^1H NMR (400 MHz, CD_2Cl_2): δ 8.10 (d, J = 8.4 Hz, 4H), 7.49 (t, J = 8.0 Hz, 4H), 6.90 (s, 8H), 6.70 (d, J = 7.2 Hz, 4H), 2.44 (s, 12H), 1.76 (s, 24H). IR (Nujol): ν 1653.8 (C=N), 1611.2 (C=N), 1056.3 (BF_4^-) cm^{-1}. Elem anal. Calcd for $C_{60}H_{56}CuBN_4F_4\cdot{}^1/_8C_5H_{12}$: C, 73.37; H, 5.84; N, 5.65. Found: C, 73.28; H, 5.90; N, 5.25. MALDI-TOF-MS: m/z 416.1 (2%) [*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN]$^+$, 479.2 (25%) [Cu(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)]$^+$, 895.4 (100%) [Cu(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)$_2$]$^+$, 983.2 (8%) [Cu(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)$_2$-(BF_4)]$^+$. UV−vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 255sh (58 240), 324 (25 950), 401sh (7820), 502 (7720), 726 (4070). Crystal data for **1**: crystal color, brown; crystal dimensions, 0.10 × 0.10 × 0.10 mm^3; $C_{60}H_{56}BCuF_4N_4$, M = 983.44 g mol^{-1}; orthorhombic; space group *Ccca*; a = 16.8876(10) Å; b = 22.1696(10) Å; c = 16.1730(10) Å; Z = 4; D_c = 1.079 g cm^{-3}; μ(Mo Kα) = 0.409 mm^{-1}; a total of 19 453 reflections; 1.84° < θ < 27.46°, 3475 independent reflections with 2256 having $I > 2\sigma(I)$; 164 parameters; final results R1 = 0.0628 and wR2 = 0.1917; GOF = 1.025; maximum residual electronic density = 0.372 e Å^{-3}.

Synthesis of [Cu(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)(NCMe)$_2$]BF_4 (3). A suspension of [Cu(NCMe)$_4$]BF_4 (0.063 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was treated with an orange solution of *o*,*o*′-*i*$Pr_2C_6H_3$-BIAN (0.1 g, 0.20 mmol) in CH_2Cl_2 (20 mL). The mixture turned quickly to brown and was left stirring overnight at room temperature. After filtration of the solution, the solvent was partially removed and petroleum ether was added. It was put in a refrigerator, and a brown microcrystalline solid was recovered after filtration and washed with petroleum ether (2 × 10 mL). A total of 0.12 g of **3** was obtained (yield 82%). Crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane in a CH_2Cl_2 solution of **3**.

^1H NMR (400 MHz, CD_2Cl_2): δ 8.12 (d, J = 8.2 Hz, 2H), 7.54−7.50 (m, 2H), 7.46−7.42 (m, 6H). 6.78 (d, J = 7.0 Hz, 2H), 3.11−2.82 (m, 4H), 2.15 (s, 6H), 1.31 (d, J = 6.6 Hz, 12H), 1.01 (d, J = 11.5 Hz, 12H). IR (Nujol): ν 2375.1, 2333.7 (Me$\underline{\text{CN}}$); 1657.2, 1614.3 (C=N); 1054.9 (BF_4^-) cm^{-1}. Elem anal. Calcd for $C_{40}H_{46}BCuF_4N_4\cdot{}^1/_8CH_2Cl_2$: C, 64.79; H, 6.27; N, 7.53. Found: C, 64.73; H, 6.31; N, 7.32. MALDI-TOF-MS: m/z 457.6 (20%) [*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN-C(Me)$_2$]$^+$, 499.7 (8%) [*o*,*o*′-*i*$Pr_2C_6H_3$-BIANH]$^+$, 563.6 (100%) [Cu(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)]$^+$, 647.5 (30%) [Cu(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)(NCMe)$_2$]$^+$, 731.06 (48%) [Cu(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)(NCMe)$_2$(BF_4)]$^+$. UV−vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 262 (42 610), 320 (15 680), 332sh (12 950), 414 (3020), 567 (260). Crystal data for **3**·2CH_2Cl_2: crystal color, brown; crystal dimensions, 0.10 × 0.10 × 0.10 mm^3; $C_{42}H_{50}BCl_4CuF_4N_4$, M = 903.01 g mol^{-1}; monoclinic; space group $P2_1/c$; a = 12.7670(3) Å; b = 14.7000(6) Å; c = 24.3370(8) Å; β = 96.4950(17)°; Z = 4; D_c = 1.322 g cm^{-3}; μ(Mo Kα) = 0.767 mm^{-1}; a total of 36 170 reflections; 1.61° < θ < 30.02°, 13 232 independent reflections with 5900 having $I > 2\sigma(I)$; 505 parameters; final results R1 = 0.1293 and wR2 = 0.3331; GOF = 1.25; maximum residual electronic density = 1.153 e Å^{-3}.

Synthesis of Silver Complexes. Synthesis of [Ag(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)$_2$]BF_4 (2). A colorless solution of [Ag(NCMe)$_4$]BF_4 (0.087 g, 0.24 mmol) in CH_2Cl_2 (10 mL) was treated with a red solution of *o*,*o*′,*p*-$Me_3C_6H_2$-BIAN (0.2 g, 0.48 mmol) in CH_2Cl_2 (20 mL). The mixture turned quickly to dark red; it was stirred overnight. After filtration of the solution, the solvent was partially removed and petroleum ether was added. The solution was put in a refrigerator. The red-orange microcrystals formed were separated by filtration and washed with petroleum ether (2 × 10 mL). A total of 0.19 g of **2** was obtained (yield 77%). Crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane in a CH_2Cl_2 solution of **2**.

^1H NMR (400 MHz, CD_2Cl_2): δ 8.08 (d, J = 8.3 Hz, 4H), 7.50 (t, J = 7.8 Hz, 4H), 6.95 (s, 8H), 6.91−6.82 (d, J = 7.1 Hz, 4H), 2.43 (s, 12H), 1.78 (s, 24H). IR (Nujol): ν 1668.3 (C=N), 1637.7 (C=N), 1053.8 (BF_4^-) cm^{-1}. Elem anal. Calcd for $C_{60}H_{56}AgBF_4N_4\cdot{}^2/_3CH_2Cl_2$: C, 67.19; H, 5.33; N, 5.17. Found: C, 67.11; H, 5.54; N, 5.09. MALDI-TOF-MS: m/z 416.2 (10%) [*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN]$^+$, 525.1(100%) [Ag(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)]$^+$, 941.3 (60%) [Ag(*o*,*o*′,*p*-$Me_3C_6H_2$-BIAN)$_2$]$^+$. UV−vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 260 (108 280), 311 (46 500), 327 (42 790), 375 (9050), 495 (12 800). Crystal data for **2**: crystal color, red; crystal dimensions, 0.10 × 0.10 × 0.10 mm^3; $C_{60}H_{56}AgBF_4N_4$, M = 1027.77 g mol^{-1}; orthorhombic; space group *Ccca*; a = 16.8436(3) Å; b = 22.5966(5) Å; c = 16.1054(3) Å; Z = 4; D_c = 1.114 g cm^{-3}; μ(Mo Kα) = 0.377 mm^{-1}; a total of 39 187 reflections; 1.80° < θ < 27.50°, 3525 independent reflections with 2751 having $I > 2\sigma(I)$; 162 parameters; final results R1 = 0.0447 and wR2 = 0.1395; GOF = 1.133; maximum residual electronic density = 0.480 e Å^{-3}.

