

Facile Oxidation-Based Synthesis of Sterically Encumbered Four-Coordinate Bis(2,9-di-*tert*-butyl-1,10-phenanthroline)copper(I) and Related Three-Coordinate Copper(I) Complexes

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A new oxidation-based synthetic route was developed for synthesis of Cu(I) complexes with weakly coordinating ligands, leading to the synthesis of the elusive $[\text{Cu}(\text{dtbp})_2]^+$ (dtbp, 2,9-di-*tert*-butyl-1,10-phenanthroline) complex that may be useful as a sensor or as a dye for dye-sensitized solar cells. An acetone solution of either 1 or 2 equiv of dtbp was added to excess Cu(0) and 1 equiv of AgY (Y is O_3SCF_3^- , BF_4^- , SbF_6^- , or $\text{B}(\text{C}_6\text{F}_5)_4^-$) in a nitrogen-filled glove box. Following filtration and evaporation under vacuum, crystallization from CH_2Cl_2 and hexanes results in X-ray quality crystals of $\text{Cu}(\text{dtbp})(\text{O}_3\text{SCF}_3)$ (**1**), $\text{Cu}(\text{dtbp})(\text{BF}_4)$ (**2**), $[\text{Cu}(\text{dtbp})(\text{acetone})][\text{SbF}_6]$ (**3**), $[\text{Cu}(\text{dtbp})_2]\text{B}(\text{C}_6\text{F}_5)_4 \cdot \text{CH}_2\text{Cl}_2$ (**4**• CH_2Cl_2), $[\text{Cu}(\text{dtbp})_2][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$ (**5**• CH_2Cl_2), and $[\text{Cu}(\text{dtbp})_2][\text{SbF}_6] \cdot \text{CH}_2\text{Cl}_2$ (**6**• CH_2Cl_2). Complexes **1–6** were characterized by X-ray crystallography and NMR. The Cu atom in complexes **1–3** exhibited distorted trigonal coordination geometries, reflecting the steric effect of the bulky *tert*-butyl substituents. The structures of the pseudotetrahedral complexes **4**, **4**• CH_2Cl_2 , **5**• CH_2Cl_2 , and **6**• CH_2Cl_2 revealed the longest average Cu–N distances (2.11 Å, 2.11 Å, 2.10 Å, and 2.11 Å, respectively) in this class of compounds—longer by more than three standard deviations from the average.

Introduction

Copper(I) has been used extensively in the synthesis of molecular machines,^{1–3} bioinspired model complexes,^{4–7} and industrial catalysts.⁸ Cu(I) complexes are challenging to synthesize due to the intrinsic instability of the cuprous oxidation state; under many conditions disproportionation of Cu(I) to Cu(0) and Cu(II) is thermodynamically favored. Nevertheless, the ligand structure and solution conditions

may be tailored to favor the formation of Cu(I) complexes, forming the basis of most Cu(I) complex synthesis.

Copper(I) complexes of the formula $[\text{CuL}_2]^+$, where L is a 2,9-disubstituted-phenanthroline, display interesting photophysical properties that result from a metal-to-ligand charge-transfer (MLCT) transition.⁹ In the excited state, the Cu atom is formally in the +2 oxidation state, and relaxation occurs either through nonemissive geometric reorganization toward square planar geometry or through radiative emission. Maximum radiative emission is achieved by preventing the nonemissive geometric reorganization path, typically by increasing the steric bulk of the substituents at the 2 and 9 positions of the phenanthroline ligand. A synthetic goal has been to maximize the size of the substituents while retaining the two bidentate phenanthroline ligands on the metal center, which give rise to the MLCT.^{9–13}

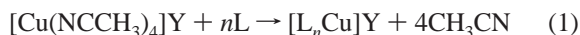
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- (1) Poleschak, I.; Kern, J.-M.; Sauvage, J.-P. *Chem. Commun.* **2004**, 4, 474–476.
- (2) Weber, N.; Hamann, C.; Kern, J.-M.; Sauvage, J.-P. *Inorg. Chem.* **2003**, 42, 21, 6780–6792.
- (3) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, 34, 6, 477–487.
- (4) Aboelella, N. W.; Kryatov, S. V.; Gherman, B. F.; Brennessel, W. W.; Young, V. G., Jr.; Sarangi, R.; Rybak-Akimova, E. V.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2004**, 126, 51, 16896–16911.
- (5) Aboelella, N. W.; Reynolds, A. M.; Tolman, W. B. *Science* **2004**, 304, 5672, 836–837.
- (6) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, 104, 2, 1047–1076.
- (7) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, 104, 2, 1013–1045.
- (8) Kim, Y. I.; Salim, S.; Huq, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1991**, 113, 25, 9561–9563.

- (9) Scaltrito, D. V.; Thompson, D. W.; O'Callaghan, J. A.; Meyer, G. J. *Coord. Chem. Rev.* **2000**, 208, 243–266.
- (10) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, 34, 11, 2833–2840.
- (11) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *J. Am. Chem. Soc.* **1999**, 121, 17, 4292–4293.
- (12) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *Angew. Chem., Int. Ed.* **1998**, 37, 11, 1556–1558.

These $[\text{CuL}_2]^+$ complexes have potential applications as inexpensive and environmentally benign solar energy conversion devices or sensors.^{14–16} In this class of compounds, the homoleptic complexes $[\text{Cu}(\text{dnpp})_2]^+$ and $[\text{Cu}(\text{dsbp})_2]^+$ and the heteroleptic complex $[\text{Cu}(\text{dtbp})(\text{dmp})]^+$ employ the sterically bulkiest substituents at the 2 and 9 positions of the phenanthroline ligand.¹⁷ These complexes demonstrate the most useful photophysical properties: long excited-state lifetimes and high quantum efficiencies.^{10,11} Two phenanthroline ligands are not necessary; Cu(I) complexes with one phenanthroline ligand and bulky auxiliary ligands such as triphenylphosphine and bis[2-(diphenylphosphino)phenyl] ether also exhibit excellent photophysical properties.^{18–21} To optimize excited-state lifetimes and quantum efficiencies, it is necessary to confront the considerable synthetic challenge of incorporating highly bulky ligands into Cu(I) complexes.

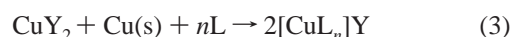
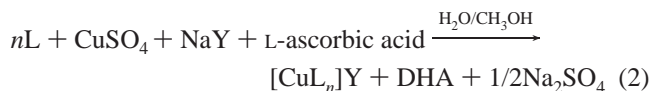
The most common method for the synthesis of Cu(I) complexes has been addition of the desired ligand to $[\text{Cu}(\text{NCCH}_3)_4]\text{Y}$ (where Y is PF_6^- , ClO_4^- , SbF_6^- , or SO_3CF_3^- , reaction 1). This synthetic method has been used successfully to prepare many sterically congested Cu(I) systems,^{22,23} including both homoleptic and heteroleptic bis(phenanthroline)-Cu(I) complexes.^{10,11,12,24–26} For example, this route was used to synthesize the homoleptic complexes $[\text{Cu}(\text{phen})_2]^+$, $[\text{Cu}(\text{dmp})_2]^+$, $[\text{Cu}(\text{dpp})_2]^+$,