Synthesis of [Ag(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)(NCMe)$_2$]BF_4 (4). A colorless solution of [Ag(NCMe)$_4$]BF_4 (0.14 g, 0.4 mmol) in CH_2Cl_2 (10 mL) was treated with an orange solution of *o*,*o*′-*i*$Pr_2C_6H_3$-BIAN (0.2 g, 0.4 mmol) in CH_2Cl_2 (20 mL). The mixture turned quickly to a red-orange color; it was stirred overnight, until everything was dissolved. After filtration of the solution, the solvent was partially removed and petroleum ether was added. The solution was put in a refrigerator. The orange microcrystals formed were separated by filtration and washed with petroleum ether (2 × 10 mL). A total of 0.25 g of **4** was obtained (yield 81%).

^1H NMR (400 MHz, CD_2Cl_2): δ 8.14 (d, J = 8.3 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.47−7.41 (m, 6H), 6.78 (d, J = 7.3 Hz, 2H), 2.95−2.86 (m, 4H), 2.13 (s, 6H), 1.30 (d, J = 6.8 Hz, 12H), 1.03 (d, J = 6.8 Hz, 12H). IR (Nujol): ν 2303.1 (Me$\underline{\text{CN}}$), 2276.9 (Me$\underline{\text{CN}}$), 1668.3 (C=N), 1655.2 (C=N), 1633.3 (C=N), 1056 (BF_4^-) cm^{-1}. Elem anal. Calcd for $C_{40}H_{46}AgBF_4N_4\cdot{}^2/_5CH_2Cl_2$: C, 59.80; H, 5.81; N, 6.90. Found: C, 59.76. H, 5.83. N, 6.56. MALDI-TOF-MS: m/z 457.2 (100%) [*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN-C(Me)$_2$]$^+$, 500.0 (35%) [*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN]$^+$, 607.2 (20%) [Ag(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)]$^+$, 735.1 (14%) [Ag(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)(NCMe)(BF_4)]$^+$, 1235.4 (10%) [Ag(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)$_2$(NCMe)(BF_4)]$^+$. UV−vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 262 (33 090), 315 (13 000), 331 (11 990), 398 (2350), 426sh (1690), 483 (410).

Synthesis of [Ag(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)$_2$]BF_4 (5). A colorless solution of [Ag(NCMe)$_4$]BF_4 (0.07 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was treated with an orange solution of *o*,*o*′-*i*$Pr_2C_6H_3$-BIAN (0.2 g, 0.4 mmol) in CH_2Cl_2 (20 mL). The mixture turned quickly to a red-orange color; it was stirred overnight, until everything was dissolved. After filtration of the solution, the solvent was partially removed and petroleum ether was added. The solution was put in a refrigerator. The red microcrystals formed were separated by filtration and washed with petroleum ether (2 × 10 mL). A total of 0.2 g of **5** was obtained (yield 84%). Crystals suitable

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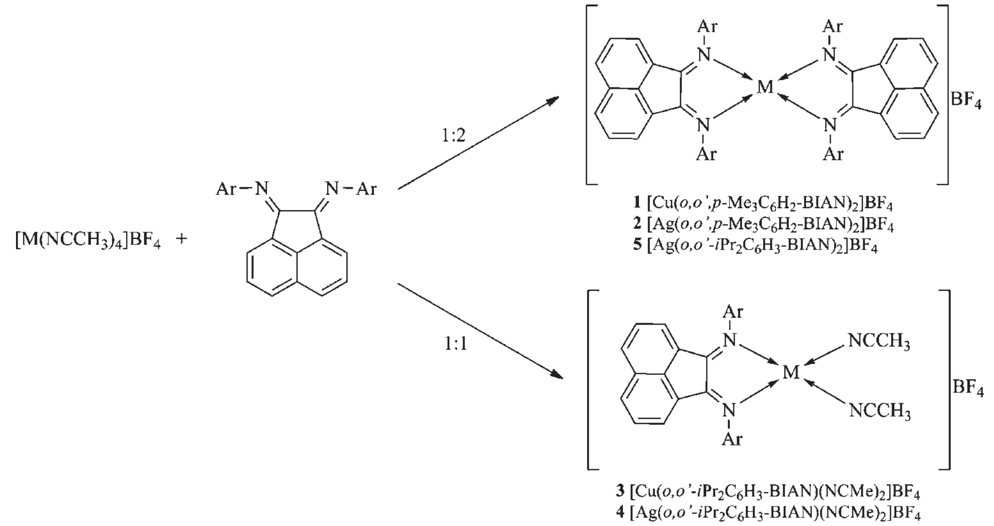
Scheme 1. Synthetic Pathways for Complexes



1 $[Cu(o,o',p\text{-}Me_3C_6H_2\text{-}BIAN)_2]BF_4$
2 $[Ag(o,o',p\text{-}Me_3C_6H_2\text{-}BIAN)_2]BF_4$
5 $[Ag(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-}BIAN)_2]BF_4$

3 $[Cu(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-}BIAN)(NCMe)_2]BF_4$
4 $[Ag(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-}BIAN)(NCMe)_2]BF_4$

for X-ray diffraction were obtained by the slow diffusion of pentane in a CH_2Cl_2 solution of **5**.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.11 (d, J = 8.4 Hz, 4H), 7.53−7.38 (m, 16H), 6.76 (d, J = 7.3 Hz, 4H), 2.94 (sep, J = 6.9 Hz, 8H), 1.31 (d, J = 6.8 Hz, 24H), 0.97 (d, J = 6.8 Hz, 24H). IR (Nujol): ν 1655.2, 1632.1 (C=N); 1062.5 (BF_4^-) cm^{-1}. Elem anal. Calcd for $C_{72}H_{80}AgBF_4N_4\cdot CH_2Cl_2$: C, 68.44; H, 6.45; N, 4.37. Found: C, 68.50; H, 6.82; N, 4.40. MALDI-TOF-MS: m/z 457.6 (100%) $[o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN-C(Me)}_2]^+$, 500.6 (25%) $[o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIANH}]^+$, 607.5 (25%) $[Ag(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})]^+$, 1235.3 (5%) $[Ag(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})_2(NCMe)(BF_4)]^+$. UV−vis [$\lambda_{max}$/nm ($\varepsilon$/M^{-1} cm^{-1})]: 256 (181 170), 313 (8860), 325 (8580), 380 (1040), 423sh (1700), 478 (250). Crystal data for $\mathbf{5}\cdot{}^5/_2CH_2Cl_2$: crystal color, red orange; crystal dimensions, 0.20 × 0.12 × 0.10 mm^3; $C_{74.5}H_{85}AgBCl_5F_4N_4$, M = 1408.40 g mol^{-1}; monoclinic; space group $P2_1/c$; a = 20.886(3) Å; b = 15.096(4) Å; c = 25.225(6) Å; β = 101.8980(10)°; Z = 4; D_c = 1.202 g cm^{-3}; μ(Mo Kα) = 0.481 mm^{-1}; a total of 17 793 reflections; 1.58° < θ < 27.49°, 17 793 independent reflections with 9502 having $I > 2\sigma(I)$; 803 parameters; final results R1 = 0.0931 and wR2 = 0.2544; GOF = 1.248; maximum residual electronic density = 1.473 e Å^{-3}.