$[\text{Cu}(\text{bcp})_2]^+$, and $[\text{Cu}(\text{bfp})_2]^+$.^{12,27} Larger substituents at the 2 and 9 positions of the phenanthroline, i.e., *tert*-butyl, impair the ability of a second **dtbp** ligand to compete effectively with acetonitrile for coordination to Cu(I), rendering $[\text{Cu}(\text{dtbp})_2]^+$ inaccessible.^{10,11} However, subsequent addition of

a less bulky phenanthroline ligand, i.e., **dmp**, to a solution containing **dtbp** and $[\text{Cu}(\text{NCCH}_3)_4]^+$ allows for the synthesis of the heteroleptic complex $[\text{Cu}(\text{dtbp})(\text{dmp})]^+$.¹¹ This approach, dubbed HETPHEN, has been used to great advantage in the preparation of supramolecular assemblies.^{28–30}

Other commonly used synthetic methods for the preparation of Cu(I) complexes include reduction of Cu(II), comproportionation, and metathesis. Often used in the syntheses of Cu(I) phenanthroline complexes is the reduction of Cu(II) starting materials by L-ascorbic acid in the presence of ligands (reaction 2).^{13,24,25} Since this reaction is carried out in alcohol and water mixtures, it is not suitable for preparing water sensitive compounds. Some Cu(I) complexes are



Y = SO_3CF_3^- , BF_4^- , SbF_6^- , $\text{B}(\text{C}_6\text{F}_5)_4^-$, DHA = dehydroascorbic acid, X = halide

prepared by the comproportionation of Cu(II) and Cu(0) in the presence of an appropriate ligand (reaction 3).^{25,26} Because the formation of Cu(I) from Cu(II) and Cu(0) is unfavorable,³¹ these methods rely heavily on the ability of the ligand to stabilize the Cu(I) ion. Finally, metathesis is broadly used to exchange anionic ligands: a halide ion is abstracted from the metal-halide precursor of the desired complex by a Ag(I) salt, producing a Cu(I) complex with a different coordinated anion (reaction 4). This method is less often employed in Cu(I) complex syntheses; Hamilton and co-workers provide the only successful implementation of metathesis reactions for the synthesis of Cu(I)-phenanthroline complexes.³²

In this paper we present an oxidation-based method for the synthesis of Cu(I) complexes. This new approach allows weakly binding ligands access to the metal center of Cu(I)-(**dtbp**) complexes to form three- and four-coordinate Cu(I) complexes. Our synthetic route has enabled us to generate a series of three-coordinate Cu(I)-phenanthroline complexes, a class of complexes which are challenging to prepare. Only 4.3% of structurally characterized Cu(I) complexes are three-coordinate.³³ The $[\text{Cu}(\text{dtbp})_2]^+$ complex, which was believed to be synthetically inaccessible, was also synthesized. This

- (13) McMillin, D. R.; Buckner, M. T.; Ahn, B. T. *Inorg. Chem.* **1977**, *16*, 943–945.
 (14) Rogers, C. W.; Wolf, M. O. *Coord. Chem. Rev.* **2002**, *233–234*, 341–350.
 (15) O'Regan, B.; Graetzel, M. *Nature* **1991**, *353*, 6346, 737–740.
 (16) Miller, M. T.; Karpishin, T. B. *Sens. Actuators, B* **1999**, *B61*, 1–3, 222–224.
 (17) phen, 1,10-phenanthroline; dnpp, 2,9-dineopentyl-1,10-phenanthroline; dsbp, 2,9-di-*sec*-butyl-1,10-phenanthroline; dtp, 2,9-di-*tert*-butyl-1,10-phenanthroline; dmp, 2,9-dimethyl-1,10-phenanthroline; dpp, 2,9-diphenyl-1,10-phenanthroline; bcp, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; bfp, 2,9-bis-trifluoromethyl-1,10-phenanthroline.
 (18) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 19, 5906–5912.
 (19) Palmer, C. E. A.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 23, 3837–3840.
 (20) Cuttall, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 1, 6–7.
 (21) Kuang, S.-M.; Cuttall, D. G.; McMillin, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2002**, *41*, 12, 3313–3322.
 (22) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 24, 6307–6321.
 (23) Spencer, D. J. E.; Aboeella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10, 2108–2109.
 (24) Kovalevsky, A. Y.; Gembicky, M.; Coppens, P. *Inorg. Chem.* **2004**, *43*, 26, 8282–8289.
 (25) Kovalevsky, A. Y.; Gembicky, M.; Novozhilova, I. V.; Coppens, P. *Inorg. Chem.* **2003**, *42*, 26, 8794–8802.
 (26) Hirsch, J.; George, S. D.; Solomon, E. I.; Hedman, B.; Hodgson, K. O.; Burstyn, J. N. *Inorg. Chem.* **2001**, *40*, 10, 2439–2441.
 (27) Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 22, 6406–6412.

- (28) Kalsani, V.; Schmittel, M.; Listorti, A.; Accorsi, G.; Armaroli, N. *Inorg. Chem.* **2006**, *45*, 5, 2061–2067.
 (29) Schmittel, M.; Ganz, A.; Fenske, D. *Org. Lett.* **2002**, *4*, 14, 2289–2292.
 (30) Schmittel, M.; Kalsani, V.; Fenske, D.; Wiegrefe, A. *Chem. Commun.* **2004**, *5*, 490–491.
 (31) Cotton, F. A.; Wilkinson, G.; Bochmann, M.; Murillo, C. *Advanced Inorganic Chemistry*, 6th ed.; 1998.
 (32) Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. *Chem. Commun.* **2004**, *14*, 1628–1629.
 (33) A Cambridge Structural Database (updated November 2004) search of three-coordinate Cu(I) complexes resulted in 195 complexes, and a search for all Cu(I) complexes resulted in 4530 complexes.

latter complex may have potential as a dyestuff for dye-sensitized solar cells and as a sensor for small molecules.

Experimental Section

General Methods and Materials. All chemicals were purchased from Aldrich and used without further purification unless otherwise stated. $K[B(C_6F_5)_4]$ was purchased from Boulder Scientific Co., copper powder from STREM, and MnO_2 from Fluka; all were used as received. Solvent grade acetone and hexanes were purchased from Columbus Chemical Industries, Inc., and spectrophotometric grade CH_2Cl_2 was from Burdick and Jackson. All syntheses and crystallizations were performed in a glove box under a nitrogen atmosphere. Acetone, distilled from Drierite, and CH_2Cl_2 and hexanes, distilled from calcium hydride, were degassed before use. The ligand, **dtbp**, was synthesized as described previously.¹⁰ $AgBF_4$ and $Ag[B(C_6F_5)_4]$ were synthesized from AgF and $(CH_3CH_2)_2O \cdot BF_3$ and $AgNO_3$ and $K[B(C_6F_5)_4]$, respectively.³⁴ 1H and ^{13}C NMR spectra were recorded at room temperature (22 °C) on a Varian Mercury-300 MHz spectrometer. Chemical shifts were referenced to the residual protons in the deuterated solvent or to the solvent carbons and are reported in parts per million versus Me_4Si . Infrared spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses were performed by Desert Analytics.

Synthesis of $Cu(dtbp)(CF_3SO_3)$ (1). An acetone solution (5 mL) of **dtbp** (100 mg, 0.342 mmol) was added to a vial charged with 87.9 mg (0.342 mmol) of $AgCF_3SO_3$ and an excess of Cu powder (approximately 1 g). The mixture was allowed to stir for 30 min. The brown slurry was filtered through Celite and glass wool to remove the black-brown solid. The resulting orange-yellow filtrate was evaporated to dryness under vacuum. The orange solid was dissolved in CH_2Cl_2 and filtered through Celite and glass wool to clarify. Slow evaporation of a CH_2Cl_2 /hexanes solution yielded 158 mg (92%) of large (4 mm × 4 mm × 1 mm) light-orange X-ray quality plates of **1**. 1H NMR (300 MHz, CD_2Cl_2): δ 1.756 (s, 18H, CH_3), δ 7.853 (s, 2H, CH), δ 8.024 (d, J = 8.4 Hz, 2H, CH), δ 8.410 (d, J = 8.7 Hz, 2H, CH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 30.70, 38.64, 122.36, 126.15, 127.55, 138.95, 143.72, 170.11 ppm. IR (cm^{-1}): $CF_3SO_3^-$, 1234, 1217, 1180, 1161, 1028, 630. Anal. Calcd for $C_{21}H_{24}N_2CuSO_3F_3$: C, 49.94; H, 4.79; N, 5.55. Found: C, 49.58; H, 4.91; N, 5.31.

Synthesis of $Cu(dtbp)(BF_4)$ (2). An acetone solution (5 mL) of **dtbp** (100 mg, 0.342 mmol) was added to a vial containing 66.3 mg (0.342 mmol) of $AgBF_4$ and an excess of Cu powder (approximately 1 g). The mixture was allowed to stir for 30 min. The brown slurry was filtered through Celite and glass wool to remove the black-brown solid. The resulting yellow filtrate was evaporated to dryness under vacuum. The orange solid was dissolved in CH_2Cl_2 and filtered again to remove any residual solid. This complex was challenging to purify. Precipitation from CH_2Cl_2 /hexanes yielded 143 mg (94.4%) of small thin yellow needles of impure **2**. A poor yield of X-ray quality plates was obtained upon slow evaporation of a CH_2Cl_2 /hexanes solution. 1H NMR (300 MHz, CD_2Cl_2): δ 1.731 (s, 18H, CH_3), δ 7.917 (s, 2H, CH), δ 8.064 (d, J = 8.7 Hz, 2H, CH), δ 8.479 (d, J = 8.4 Hz, 2H, CH) ppm. IR (cm^{-1}): BF_4^- , 1138, 1089, 1054, 1024, 1013. This compound could not be obtained in high analytical purity, and, thus, a satisfactory elemental analysis was not obtained.

Synthesis of $[Cu(dtbp)((CH_3)_2CO)][SbF_6]$ (3). An acetone solution (5 mL) of **dtbp** (100 mg, 0.342 mmol) was added to a vial containing 119.6 mg (0.349 mmol) of $AgSbF_6$ and an excess

of Cu powder (approximately 1 g). The mixture was stirred for 1 h and was then filtered through Celite and glass wool. The black-brown solid was removed, yielding a yellow solution that was evaporated to dryness under vacuum. The resulting yellow powder was dissolved in CH_2Cl_2 and filtered again to clarify, and the solvent was removed. The yellow solid was redissolved in acetone; recrystallization from acetone/hexanes yielded 196 mg (88%) of thin yellow needles of **3**. 1H NMR (300 MHz, CD_2Cl_2): δ 1.677 (s, 18H, CH_3), δ 2.460 (s, 6H, CH_3), δ 7.966 (s, 2H, CH), δ 8.091 (d, J = 8.7 Hz, 2H, CH), δ 8.537 (d, J = 8.4 Hz, 2H, CH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 30.64, 32.44, 38.27, 122.60, 126.56, 128.02, 139.91, 143.58, 169.41, 185.99 ppm. IR (cm^{-1}): SbF_6^- , 654. Anal. Calcd for $C_{22}H_{30}N_2CuOSbF_6$: C, 42.51; H, 4.65; N, 4.31. Found: C, 42.79; H, 4.44; N, 4.15.

New Method for Synthesis of $[Cu(dtbp)(dmp)][BF_4]$. An acetone solution (5 mL) of **dtbp** (50 mg, 0.171 mmol) was added to a vial containing 33.1 mg (0.171 mmol) of $AgBF_4$ and an excess of Cu powder (approximately 1 g). The mixture was allowed to stir for 1 h and was filtered through Celite and glass wool. A black-brown solid was removed, yielding a yellow solution of $[Cu(dtbp)-((CH_3)_2CO)][BF_4]$ (**3**). Upon addition of 2,9-dimethyl-1,10-phenanthroline (35.6 mg, 0.171 mmol), an intense orange-red color resulted. Crystallization from acetone/hexanes yielded 97.3 mg (87.4%) of orange blocks of $[Cu(dmp)(dtbp)][BF_4]$. The composition was confirmed by comparison with previously reported NMR spectra.¹¹

Synthesis of $[Cu(dtbp)_2][B(C_6F_5)_4] \cdot CH_2Cl_2$ ($4 \cdot CH_2Cl_2$). An acetone solution (5 mL) of **dtbp** (89.6 mg, 0.254 mmol) was added to a vial containing 100 mg (0.127 mmol) of $Ag[B(C_6F_5)_4]$ and an excess of Cu powder (approximately 1 g). The mixture was allowed to stir for 30 min and was filtered through Celite and glass wool. A black-brown solid was removed, yielding a yellow-orange solution that was evaporated to dryness under vacuum. The orange solid was dissolved in CH_2Cl_2 and filtered to clarify, producing a clear orange solution. Large bright orange X-ray quality blocks of $4 \cdot CH_2Cl_2$ (146.3 mg, 81.5%) were isolated by layering with hexanes or by addition of hexanes followed by slow evaporation. 1H NMR (300 MHz, CD_2Cl_2): δ 1.214 (s, 36H, CH_3), δ 7.996 (s, 4H, CH), δ 8.071 (d, J = 9.0 Hz, 4H, CH), δ 8.484 (d, J = 8.7 Hz, 4H, CH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 30.69, 39.17, 124.60, 127.55, 129.49, 138.76, 143.61, 169.01 ppm. IR (cm^{-1}): $[B(C_6F_5)_4]^-$, 1511, 1462, 1274, 1087, 979, 774, 768, 756, 683, 660. Anal. Calcd for $C_{64}H_{48}N_4CuBF_2O \cdot 1/3CH_2Cl_2$: C, 56.99; H, 3.62; N, 4.13. Found: C, 57.03; H, 3.83; N, 4.24.

Synthesis of $[Cu(dtbp)_2][BF_4] \cdot CH_2Cl_2$ ($5 \cdot CH_2Cl_2$). An acetone solution (5 mL) of **dtbp** (100 mg, 0.342 mmol) was added to a vial containing 33.2 mg (0.171 mmol) of $AgBF_4$ and an excess of Cu powder (approximately 1 g). The mixture was allowed to stir for 30 min and then filtered through Celite and glass wool. The resulting clear orange solution was evaporated to dryness under vacuum. The orange solid was dissolved in CH_2Cl_2 and filtered to clarify. Layering with hexanes yielded 130.6 mg (93.1%) of large bright orange needles of $5 \cdot CH_2Cl_2$. 1H NMR (300 MHz, CD_2Cl_2): δ 1.225 (s, 36H, CH_3), δ 8.043 (s, 4H, CH), δ 8.096 (d, J = 8.7 Hz, 4H, CH), δ 8.534 (d, J = 8.7 Hz, 4H, CH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 30.73, 39.13, 124.62, 127.63, 129.60, 138.85, 169.26 ppm. IR (cm^{-1}): BF_4^- , 1072.73, 1057.27, 1030.78, 633.99. Anal. Calcd for $C_{40}H_{48}N_4CuBF_4$: C, 60.04; H, 6.15; N, 6.83. Found: C, 60.29; H, 6.57; N, 6.70.