Results and Discussion

Synthesis and Characterization of Complexes. Monochelate complexes $[M(Ar\text{-}BIAN)(NCMe)_2]BF_4$ and bischelate complexes $[M(Ar\text{-}BIAN)_2]BF_4$, where M = Cu^I and Ag^I and Ar-BIAN = bis(aryl)acenaphthenequinonediimine ligands ($o,o'\text{-}i\text{Pr}_2C_6H_3$-BIAN and $o,o',p\text{-}Me_3C_6H_2$-BIAN), were synthesized by the direct reaction of $[M(NCMe)_4]BF_4$ with a 1:1 or 1:2 mole ratio of the corresponding Ar-BIAN ligand in dried CH_2Cl_2 at room temperature under an argon atmosphere, in 70−90% yield (Scheme 1).

In all cases, a rapid reaction occurred with an immediate color change. Silver complexes show colors changing from orange to bright red, while copper complexes show dark-brown colors. Silver(I) complexes are light-sensitive, while copper(I) complexes are air-sensitive. Exposure of solutions of the copper(I) complexes to air results in the broadening of ^{1}H NMR signals due to the formation of paramagnetic copper(II).

Ligand stereochemistry, as well as the size of the cationic metal, influences the formation of the bis- or monochelate complexes. For instance, when the less bulky ligand $o,o',p\text{-}Me_3C_6H_2$-BIAN was used, the bischelate complexes of copper(I) and silver(I), compounds **1** and **2**, were easily formed. Attempts to obtain the monochelate using a 1:1 stoichiometry gave instead mixtures of the starting material $[M(NCMe)_4]BF_4$, where M = Cu^I and Ag^I, and the mono- and bischelate complexes. Separation of the components of the mixture by recrystallization was not possible because of the similar solubility of the complexes, and no further efforts were made. The preferential formation of the bischelate complexes, even at a 1:1 stoichiometry, can be explained by the "chelate effect", which favors the substitution of two acetonitrile molecules by one $o,o',p\text{-}Me_3C_6H_2$-BIAN ligand. This is in agreement with theoretical calculations as discussed further in this paper. Reactions of $[Ag(NCMe)_4]BF_4$ with the bulkiest $o,o'\text{-}i\text{Pr}_2C_6H_3$-BIAN in a 1:1 stoichiometry gave the intermediate monochelate compound **4**. When a 1:2 stoichiometry was used, the bischelate compound **5** was formed. However, in the case of the smallest copper(I), the bischelate compound was not obtained even using a large excess of ligand; only the monochelate complex **3** was obtained, in a yield of about 80%. Conversion of $[M(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})(NCMe)_2]^+$ to $[M(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})_2]^+$ complexes is difficult, having higher energy values for copper than for silver (+15 and +5 kcal mol^{-1}, respectively), as discussed later in the theoretical calculations.

All synthesized compounds have been characterized by elemental analyses, MALDI-TOF-MS spectrometry, and IR, UV−vis, and ^{1}H NMR spectroscopy, and the results are shown in the Experimental Section.

The IR spectra of the complexes recorded as Nujol mulls display medium absorption bands in the region ν 1668−1611 cm^{-1}, which is the absorption region for ν(C=N). Bands assigned to C=N stretching vibrations of the free ligand were observed in the region ν 1674−1637 cm^{-1}. The bands in the complexes are shifted to lower wave numbers, which suggested coordination of both diimine nitrogen atoms of the Ar-BIAN ligands to the metal ion.

MALDI-TOF-MS spectra of all of the complexes show peaks assigned to the free ligands at m/z 416.2 for $o,o',p\text{-}Me_3C_6H_2$-BIAN and at m/z 500.0 for $o,o'\text{-}i\text{Pr}_2C_6H_3$-BIAN.

In the case of complexes bearing *o,o′*-*i*$Pr_2C_6H_3$-BIAN, a peak due to fragmentation of the ligand at *m*/*z* 457.2 is also observed, which can be explained by the loss of one $CH(Me)_2$ group. The spectrum of complex **1** shows the most intense peak at *m*/*z* 895.4 assigned to $[Cu(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})_2]^+$, and the peak at *m*/*z* 479.2 is due to the loss of one ligand, corresponding to $[Cu(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})]^+$. At a high mass region, a peak at *m*/*z* 983.2, corresponding to the bischelate complex and the counterion $[Cu(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})_2(BF_4)]^+$, was found. Similar peaks and fragmentations were observed for complex **3**.

In the case of complexes **2** and **5**, the peaks at *m*/*z* 941.3 and 1235.3 were assigned to the bischelate species $[Ag(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})_2]^+$ and $[Ag(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})_2(NCMe)(BF_4)]^+$, respectively. A similar fragmentation was observed for complex **4**.

Spectrophotometric Studies. All of the reported compounds and the free ligands *o,o′,p*-$Me_3C_6H_2$-BIAN and *o,o′*-*i*$Pr_2C_6H_3$-BIAN were spectroscopically characterized in a CH_2Cl_2 solution at 298 K at concentrations between 10^{-6} and 10^{-4} M. Optical data are summarized in Table S1 (Supporting Information).

As was previously reported for a diiminenaphthalene derivative,[24] the absence of bands in the IR region of the absorption spectra observed for the ligands *o,o′,p*-$Me_3C_6H_2$-BIAN and *o,o′*-*i*$Pr_2C_6H_3$-BIAN confirms that no anionic states, due to reduction of the bonds, are present.[25]

Figure S1 (Supporting Information) shows the UV−vis spectra of complex **2** at different concentrations, in a freshly prepared dichloromethane solution. Bands at 260, 311, 327, 375, and 495 nm are observed. The band observed at 495 nm could be assigned to the metal-to-ligand charge-transfer (MLCT) transitions from the metal center to the π^* orbital of *o,o′,p*-$Me_3C_6H_2$-BIAN. In general, all bands are red-shifted compared with the free ligand; the bands in the UV region at 260, 311, and 327 nm could be assigned to the $\pi-\pi^*$ transitions in the acenaphthylene and aryl moieties (intraligand transitions), which were also observed in the free diimine compound and in the previously published palladium(II) complexes with a naphthalene derivative.[24]

The stoichiometry of complex **3** in solution was studied by a titration experiment consisting of the addition of a dichloromethane solution of copper(I) to a freshly prepared dichloromethane solution of the free ligand *o,o′*-*i*$Pr_2C_6H_3$-BIAN. The results are shown in Figure 1. The band centered at 335 nm is red-shifted after metal complexation, confirming that metal complexation takes place. A detailed inspection of the inset in Figure 1 shows a plateau reached after the addition of 1 equiv of copper(I), which confirms that one *o,o′*-*i*$Pr_2C_6H_3$-BIAN coordinates to one Cu^I ion. This stoichiometry was further confirmed in the solid state using X-ray diffraction. For the rest of the metal titrations, the plateau suggests the formation of a 0.5:1 M/L complex in dichloromethane.