Synthesis of $[Cu(dtbp)_2][SbF_6] \cdot CH_2Cl_2$ ($6 \cdot CH_2Cl_2$). An acetone solution (5 mL) of **dtbp** (100 mg, 0.342 mmol) was added to a vial containing 59.8 mg (0.171 mmol) of $AgSbF_6$ and an excess of

(34) Green, O.; Santiago-Cintron, M.; Burstyn, J. N. Manuscript in preparation.

Table 1. X-ray Crystallographic Data for Cu(dtbp)(OTf) (1), Cu(dtbp)(BF₄) (2), [Cu(dtbp)((CH₃)₂CO)][SbF₆] (3), [Cu(dtbp)₂][B(C₆F₅)₄•CH₂Cl₂(4•CH₂Cl₂)], [Cu(dtbp)₂][BF₄•CH₂Cl₂(5•CH₂Cl₂)], and [Cu(dtbp)₂][SbF₆•CH₂Cl₂(6•CH₂Cl₂)]

	1	2	3	4•CH ₂ Cl ₂	5•CH ₂ Cl ₂	6•CH ₂ Cl ₂
formula	C ₂₁ H ₂₄ N ₂ CuSO ₃ F ₃	C ₂₀ H ₂₄ N ₂ CuBF ₄	C ₂₂ H ₃₀ N ₂ CuOSbF ₆	C ₆₅ H ₅₀ N ₄ CuBF ₂₀ Cl ₂	C ₄₁ H ₅₀ N ₄ CuBF ₄ Cl ₂	C ₄₁ H ₅₀ N ₄ CuSbF ₆ Cl ₂
formula weight	505.02	442.76	649.78	1412.34	820.10	884.11
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	11.1025(7)	6.800(1)	14.337(2)	14.704(2)	14.754(1)	12.200(1)
<i>b</i> (Å)	10.3858(7)	19.943(3)	6.8138(9)	25.882(3)	15.138(1)	13.628(1)
<i>c</i> (Å)	19.158(1)	14.035(2)	26.391(3)	16.704(2)	17.956(1)	14.403(1)
α (°)	90	90	90	90	90.459(1)	92.833(1)
β (°)	97.848(1)	92.709(2)	104.818(2)	108.057(2)	91.190(1)	109.737(1)
γ (°)	90	90	90	90	98.885(1)	107.814(1)
<i>V</i> (Å ³)	2188.4(2)	1901.1(4)	2492.4(6)	6043.8(10)	3961.3(4)	2114.3(2)
<i>Z</i>	4	4	4	4	4	2
<i>D</i> _{calc} (g/cm ³)	1.533	1.547	1.732	1.552	1.375	1.389
μ (mm ⁻¹)	1.144	1.194	2.000	0.558	0.740	1.199
<i>F</i> (000)	1040	912	1296	2864	1712	900
crystal size (mm ³)	0.34 × 0.22 × 0.14	0.32 × 0.12 × 0.11	0.40 × 0.17 × 0.08	0.25 × 0.20 × 0.10	0.45 × 0.45 × 0.09	0.18 × 0.15 × 0.11
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0309, 0.0787	0.0489, 0.1170	0.0389, 0.0913	0.0552, 0.1274	0.0539, 0.1425	0.0315, 0.0753
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0375, 0.0827	0.0683, 0.1278	0.0514, 0.0976	0.0882, 0.1447	0.0637, 0.1489	0.0398, 0.0785

Cu powder (approximately 1 g). The mixture was allowed to stir for 30 min and then filtered through Celite and glass wool. The resulting clear orange solution was evaporated to dryness under vacuum. The orange solid was dissolved in CH₂Cl₂ and filtered to clarify. Layering with hexanes yielded 132.4 mg (87.6%) of large bright orange crystals of **6•CH₂Cl₂**. ¹H NMR (300 MHz, CD₂Cl₂): δ 1.221 (s, 36H, CH₃), δ 8.028 (s, 4H, CH), δ 8.088 (d, *J* = 8.4 Hz, 2H, CH), δ 8.517 (d, *J* = 8.7 Hz, 2H, CH) ppm. ¹³C NMR (75 MHz, CD₂Cl₂): δ 29.74, 36.22, 123.67, 126.45, 128.52, 137.66 ppm. IR (cm⁻¹): SbF₆⁻, 656.32. Anal. Calcd for C₂₄H₄₈N₄CuSbF₆•1/2CH₂Cl₂: C, 52.50; H, 5.33; N, 6.05. Found: C, 52.04; H, 5.39; N, 5.76.

X-ray Structure Determination. Suitable crystals were selected under oil in air at room temperature. The crystals were mounted on the tip of a Nylon loop and immediately placed in a stream of nitrogen at 100(2) K. The data collection was performed on a Bruker CCD-1000 diffractometer with Mo K α (λ = 0.71073 Å) radiation. The detector was placed at a distance of 4.9 cm from the crystal. The data frames were integrated with the Bruker SAINT-Plus software package and corrected for absorption effects using SADABS.³⁵ Crystal structures for compounds **1–4** and **4•CH₂Cl₂** were solved by direct methods, and all non-hydrogen atoms were identified on the initial electron density map. The non-hydrogen atoms were subsequently refined by full-matrix least-squares methods with anisotropic displacement coefficients. All hydrogen atoms were calculated at idealized positions and were refined as riding atoms with individual isotropic coefficients. Further details of the data collection and refinement are listed in Table 1.

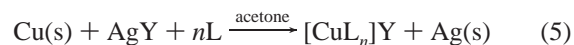
Under the microscope, several seemingly suitable single crystals of **5•CH₂Cl₂**, all of which showed strong reflections with no evidence of twinning, were selected under oil in air at room temperature. Bruker's SMART software was unable to determine a unit cell after matrix collections for any of the crystals. After a full data collection of one crystal, CellNow was executed, finding a two part twinned crystal.³⁶ The two domains of 52.6% and 47.4% proportions were related by 180° rotation. The data frames were integrated with the Bruker SAINT-Plus software package and the

unit cell parameters obtained from CellNow and corrected for absorption effects using TWINABS. The solution and refinement were carried out as described for **1–4•CH₂Cl₂** once the corrected reflection file was obtained.

There were two partially occupied solvate molecules of CH₂Cl₂ present in the asymmetric unit of **6•CH₂Cl₂**. A significant amount of time was invested in identifying and refining the disordered molecules. Bond-length restraints were applied to model the molecules, but the resulting unusually large isotropic displacement coefficients suggested the molecules were mobile. Option SQUEEZE of program PLATON was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecule.³⁷ PLATON calculated the upper limit of volume that can be occupied by the solvent to be 366.1 Å³ or 17.3% of the unit cell volume. The program calculated 90 electrons in the unit cell for the diffuse species. This approximately corresponds to two solvate CH₂Cl₂ molecules in the unit cell (84 electrons). It is very likely that this solvate molecule is disordered over several positions. All derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

Results

Facile Synthesis of Cu(I) Complexes with Hindered Phenanthroline Ligands. Controlled oxidation of metallic copper by stoichiometric amounts of silver salt in the presence of ligand results in the facile synthesis of Cu(I) complexes of hindered phenanthrolines. When excess copper metal is stirred with 1 equiv of a Ag(I) salt and 1 or 2 equiv of 2,9-di-*tert*-butyl-1,10-phenanthroline (dtbp), Cu(I) complexes bearing either one or two bulky phenanthroline ligands may be isolated in high yield (reaction 5). Reaction progress may be easily monitored by eye; reduction of the Ag(I) is observable via formation of a black Ag(0) precipitate, while oxidation of the Cu(0) results in formation of the yellow or orange Cu(I)L_{*n*}Y (*n* = 1 or 2) species.



This method provides a facile route to Cu(I)(dtbp)Y complexes, where Y⁻ is one of a variety of weakly

(35) Bruker-AXS. *SADABS V.2.05*, *T.*, *SAINT V.6.22*, *SHELXTL V.6.10*, & *SMART V.5.622 Software Reference Manuals*; Bruker-AXS: Madison, WI, U.S.A., 2000–2004.

(36) Sheldrick, G. M. *CellNow*; University of Göttingen: Göttingen, Germany, 2005.

(37) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *A46*, 3, 194–201.

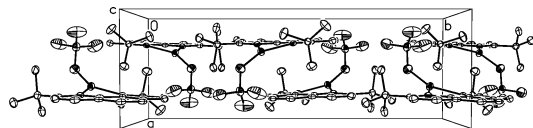


Figure 1. Packing diagram of the unit cell of three-coordinate $\text{Cu}(\text{dtbp})\text{-(BF}_4\text{)}$ (**2**) shown along the c -axis with 50% probability thermal ellipsoids. Note the occurrence of π -stacking between the phenanthroline planes of two inverted cations. H atoms have been omitted for clarity.

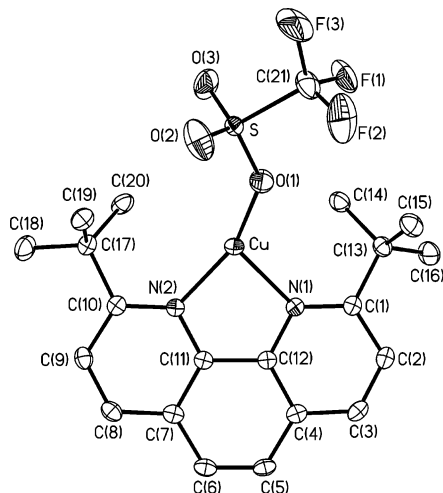


Figure 2. Face-on molecular drawing of three-coordinate $\text{Cu}(\text{dtbp})(\text{SO}_3\text{-CF}_3)$ (**1**) shown with 50% probability thermal ellipsoids. H atoms have been omitted for clarity.

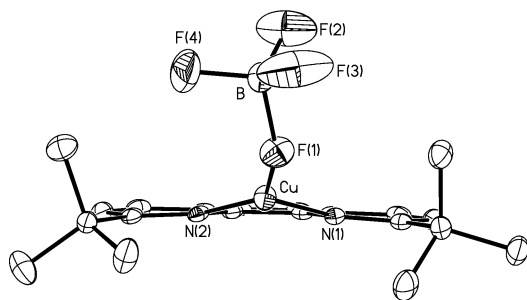


Figure 3. Side-on molecular drawing of three-coordinate $\text{Cu}(\text{dtbp})(\text{BF}_4)$ (**2**) shown with 50% probability thermal ellipsoids. Note the orientation of the *tert*-butyl methyl groups and the bending of the Cu atom and BF_4^- ion away from the upward-facing methyl groups.

coordinating anions. Mixtures of AgCF_3SO_3 , AgBF_4 , or AgSbF_6 with **dtbp** in a 1:1 molar ratio react with $\text{Cu}(0)$ to give the mono-**dtbp** $\text{Cu}(\text{I})$ complexes **1–3** (92%, 94%, and 88% yields, respectively). These are solvent-facilitated reactions; the redox process will not occur efficiently unless the solvent is of modest polarity and coordinating ability. In acetone and ethanol the redox reaction is complete in minutes, whereas in THF the reaction occurs over the course of hours, and in dichloromethane the reaction may go to completion in days to weeks. We believe that the reaction product is a solvato complex in coordinating solvents, but the coordinated solvent molecule may be lost upon workup if an alternate ligand is present, as occurs in complexes **1** and **2**.

The method is particularly well-suited to the clean preparation of mixed ligand complexes of the hindered phenanthroline ligand, **dtbp**. The complex, $[\text{Cu}(\text{dmp})\text{-(dtbp)}]^+$, where dmp is 2,9-dimethyl-1,10-phenanthroline,

may be isolated in high yield and purity, improving on a prior synthesis. Reaction of 1 equiv AgBF_4 and 1 equiv of **dtbp** in the presence of excess $\text{Cu}(0)$ in acetone produces $[\text{Cu}(\text{dtbp})((\text{CH}_3)_2\text{CO})][\text{BF}_4]$. Direct addition of 1 equiv of dmp to the yellow $[\text{Cu}(\text{dtbp})((\text{CH}_3)_2\text{CO})][\text{BF}_4]$ solution resulted in the desired deep orange complex $[\text{Cu}(\text{dmp})(\text{dtbp})][\text{BF}_4]$ in 87% yield. The ^1H NMR of this product showed no evidence of $[\text{Cu}(\text{dmp})_2]^+$, an impurity reported in the prior synthesis.¹¹ The order of ligand addition and the steric bulk of **dtbp** are key to the success of this method: when 1 equiv of AgCF_3SO_3 and 1 equiv of dmp were mixed together and allowed to react with excess $\text{Cu}(0)$, the only product was 1/2 of an equiv of $[\text{Cu}(\text{dmp})_2][\text{CF}_3\text{SO}_3]$.

Remarkably, this oxidation-based method can be used to prepare the heretofore elusive complex cation $[\text{Cu}(\text{dtbp})_2]^+$. Mixtures of the silver salts $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$, AgBF_4 , or AgSbF_6 with **dtbp** in a 1:2 ratio react with excess $\text{Cu}(0)$ to afford the $[\text{Cu}(\text{dtbp})_2]^+$ complexes **4**• CH_2Cl_2 , **5**• CH_2Cl_2 , and **6**• CH_2Cl_2 in good yields (82%, 93%, and 88%, respectively). The process by which the $[\text{Cu}(\text{dtbp})_2]^+$ cation is formed is complex and highly solvent dependent. The $[\text{Cu}(\text{dtbp})_2]^+$ product is only formed if the oxidation reaction is carried out in acetone, ethanol, or THF. In CH_2Cl_2 or toluene no color change is observed on the same time scale. The initial product in successful reactions is the $[\text{Cu}(\text{dtbp})(\text{solvato})]^+$ complex; the $[\text{Cu}(\text{dtbp})_2]^+$ species is formed when the solvent is removed. In acetone, the initial product is pale yellow, similar to acetone solutions of **3**. The second ligand appears to bind as acetone is removed: as the solvent volume decreases the solution darkens, tending toward orange, and the residual solid varies from dark yellow to orange. This solid dissolves to produce a bright orange solution in CH_2Cl_2 and yields bright orange crystals upon precipitation with hexanes.