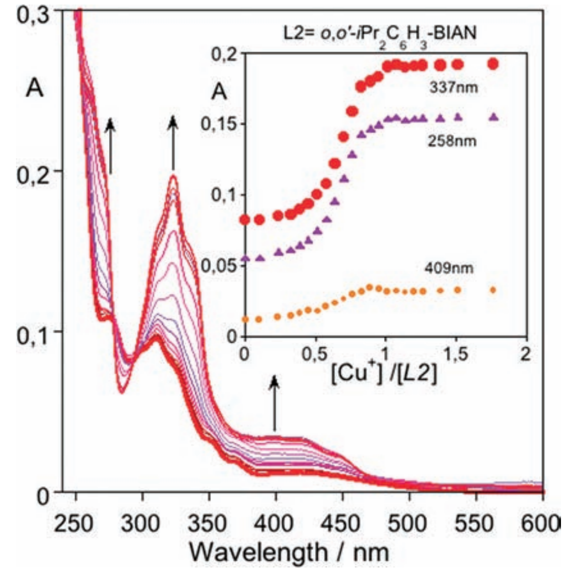


Figure 1. Spectrophotometric titration of ligand *o,o′*-*i*$Pr_2C_6H_3$-BIAN with an increasing amount of $[Cu(NCMe)_4]BF_4$ in a freshly dried dichloromethane solution at room temperature. [*o,o′*-*i*$Pr_2C_6H_3$-BIAN] = 1.0×10^{-5} M.

This stoichiometry was confirmed in the solid state by the X-ray structures of complexes **1**, **2**, and **5**.

In order to study the possible fluorescence emission, each metal complex was excited in the MLCT bands (440−470 nm) or in the $\pi-\pi^*$ bands (325−335 nm), but no emission was observed. All complexes appear not to be luminescent in dichloromethane at room temperature and 77 K. The expected fluorescence emission for the full-shell transition-metal elements silver(I) and copper(I) is totally quenched.[26] This quenching is probably due to the absence of a spacer between the emissive unit and the chelating unit (imine nitrogen) that permits a fast electron transfer from the lone pair of electrons present in the imine nitrogen atoms to the emissive chromophores.[27] Similar results were previously reported for zinc(II) and palladium(II) complexes bearing Schiff-base naphthalene ligands.[24]

Crystal Structure Descriptions. Complexes **1**−**3** and **5** formed single crystals by the slow diffusion of pentane or petroleum ether in CH_2Cl_2 solutions.

Complexes **1** and **2** crystallize in the orthorhombic space group *Ccca* (No. 68). The ORTEP views and selected distances and angles of both complexes are shown in Figure 2. The angle between planes containing MN_2C_2 units around metal centers (ω) is drawn in the insets. Both crystal structures are isotopic and show unambiguously that the metal center has a distorted tetrahedral geometry, with classical distances and angles. Moreover, the sp^2 nature of the C1−N1 (and equivalent) bonds is confirmed by the average N−C distance of 1.28(1) Å. In both

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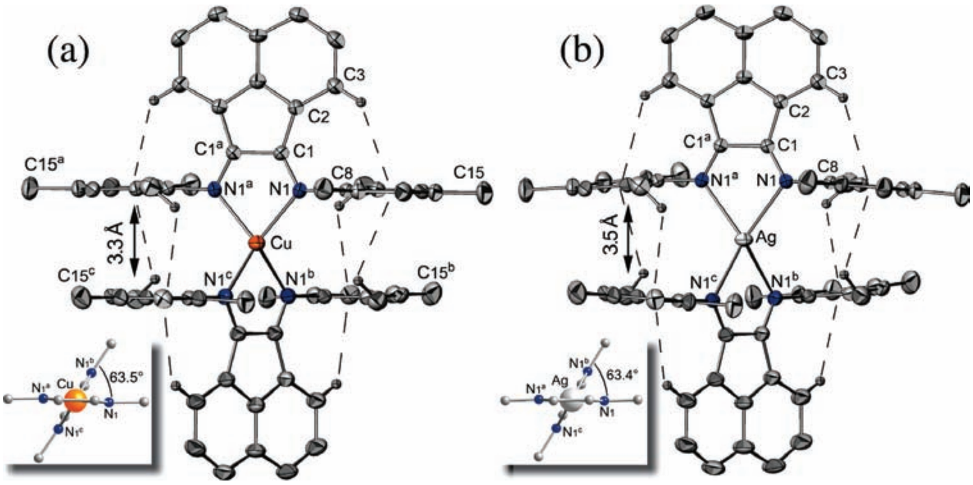

Figure 2. ORTEP views of complexes **1** and **2** with partial labeling schemes. Counteranions and the main hydrogen atoms have been omitted for clarity. Dashed lines represent CH−π interactions. The ellipsoids enclose 50% of the electronic density. Symmetry codes for equivalent positions: a = $-x + 1, y, -z + {}^1/_2$, b = $x, -y + {}^1/_2, -z + {}^1/_2$, c = $-x + 1, -y + {}^1/_2, z$. Selected distances (Å) and angles (deg): (a) Cu−N1 2.098(2), N1−C1 1.283(3), C1−C1^a 1.494(5); N1^a−Cu−N1 80.2(1), N1^a−Cu−N1^c 113.6(1), N1^a−Cu−N1^b 140.4(1), C1−N1−C8 116.8(2); (b) Ag−N1 2.329(2), N1−C1 1.274(3), C1−C1^a 1.526(4), N1^a−Ag−N1 73.28(8), N1^a−Ag−N1^c 118.74(9), N1^a−Ag−N1^b 143.79(9), C1−N1−C8 120.36(18). The insets show the angle ω between metal−N−C−C−N−metal planes.

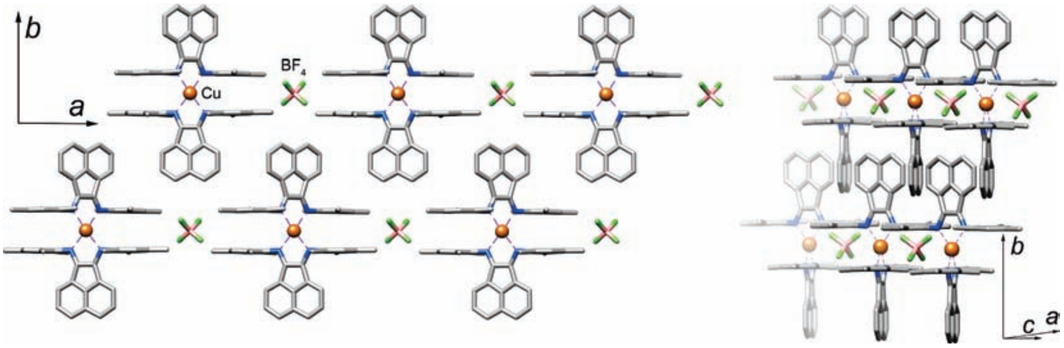

Figure 3. Selected view of the packing diagram of complex **1**. Hydrogen atoms have been omitted for clarity.

complexes, the naphthalene moieties are perpendicular to the mesityl groups. Numerous nonclassical hydrogen bonds (CH−π) have been detected in these crystal structures (see also Figure 2).