Structures of $\text{Cu}(\text{dtbp})(\text{CF}_3\text{SO}_3)$ (1**) and $\text{Cu}(\text{dtbp})(\text{BF}_4)$ (**2**).** The structures of **1** and **2** confirm the 1:1 $\text{Cu}:\text{dtbp}$ stoichiometry and reveal that the counterion binds to the metal. Compounds **1** and **2** crystallize in the $P2_1/n$ and $P2_1/c$ space groups, respectively, with four formula units occupying the unit cell and no solvent molecules present. The unit cell compositions are thus consistent with a +1 oxidation state for the metal ion. Furthermore, the anomalous scattering properties of the heavy atoms and the elemental analyses are consistent with the lighter Cu atom and not the heavier Ag atom in the complexes. Both compounds participate in π -stacking but in different ways. The crystal packing of **2**, illustrated in Figure 1, reveals that the phenanthroline rings engage in infinitely long π -stacking interactions. Between any two stacking molecules lies an inversion center; thus, each molecule is inverted with respect to both of its stacking partners. The phenanthroline planes are stacked at average perpendicular distances of 3.4 Å and are offset with respect to one another. The packing diagram of complex **1** (Figure S1) reveals that the molecules engage only in pairwise π -stacking interactions. In each pair, the two molecules are offset and inverted with respect to one another.

The geometry about the metal ions is distorted trigonal planar. The metal ion in each complex is three coordinate,

Table 2. Significant Bond Distances (in Å) of Cu(dtbp)(OTf) (**1**), Cu(dtbp)(BF₄) (**2**), [Cu(dtbp)((CH₃)₂CO)][SbF₆] (**3**), [Cu(dtbp)₂][B(C₆F₅)₄] (**4**), [Cu(dtbp)₂][B(C₆F₅)₄]•CH₂Cl₂(**4**•CH₂Cl₂), [Cu(dtbp)₂][BF₄]•CH₂Cl₂(**5**•CH₂Cl₂), and [Cu(dtbp)₂][SbF₆]•CH₂Cl₂(**6**•CH₂Cl₂)

	1	2	3	4	4 •CH ₂ Cl ₂	5 •CH ₂ Cl ₂	6 •CH ₂ Cl ₂
Cu–N(1)	2.102(2)	2.040(3)	2.056(3)	2.130(1)	2.096(3)	2.081(2)	2.072(2)
Cu–N(2)	1.990(2)	2.019(3)	2.012(3)	2.096(1)	2.115(3)	2.105(2)	2.079(2)
Cu–N(3)				2.103(1)	2.076(3)	2.104(2)	2.145(2)
Cu–N(4)				2.120(1)	2.139(3)	2.114(2)	2.149(2)
Cu–F or O	1.927(2)	2.012(2)	1.929(3)				
av Cu–N	2.0462(16)	2.030(3)	2.034(3)	2.1121(12)	2.107(3)	2.103(2)	2.1108(19)

with the two nitrogens of the phenanthroline (dtbp) and either an O atom (CF₃SO₃[−], **1**) or an F atom (BF₄[−], **2**) as ligands. The coordination environment of the Cu(I) is shown in Figure 2 for complex **1**. The Cu–N(1) and Cu–N(2) distances are 2.102(2) Å and 1.990(2) Å, respectively, for **1** and 2.040(3) Å and 2.019(3) Å, respectively, for **2**. The distances from the Cu(I) to the coordinating atoms of the anions are 1.927(2) Å for **1** (O(1)) and 2.012(2) Å for **2** (F(1)). These bond lengths are listed in Table 2. The metal ion and counterion-derived ligand reside above the plane of the phenanthroline, as shown in the packing diagram of **2** in Figure 1, and when the molecule is viewed along the plane of the phenanthroline ligand in Figure 3 (complex **1**, Figure S2). The plane containing the Cu and the two phenanthroline nitrogen atoms is coplanar neither with the phenanthroline aryl rings nor with the Cu–X (anion atom) bond. The angle between the N–Cu–N plane and the phenanthroline aryl plane is 22.4° in **1** and 14.2° in **2**. The angle between the N–Cu–N plane and the Cu–X bond is 16.3° in **1** and 10.9° in **2**. Two pairs of methyl groups point downward, away from the counterion ligand, while the third pair of methyl groups points upward. The counterion is nestled into the cleft created by the upward facing methyl groups. Similar to the previous ¹H NMR observations of dnpp complexes, the chemical shifts of the methyl groups of the substituents of dtbp in **1** (δ 1.756 ppm) and **2** (δ 1.731 ppm) are shifted downfield with respect to that of free dtbp ligand (δ 1.58 ppm); this shift is expected due to the inductive effect upon complexation of the ligand to a Lewis acidic, electropositive center such as Cu(I).^{10,11}

Structure of [Cu(dtbp)((CH₃)₂CO)][SbF₆] (3**).** In contrast, the counterion in **3** does not serve as a ligand, rather, a solvent molecule binds to the metal. Compound **3** crystallized in a *P2₁/c* space group, with four formula units, i.e., four [Cu(dtbp)((CH₃)₂CO)]⁺ cations and four SbF₆[−] anions, occupying the unit cell. The complex cation is shown in Figure 4 and the packing diagram with the unit cell is shown in Figure 5. The anomalous scattering properties of the heavy atom and elemental analysis are only consistent with the presence of a Cu atom in the complex, and the contents of the unit cell are again consistent with the Cu(I) oxidation state of metal ion. Comparison of the packing arrangements between **2** (Figure 1) and **3** (Figure 5), which crystallize in the same space group, reveals similar infinite stacking interactions of the Cu-phenanthroline units: the distance between the phenanthroline planes of the two inverted cations in the center of Figure 5 is 3.4 Å. Interestingly, however, the stacking axes are different between the two crystal structures (*a* for **2** and *b* for **3**). In **3**, the distance of closest approach between the Cu atom and an F atom of the SbF₆[−]

counterion is 5.072 Å; the shortest distance between the Cu atom and the Sb atom is 6.764 Å.

The coordination sphere of the metal ion in **3** is composed of the two nitrogen atoms of the phenanthroline and the carbonyl oxygen atom of the acetone molecule. The Cu–N(1) and Cu–N(2) distances are 2.056(3) Å and 2.012(3) Å, respectively; the Cu(I)–O bond distance is 1.929(3) Å. The coordination sphere of the metal center is distorted trigonal planar, with the metal ion and the acetone ligand above the plane of the phenanthroline. In **3**, the angle between the N–Cu–N plane and the phenanthroline aryl plane is 19.6°, and the angle between the N–Cu–N plane and the Cu–O bond is 23.1°. Similar to the structures of **1** and **2**, the methyl groups of the *tert*-butyl substituents are rotated such that there is only one methyl group on the face of the phenanthroline where the Cu(I)-acetone moiety resides. As expected, the chemical shift of the methyl group of the dtbp in complex **3** is also shifted downfield (δ 1.677 ppm) compared to that of free dtbp. The protons of the ligated acetone can be observed by NMR at δ 2.460 ppm.