Although complexes **1** and **2** share the same ligand and geometry, a small difference (clearly shown in Figure 2) can be pointed out: the C1−N1−C8 angle is 116.8(2)° in the case of **1** and 120.36(18)° in **2**.

For complex **1**, the ORTEP view (Figure 2) clearly shows that the mesityl groups are practically parallel to each other, with an average angle of 2° and a distance of 3.3 Å, while in complex **2**, the mesityl groups are slightly incurved with an average angle of 11° and a distance between planes of 3.5 Å. This relative position of the mesityl groups seems to be correlated to the M−N distance [Cu−N = 2.098(2) Å and Ag−N = 2.329(2) Å]. This can be explained by the fact that, to minimize the energy, the angle will be closed to the free ligand angle, with a C1−N1−C8 angle of 123.3(4)°.[28] Because the silver atom is bigger than the copper one, the complex gains more "elasticity". A packing diagram of complex **1** is presented in Figure 3.

Complexes $3 \cdot 2CH_2Cl_2$ and $5 \cdot {}^5/_2CH_2Cl_2$ crystallize in the monoclinic space group $P2_1/c$ (No. 14). The ORTEP views and selected distances and angles of both complexes are shown in Figures 4 and 5. The sp^2 nature of the C1−N1 (and equivalent) bonds is also confirmed in these two complexes by the average N−C distance of 1.28(1) Å. Complexes **3** and **5** exhibit a distorted tetrahedral geometry around the metal center. In the case of complex **5**, numerous nonclassical hydrogen bonds (CH−π) have been detected.

Crystal data and refinement details for **1**, **2**, $3 \cdot 2CH_2Cl_2$, and $5 \cdot {}^5/_2CH_2Cl_2$ (T = 173 K; λ(Mo Kα) = 0.710 73 Å) are shown in Table S2 (Supporting Information).

Computational Discussion. We have performed theoretical calculations in order to evaluate the thermodynamic feasibility of the synthesis of BIAN complexes in solution. Complexes containing an Ar-BIAN ligand in which aryl groups are o,o',p-$Me_3C_6H_2$ or o,o'-$i$$Pr_2C_6H_3$ have been computed. A C_6H_5 group was also included to estimate the contribution of the unsubstituted aryl rings. We focus not only on the energetic features but also on the structural parameters for optimized structures to determine the experimental behavior.

Molecular Geometry. We have optimized the molecular geometry for complexes [M(Ar-BIAN)(NCMe)]$^+$,

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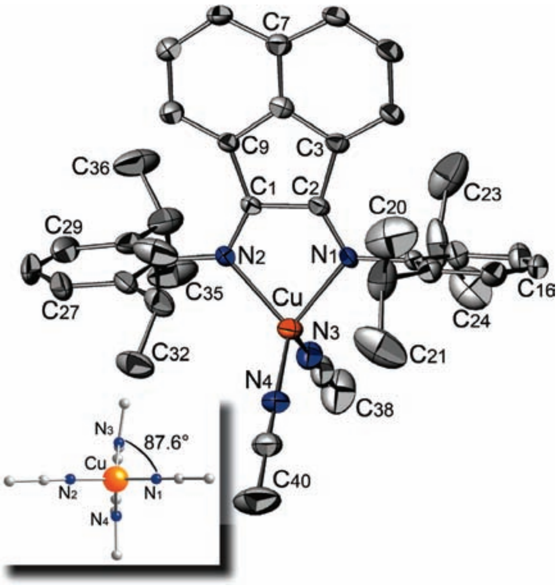

Figure 4. ORTEP view of complex **3** with a partial labeling scheme. The counteranion and main hydrogen atoms have been omitted for clarity. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles (deg): Cu−N1 2.108(4), Cu−N2 2.095(5), Cu−N3 1.949(6), Cu−N4 1.948(6), N1−C2 1.277(7), N2−C1 1.280(7), C1−C2 1.492(8); N1−Cu−N2 80.39(17), N2−Cu−N3 116.2(2), N3−Cu−N4 109.4(3), N1−Cu−N4 118.9(2). The inset shows the angle ω between the Cu−N−C−C−N−Cu and CH_3CN−Cu−$NCCH_3$ planes.

$[M(Ar\text{-}BIAN)(NCMe)_2]^+$, and $[M(Ar\text{-}BIAN)_2]^+$ in which M = Cu or Ag and Ar = C_6H_5, *o,o′,p*-$Me_3C_6H_2$, or *o,o′*-*i*$Pr_2C_6H_3$. Atomic coordinates of optimized complexes and ligands are available in Tables S3−S5 (Supporting Information). Their main geometrical parameters are shown in Table 1, together with $[M(NCMe)_n]^+$ (M = Cu, Ag; n = 2, 3, or 4) and uncoordinated Ar-BIAN ligands. In general, theoretical and experimental geometries are in agreement, with only a slight lengthening of the metal−ligand bond distances.

The molecular geometry around the transition metal in the $[M(NCMe)_n]^+$ species can be perfectly described as linear (n = 2), trigonal (n = 3), and tetrahedral (n = 4).[29] In general, M−N_a distances increase with the coordination number in the series $[M(NCMe)_n]^+$ and also in $[M(Ar\text{-}BIAN)(NCMe)_n]^+$, and similar results are obtained for M−N_b in later complexes. This trend can be confirmed by a search of $[M(NCMe)_n]^+$ (M = Cu, Ag) complexes in the Cambridge Structural Database (Table S6 in the Supporting Information). However, it can be seen that M−N_a decreases when two acetonitriles are replaced by one BIAN ligand, keeping the coordination number of the transition metal, probably by a rehybridation of valence orbitals in the metal.

In all complexes with Ar-BIAN, the ligand behaves as bidentate, having a five-membered MN_2C_2 chelate ring. Mixed compounds with an acetonitrile ligand such as $[M(Ar\text{-}BIAN)(NCMe)_n]^+$ (n = 1 or 2) present minimal geometric variations with a change of the coordination number of the metal. Complexes of the type $[M(Ar\text{-}BIAN)(NCMe)]^+$ are practically planar, having less than 1° deviation in the MN_3 unit, and similar distances and bond angles for both metals are found. Analogously, in $[M(Ar\text{-}BIAN)(NCMe)_2]^+$ complexes, the metal exhibits a pseudotetrahedral environment in which N_a−M−N_a decreases by about 4° when the aryl groups of the BIAN ligands are changed (C_6H_5 > *o,o′,p*-$Me_3C_6H_2$ > *o,o′*-*i*Pr_2-C_6H_3). The influence of the bulk of the aryl group substituents has also been obtained for $[M(Ar\text{-}BIAN)_2]^+$ systems, in which an increase of the M−N_b distances is found because of the steric requirements of the BIAN ligands.