Structures of [Cu(dtbp)₂][B(C₆F₅)₄]•CH₂Cl₂ (4**•CH₂Cl₂), [Cu(dtbp)₂][BF₄]•CH₂Cl₂ (**5**•CH₂Cl₂), and [Cu(dtbp)₂][SbF₆]•CH₂Cl₂ (**6**•CH₂Cl₂).** The previously elusive Cu(I)-(dtbp)₂ cation is largely similar in structure to other members of this class of compounds; the exceptional features are the elongated Cu–N bonds. As observed in the illustration of a single formula unit in Figure 6, two bulky dtbp ligands coordinate the Cu(I) atom. Crystals of **4**•CH₂Cl₂ contain four [Cu(dtbp)₂]⁺ cations, four [B(C₆F₅)₄][−] anions, and four CH₂Cl₂ solvent molecules in the unit cell in the *P2₁/c* space group. The contents of the unit cell are consistent with a +1 oxidation state of the Cu center. Elemental analysis and the anomalous scattering of the heavy atom are consistent with the presence of a Cu atom. The bulky cation and anion are well separated from one another; the distance of closest approach between the Cu atom and an F atom of [B(C₆F₅)₄][−] is 5.500 Å. The shortest distance between the centroids of the cation and anion is 9.416 Å.

The coordination geometry of the metal is pseudotetrahedral. The complex exhibits elongated Cu–N bonds resulting in a significant *D_{2d}* distortion along one axis. The Cu–N(*x*) (where *x* = 1–4) bond distances are 2.096(3) Å, 2.115(3) Å, 2.076(3) Å, and 2.139(3) Å, respectively, for an average distance of 2.11 Å. The intraligand N–Cu–N angles are 84.53(10)° and 84.43(10)°, while the interligand N–Cu–N angles are 123.97(10)°, 125.12(10)°, 121.09(10)°, and 122.70(10)°. One phenanthroline ligand is slightly distorted from its position in an idealized *D_{2d}* geometry. As illustrated in Figure 7, the plane of one phenanthroline is tilted slightly downward and displaced to one side. Another

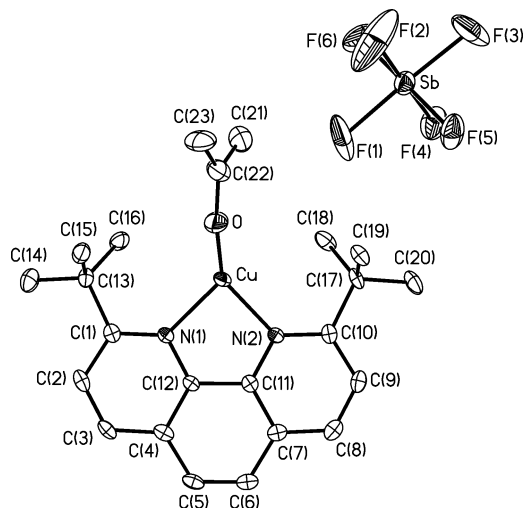


Figure 4. View of the three-coordinate $[\text{Cu}(\text{dtbp})((\text{CH}_3)_2\text{CO})][\text{SbF}_6]$ (**3**) shown with 50% probability thermal ellipsoids. The Cu atom and the acetone ligand are out of the plane of the phenanthroline ligand, similar to complex **2**, as shown in Figure 3. H atoms have been omitted for clarity.

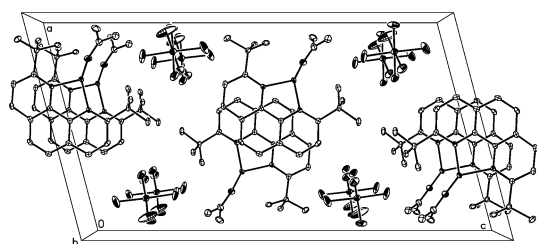


Figure 5. Packing diagram of the unit cell of the three-coordinate $[\text{Cu}(\text{dtbp})((\text{CH}_3)_2\text{CO})][\text{SbF}_6]$ shown along the b -axis with 30% probability thermal ellipsoids. Note the occurrence of π -stacking between the phenanthroline planes of two inverted cations in the center. H atoms have been omitted for clarity.

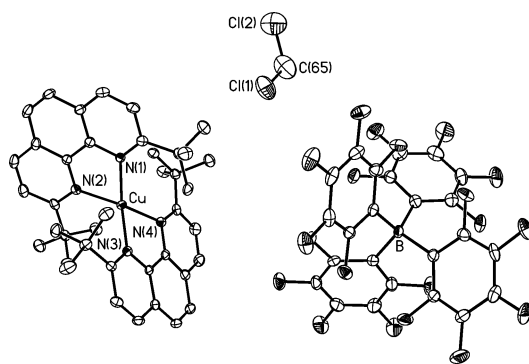


Figure 6. View of the four-coordinate $[\text{Cu}(\text{dtbp})_2][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{CH}_2\text{Cl}_2$ (**4**• CH_2Cl_2) formula unit shown with 50% probability thermal ellipsoids. The two **dtbp** ligands are arranged in a pseudotetrahedral fashion. H atoms have been omitted for clarity.

crystal form of **4**, without a solvent molecule, was obtained; the structure of the cation was similar, though the extent of distortion of the phenanthroline ligand was different. This second structure was of a more idealized D_{2d} cation; minimal distortion of the phenanthroline ligands and smaller deviations among the Cu–N bond distances were observed (Table S1). The average Cu–N bond length in this second structure was 2.11 Å. This second crystal form was a less frequently observed morphology for crystals of this compound.

The $[\text{Cu}(\text{dtbp})_2]^+$ cation in **5**• CH_2Cl_2 is similar to that in **4**• CH_2Cl_2 . The unit cell contains four formula units, i.e., four

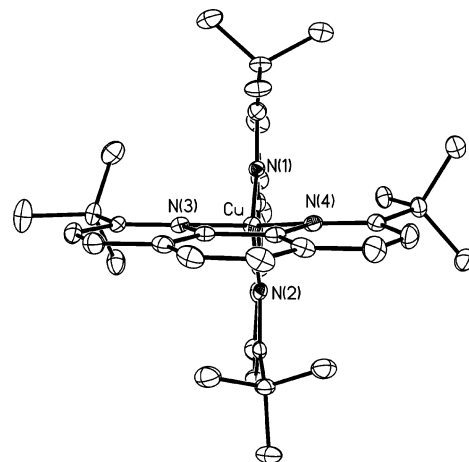


Figure 7. Drawing of the $[\text{Cu}(\text{dtbp})_2]^+$ cation of complex **4**• CH_2Cl_2 shown with 50% probability thermal ellipsoids. Only slight distortions from pseudotetrahedral D_{2d} geometry are observed, with one **dtbp** ligand tilted down and displaced sideways. H atoms have been omitted for clarity.

$[\text{Cu}(\text{dtbp})_2]^+$ cations, four BF_4^- anions, and four CH_2Cl_2 solvent molecules in a $P\bar{1}$ space group; the asymmetric unit contains two formula units. The average Cu–N bond distance in the two independent molecules is 2.10 Å; individual bond distances are listed in Table 2. The structure of the cation in **5**• CH_2Cl_2 is similar to the second, less common isomorph of **4**, which has a more idealized D_{2d} geometry. The distances between the cations and anions in the structure of **5**• CH_2Cl_2 are shorter than those of **4**• CH_2Cl_2 , as expected for the smaller anion: Cu–F is 6.29 Å and 7.72 Å; Cu–B is 7.35 Å and 8.80 Å, respectively, for the two molecules in the asymmetric unit. A picture of one of the molecules of the asymmetric unit is included in the Supporting Information (Figure S3).