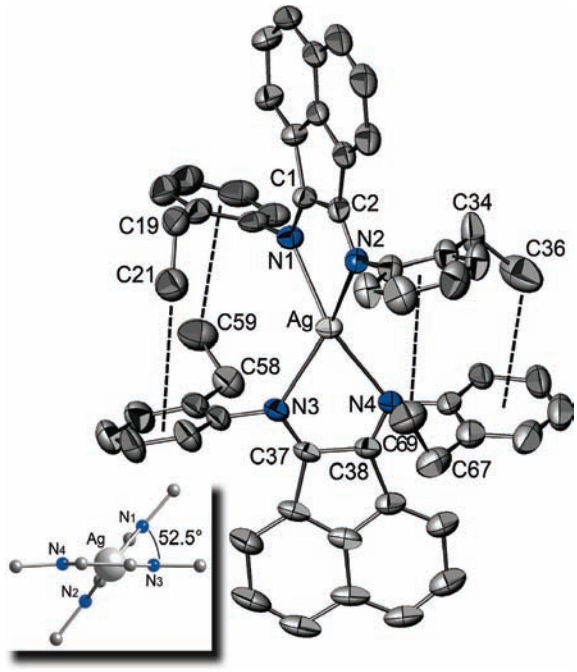

Figure 5. ORTEP view of complex **5** with a partial labeling scheme. The counteranion and main hydrogen atoms have been omitted for clarity. Dashed lines represent CH−π interactions. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles (deg): Ag−N1 2.356(5), Ag−N2 2.465(5), Ag−N3 2.440(5), Ag−N4 2.374(5), N1−C1 1.268(7), N2−C2 1.286(7), C1−C2 1.526(8); N1−Ag−N2 71.66(16), N3−Ag−N4 71.47(18), N1−Ag−N3 115.03(17), N1−Ag−N4 118.15(18), N1−Ag−N4 149.55(19). The inset shows the angle ω between the Ag−N−C−C−N−Ag planes.

The four M−N_b distances in $[M(Ar\text{-}BIAN)_2]^+$ are not strictly equal, and a small difference is always observed between both donor atoms of the same chelating ligand (less than 0.09 Å). An exception was found in the case of $[Cu(o,o'\text{-}iPr_2C_6H_3\text{-}BIAN)_2]^+$, which presents an asymmetric coordination with Cu−N_b distances of 2.10 and 2.51 Å. The last value is too large compared with the sum of the radii (2.16 Å)[30] but too short to ignore this interaction.

The analysis of the conformation for BIAN ligands shows an important variation in the relative orientation between aryl and acenaphthylene groups, defined by the τ angle in Chart 1.[24] In general, complexes having substituted aryl groups (Ar = *o,o′,p*-$Me_3C_6H_2$, *o,o′*-*i*$Pr_2C_6H_3$) show a high perpendicularity between both groups having values of τ of less than 98°. However, unsubstituted aryls such as phenyl complexes have the largest values of τ (>114°). This trend has also been found in free ligands, with τ values of 94 and 109° for substituted and unsubstituted aryl rings, respectively.

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(29) Carvajal, M. A.; Novoa, J. J.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1465–1477.

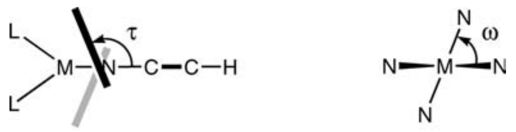
(30) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

Table 1. Structural Parameters for Optimized Complexes of the Type $[M(Ar\text{-}BIAN)_m(NCMe)_n]^+$ (M = Cu, Ag; Ar = C_6H_5, *o*,*o*′,*p*-$Me_3C_6H_2$, *o*,*o*′-*i*$Pr_2C_6H_3$)[a]

	Cu						Ag					
complex	$M-N_b$	$M-N_a$	N_b-M-N_b	τ^b	N_a-M-N_a	ω^c	$M-N_b$	$M-N_a$	N_b-M-N_b	τ^b	N_a-M-N_a	ω^c
$[M(Ph\text{-}BIAN)_2]^+$	2.109		80.4	124.9		77.4	2.401		71.4	114.4		82.4
$[M(Me_3C_6H_2\text{-}BIAN)_2]^+$	2.183		78.6	98.3		63.2	2.420		71.3	92.4		87.2
1 for M = Cu, **2** for M = Ag	*2.098*		*82.0*	*95.3*		*63.5*	*2.342*		*73.1*	*93.6*		*63.4*
$[M(iPr_2C_6H_3\text{-}BIAN)_2]^+$	2.303		75.6	97.0		50.0	2.516		69.4	95.7		47.9
3 for M = Ag							*2.409*		*71.9*	*100.8*		*52.5*
$[M(Ph\text{-}BIAN)(NCMe)_2]^+$	2.143	2.039	79.3	126.4	109.1	84.6	2.414	2.363	71.2	118.4	102.4	84.5
$[M(Me_3C_6H_2\text{-}BIAN)(NCMe)_2]^+$	2.150	2.049	79.9	91.4	104.9	89.3	2.413	2.370	71.9	92.8	101.3	89.4
$[M(iPr_2C_6H_3\text{-}BIAN)(NCMe)_2]^+$	2.153	2.042	79.7	92.2	105.8	89.8	2.417	2.373	71.6	92.4	97.4	90.0
5 for M = Cu	*2.097*	*1.943*	*83.4*	*96.2*	*109.4*	*87.6*						
$[M(Ph\text{-}BIAN)(NCMe)]^+$	2.089	1.914	81.5	126.5			2.354	2.193	72.9	119.0		
$[M(Me_3C_6H_2\text{-}BIAN)(NCMe)]^+$	2.094	1.916	82.0	94.2			2.356	2.197	73.6	93.8		
$[M(iPr_2C_6H_3\text{-}BIAN)(NCMe)]^+$	2.095	1.915	81.8	93.7			2.358	2.196	73.3	93.2		
$[M(NCMe)_2]^+$		1.873			180.0			2.124			180.0	
$[M(NCMe)_3]^+$		1.991			120.0			2.284			120.0	
$[M(NCMe)_4]^+$		2.071			109.5	90.0		2.377			109.5	90.0
Ph-BIAN				108.9						108.9		
$Me_3C_6H_2$-BIAN				94.3						94.3		
i$Pr_2C_6H_3$-BIAN				94.3						94.3		

[a] Distances are in angstroms and angles in degrees. N_b and N_a denote the nitrogen atom of BIAN and acetonitrile ligands, respectively. [b] Angle τ is defined between the chelate and aryl group planes. [c] Angle ω is defined between both ML_2 planes.

Chart 1. Definition of Parameter τ To Describe the Relative Orientation between Acenaphthylene and Aryl Groups and Angle ω



1 **2**

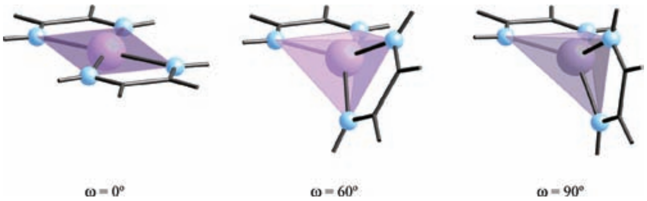


Figure 6. Rotation of the ω angle in the $[M(HN{=}CH{-}CH{=}NH)_2]^+$ complex to transform it between square-planar and tetrahedral coordination.

Another important difference in the optimized complexes are the rotation angle ω, defined in Chart 1, for tetracoordinated species such as $[M(Ar\text{-}BIAN)(NCMe)_2]^+$ and $[M(Ar\text{-}BIAN)_2]^+$. For a perfectly tetrahedral environment, $\omega = 90°$ is expected, whereas square-planar complexes should have $\omega = 0°$ (see Figure 6). Because $[M(Ar\text{-}BIAN)(NCMe)_2]^+$ complexes have values $\omega > 89°$, the coordination sphere for the transition metal is considered tetrahedral, and only for Ar = C_6H_5 is a slight distortion from an ideal geometry found when $\omega \approx 85°$. In agreement, the experimental structure of $[Cu(o,o'\text{-}iPr_2C_6H_3\text{-}BIAN)(NCMe)_2]^+$ has $\omega = 88°$. However, bischelate complexes have an important deviation from a perfect tetrahedral environment, in which ω depends on the metal and aryl groups. Calculated ω values for copper complexes (ω = 50−77°) show a higher degree of distortion from tetrahedral than those for silver complexes (ω = 48−87°), and in both cases, theoretical results would indicate that bulky aryl groups favor low values of ω. Nevertheless, the structures determined for complexes $[Cu(o,o',p\text{-}Me_3C_6H_2\text{-}BIAN)_2]^+$ and $[Ag(o,o',p\text{-}Me_3C_6H_2\text{-}BIAN)_2]^+$ show similar ω values ($\omega \approx 63°$), although for $[Ag(o,o'\text{-}iPr_2C_6H_3\text{-}BIAN)_2]^+$, a much smaller value is found ($\omega \approx 52°$).

To study the influence of the ω angle on the molecular geometry, we have analyzed the variation of this angle in simple diimine complexes $[M(RN{=}CH{-}CH{=}NR)_2]^+$ (M = Cu, Ag; R = H, Me). The full optimization of these complexes shows in all cases a clear preference for a tetrahedral environment at the transition metal (i.e., $\omega = 90°$). Figure 7 shows the relative energy of these complexes as a function of the ω angle $[M(HN{=}CH{-}CH{=}NH)_2]^+$ (M = Cu, Ag). When the ω angle is fixed at 0°, copper and silver square-planar complexes show instabilities of +11.9 and +3.9 kcal mol^{-1}, respectively. These values do not change appreciably in $[M(MeN{=}CH{-}CH{=}NMe)_2]^+$ (+12.1 and +4.3 kcal mol^{-1} for copper and silver, respectively), indicating that both methyl groups have no influence in our model complexes; see Figure S2 (Supporting Information). A comparison of tetrahedral and square-planar geometries for these model compounds shows an increase of the Cu−N (>0.11 Å) and Ag−N (0.06 Å) distances for square-planar coordination. Higher variation of the short M−N bond distances in the case of copper complexes can account for the bigger sensitivity of the relative energy as a function of ω angle, as shown in Figure 7.

Formation of Complexes. To understand the synthetic pathways of the complexes, we have planned the following sequence of balanced chemical reactions, shown in Figure 8. Because the solvent can play an important role in these reactions, we report here the obtained values in a dichloromethane solvent (Table 2), and in Table S7 (Supporting Information), we report data for the more polar acetonitrile solvent. In general, our theoretical results show small differences between the two solvents.

The first information in Table 2 is that formation of tetracoordinated species is favored for both transition metals. In general, calculated values for the incorporation of an acetonitrile molecule into copper complexes are always larger than those for silver ones (∼−9 and ∼−4 kcal mol^{-1}, respectively). A recent statistical study of the distribution for coordination numbers in d^{10} ions using the Cambridge

Structural Database,[29] has shown the higher distribution for tetrahedral compounds in copper(I) than in silver(I), which agrees with our results. The compounds isolated and obtained by us, in crystalline form, always present tetrahedral coordination. A search of the Cambridge Structural Database for copper(I) and silver(I) complexes containing acetonitrile ligands shows a marked preference for a tetracoordinated environment (Table S8 in the Supporting Information).

To evaluate the coordination competition between acetonitrile and BIAN ligands, we have studied the substitution reaction of two acetonitrile molecules by one BIAN ligand, without changing the coordination number. First, we analyze the results obtained for Ph-BIAN, and after, we compare the changes introduced by substituted aryl groups. For an unsubstituted C_6H_5-BIAN ligand, silver shows a higher tendency than copper for coordination of a chelate ligand (~ -3 and ~ -5 kcal mol^{-1} for copper and silver, respectively). However, when a Ph-BIAN ligand replaces only one acetonitrile molecule, the increase of the coordination number has a bigger effect on the energy, which is more significant for copper than for silver (~ -11 and ~ -9 kcal mol^{-1}, respectively) because of the higher preference of copper for the tetracoordination environment. Moreover, these tendencies are maintained for a second substitution.

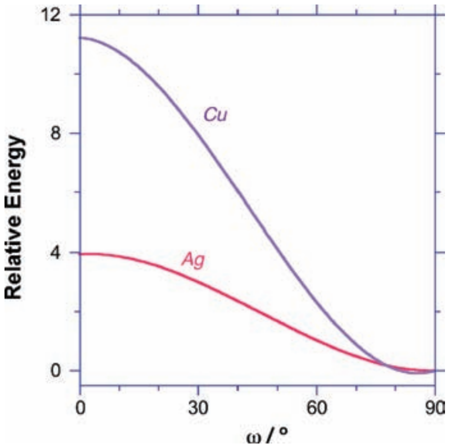


Figure 7. Relative energy (kcal mol^{-1}) as a function of the ω angle in compound $[M(HN{=}CH{-}CH{=}NH)_2]^+$ (M = Cu, Ag). Zero values for each complex are taken at the minimum ($\omega = 90°$).

We studied the changes when a substituent is introduced on the phenyl group, i.e., for o,o',p-$Me_3C_6H_2$-BIAN and o,o'-$i Pr_2C_6H_3$-BIAN. Only a slight destabilization for $[Ag(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})(NCMe)]^+$ and $[Ag(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})(NCMe)]^+$ is found compared with $[Ag(C_6H_5\text{-BIAN})(NCMe)]^+$ (on the contrary, analogous copper complexes would be stabilized by substituted aryl rings). More important changes are found in the formation of $[M(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})_2]^+$, clearly not favored for the two metals, which can be explained by the steric requirements of *i*Pr groups (values for copper complexes of about 6 and 16 kcal mol^{-1} upon going from C_6H_5-BIAN to $Me_3C_6H_2$-BIAN and from $Me_3C_6H_2$-BIAN to o,o'-$iPr_2C_6H_3$-BIAN, respectively, are roughly estimated). Finally, the conversion of $[M(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})(NCMe)_2]^+$ complexes into $[M(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})_2]^+$ species is difficult, with higher energy values for copper than for silver (+15 and +5 kcal mol^{-1}, respectively), probably because of the shorter Cu−N distance. Accordingly, the silver complexes $[Ag(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})(NCMe)_2]^+$ and $[Ag(o,o'\text{-}iPr_2C_6H_3\text{-BIAN})_2]^+$ are experimentally obtained, but in the case of copper, we could only obtain

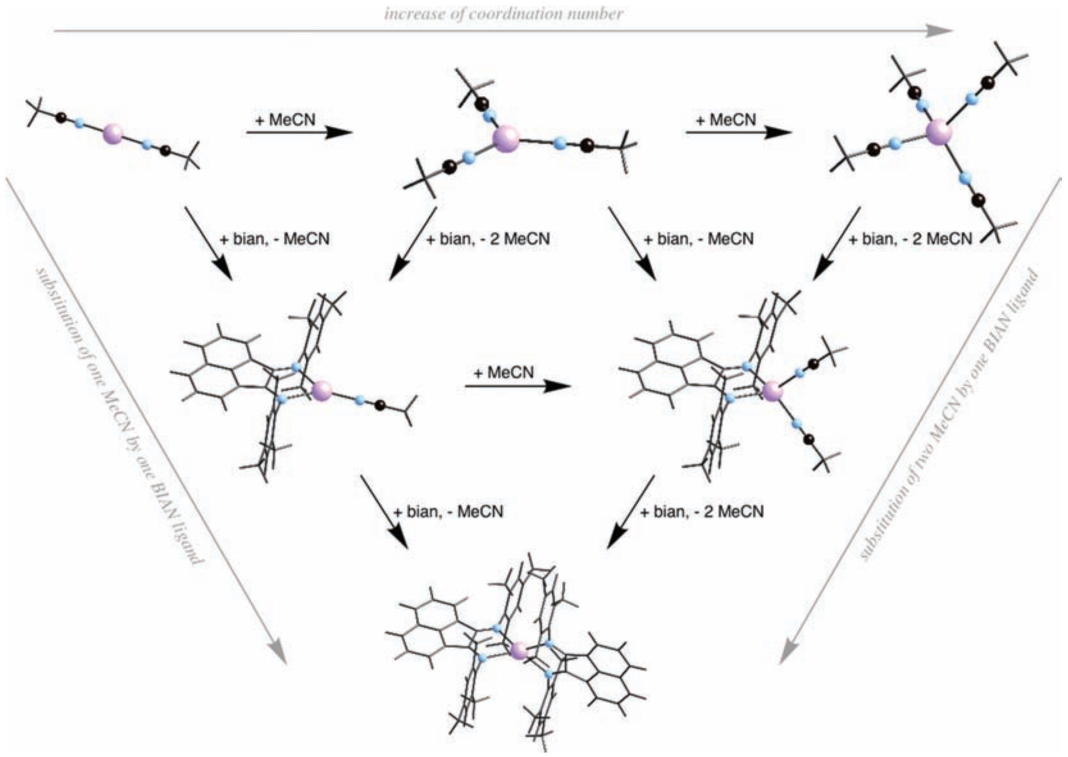


Figure 8. Schematic representation of substitution and addition reactions of ligands in $[M(Ar\text{-BIAN})_m(NCMe)_n]^+$ complexes. Molecular structures correspond to M = Ag and Ar = o,o',p-$Me_3C_6H_2$.

Table 2. Theoretical Evaluation of Energetic Changes (ΔE) for Formation Reactions in a CH_2Cl_2 Solution, Shown in Figure 8[a]

	Cu			Ag		
reaction	Ph	$Me_3C_6H_2$	$i Pr_2C_6H_3$	Ph	$Me_3C_6H_2$	$i Pr_2C_6H_3$
$[M(NCMe)_2]^+ + MeCN \Rightarrow [M(NCMe)_3]^+$	−8.78	−8.78	−8.78	−3.58	−3.58	−3.58
$[M(NCMe)_2]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)]^+ + MeCN$	−11.59	−13.28	−12.75	−8.67	−5.96	−5.32
$[M(NCMe)_2]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)_2]^+$	−19.92	−21.73	−20.16	−12.48	−12.56	−11.97
$[M(NCMe)_3]^+ + MeCN \Rightarrow [M(NCMe)_4]^+$	−8.62	−8.62	−8.62	−4.40	−4.40	−4.40
$[M(NCMe)_3]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)]^+ + 2\ MeCN$	−2.81	−4.49	−3.97	−5.09	−2.38	−1.75
$[M(NCMe)_3]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)_2]^+ + MeCN$	−11.14	−12.94	−11.38	−8.90	−8.98	−8.40
$[M(NCMe)_4]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)]^+ + 3\ MeCN$	+5.81	+4.13	+4.66	−0.69	+2.02	+2.66
$[M(NCMe)_4]^+ + BIAN \Rightarrow [M(BIAN)(NCMe)_2]^+ + 2\ MeCN$	−2.52	−4.32	−2.76	−4.50	−4.58	−3.99
$[M(BIAN)(NCMe)]^+ + MeCN \Rightarrow [M(BIAN)(NCMe)_2]^+$	−8.33	−8.45	−7.41	−3.81	−6.59	−6.65
$[M(BIAN)(NCMe)]^+ + BIAN \Rightarrow [M(BIAN)_2]^+ + MeCN$	−14.96	−8.88	+7.86	−8.84	−12.40	−1.51
$[M(BIAN)(NCMe)_2]^+ + BIAN \Rightarrow [M(BIAN)_2]^+ + 2\ MeCN$	−6.63	−0.43	+15.27	−5.03	−5.80	+5.14

[a] Energies are in kcal mol^{-1}.

$[Cu(o,o'\text{-}i Pr_2C_6H_3\text{-BIAN})(NCMe)_2]^+$, even when a stoichiometric amount of $o,o'\text{-}i Pr_2C_6H_3$-BIAN with respect to copper (2:1) or an excess of ligand was used.

Conclusions

New α-diimine compounds of copper(I) and silver(I) of formulation $[M(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})_2]BF_4$ where M = Cu^I (**1**) and Ag^I (**2**), $[M(o,o'\text{-}i Pr_2C_6H_3\text{-BIAN})(NCMe)_2]BF_4$ where M = Cu^I (**3**) and Ag^I (**4**), and $[Ag(o,o'\text{-}i Pr_2C_6H_3\text{-BIAN})_2]BF_4$ (**5**) were synthesized. The crystal structures of compounds **1**−**3** and **5** were solved by single-crystal X-ray diffraction. In all cases, copper(I) or silver(I) is in a distorted tetrahedron that consists of the four nitrogen atoms of the two α-diimine ligand or, in **3**, of one α-diimine ligand and two acetonitrile molecules. All compounds were characterized by elemental analyses, MALDI-TOF-MS spectrometry, and IR, UV−vis, and ^1H NMR spectroscopy.

Theoretical calculations of the molecular geometries show a lengthening of the metal−ligand distances with an increase of the coordination number. In the $[M(Ar\text{-BIAN})_2]^+$ species, a major distortion of the tetrahedral geometry at the transition metal is found, depending on the steric requirements of the ligands and on the size of the metal.

The formation of tetrahedral complexes is always favored for copper(I) and silver(I), and only the formation of $[M(Ar\text{-BIAN})_2]^+$ is clearly dependent on the aryl group. In this case, a methyl derivative does not introduce an appreciable change in the synthesis of $[M(o,o',p\text{-}Me_3C_6H_2\text{-BIAN})_2]^+$ complexes, whereas bulkier isopropyl groups make the formation of bischelate complexes difficult and favor $[M(o,o'\text{-}i Pr_2C_6H_3\text{-BIAN})(NCMe)_2]^+$ species, especially for small copper systems.

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Supporting Information Available: X-ray crystallographic data for complexes **1**, **2**, **3**$\cdot 2CH_2Cl_2$, and **5**$\cdot 2.5CH_2Cl_2$ in CIF format, computational details, and crystallographic and UV−vis absorption data. This material is available free of charge via the Internet at http://pubs.acs.org.