The unit cell of **6**• CH_2Cl_2 contains two formula units in the $P\bar{1}$ space group, i.e., two $[\text{Cu}(\text{dtbp})_2]^+$ cations, two SbF_6^- anions, and two CH_2Cl_2 solvent molecules. The average Cu–N bond distance is 2.11 Å, although the individual bond distances (Table 2) span the widest range of the above three complexes. The distortion of the two phenanthroline rings from idealized D_{2d} geometry is also greater than those of the above three complexes. The Cu–F distance is 5.56 Å, and the Cu–Sb distance is 7.08 Å. Figure S4 illustrates the $[\text{Cu}(\text{dtbp})_2]^+$ cation of **6**• CH_2Cl_2 . The chemical shifts of the methyl groups of the **dtbp** ligand in **4**• CH_2Cl_2 , **5**• CH_2Cl_2 , and **6**• CH_2Cl_2 (δ 1.214, 1.225, and 1.221 ppm, respectively) are shifted *upfield* relative to that of free **dtbp** ligand. This upfield shift phenomenon has previously been attributed to ring current effects on the alkyl groups.^{10,11}

Discussion

We report a novel synthetic method allowing access to Cu(I) complexes with weakly coordinated ligands, complexes that may be useful in molecular machines, biomimetic models, catalysts, or solar energy conversion devices. Conventional synthetic methods are insufficient for the synthesis of such complexes. Our method combines the oxidizing power of Ag(I) and the elegance of comproportionation reactions. Via this reaction, we synthesized Cu(I)-

(**dtbp**) complexes with either weakly coordinating counterions (**1** and **2**) or the weakly coordinating solvent acetone (**3**). Most surprisingly, the $[\text{Cu}(\text{dtbp})_2]^+$ complexes (**4–6**), which were previously reported to be impossible to synthesize, were easily and cleanly prepared via this method. The difficulty in forming $[\text{Cu}(\text{dtbp})_2]^+$, because of the great steric bulk of the substituents at the 2 and 9 positions, is evidenced by the impressive Cu(I)–N distances—the longest for this class of complexes—in the molecular structures of **4–6**.

Previous studies of complexes with the general formula $[\text{Cu}(\text{dap})(\text{B})]^+$ (dap, 2,9-dialkyl-1,10-phenanthroline; B, a less bulky phenanthroline or chloride) showed that the three-coordinate chloride adduct $\text{Cu}(\text{dap})\text{Cl}$ could only be formed with the bulky **dtbp** and dnpp ligands; reactions with all other substituted dialkylphenanthrolines resulted in only the $[\text{Cu}(\text{dap})_2]^+$ complexes.^{10,11} With dnpp, both $\text{Cu}(\text{dnpp})\text{Cl}$ and $[\text{Cu}(\text{dnpp})_2]\text{Cl}$ could be isolated. These observations revealed that only the *tert*-butyl groups are sufficiently bulky to inhibit the binding of a second **dtbp** ligand, suggesting that the second bidentate **dtbp** is a weaker ligand than monodentate chloride in these systems.

In an effort to synthesize $\text{Cu}(\text{I})(\text{dtbp})$ complexes with weakly coordinated ligands, several synthetic routes were evaluated. Direct reaction of **dtbp** with $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ only led to the formation of the three-coordinate complex $[\text{Cu}(\text{dtbp})(\text{CH}_3\text{CN})][\text{PF}_6]$, regardless of the ratio of **dtbp** used. (Data collection, refinement details, and a crystal structure of $[\text{Cu}(\text{dtbp})(\text{CH}_3\text{CN})][\text{PF}_6]$ are provided in the Supporting Information in Table S1 and Figure S5.) The *tert*-butyl substituents of the **dtbp** ligand impede effective competition with CH_3CN for ligation to the Cu(I) center. These observations demonstrate that the second bidentate **dtbp** is a weaker ligand than monodentate CH_3CN , which led previous researchers to believe that the homoleptic $[\text{Cu}(\text{dtbp})_2]^+$ complex was impossible to synthesize.¹¹ Since our goal was to prepare three-coordinate complexes with very weakly coordinating ligands, it was obvious that ligand displacement on $[\text{Cu}(\text{dtbp})(\text{CH}_3\text{CN})]^+$ was not a viable synthetic strategy.

Attempted alternative routes to the desired three-coordinate complexes were as follows: (1) preparation of a halide complex and metathesis with a silver salt of the desired anionic ligand or (2) comproportionation of Cu(0) with a Cu(II) salt. Metathesis proved ineffective due to incomplete chloride abstraction; reaction of $\text{Cu}(\text{dtbp})\text{Cl}$ with various Ag(I) salts did not produce the desired $\text{Cu}(\text{dtbp})\text{Y}$ (Y is SO_3CF_3^- , BF_4^- , SbF_6^- , or $\text{B}(\text{C}_6\text{F}_5)_4^-$) complexes. The reaction of $\text{Cu}(\text{dtbp})\text{Cl}$ with stoichiometric AgSbF_6 produced a chloride-bridged π -stacked $[(\text{Cu}(\text{dtbp}))_2\text{Cl}]^+$ species. (Data collection, refinement details, and a crystal structure of $[(\text{Cu}(\text{dtbp}))_2\text{Cl}][\text{SbF}_6]$ are in the Supporting Information in Table S1 and Figure S6.) In these systems it was thermodynamically unfavorable for stoichiometric chloride abstraction to take place. When the Ag(I) salt was present in excess, Ag(I) ions in solution inevitably underwent reduction, resulting in oxidation of Cu(I) to Cu(II), as observed by the color change from yellow to green. Similarly, the commonly utilized comproportionation strategy, where Cu(0) is oxidized

by a Cu(II) salt in the presence of **dtbp**, proved fruitless for this system. Reactions of this type in a variety of solvents were unpredictable and never resulted in the desired products; the reaction solutions were consistently blue to green in color, indicative of Cu(II) products. This observation suggests that Cu(II) is not a strong enough oxidant to oxidize Cu(0) to Cu(I) in the presence of **dtbp**. It should be noted that the only Cu(II) source tested was the commercially available $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, and the waters of hydration may inhibit comproportionation.

The logical substitution of Cu(II) with Ag(I) as an oxidizing agent for excess Cu(0) provides a novel and straightforward path to Cu(I) complexes.³⁸ In this high-yielding one-pot reaction, Cu(0) is oxidized to Cu(I), the ligand is bound to Cu(I), the Cu(I) complex is charge-balanced with a desirable counterion, and, conveniently, Ag(0) and the remaining Cu(0) are removed by filtration. The reaction proceeds more quickly in a polar coordinating solvent such as acetone than in a less polar solvent such as CH_2Cl_2 . The fact that the solvato complex **3** is the product in reaction of AgSbF_6 , **dtbp** and Cu(0) strongly suggests that acetone temporarily binds to and stabilizes the newly formed Cu(I) ion. The absence of solvent coordination likely explains the slow rate of reaction in CH_2Cl_2 . The beauty of this reaction is that it allows the synthesis of a variety of coordinatively unsaturated Cu(I) complexes via a simple reaction in which unwanted species are easily separated. Our method appears to be general and should be applicable to the preparation of otherwise inaccessible Cu(I) complexes with a variety of ligands. A further advantage is the wide variety of commercially available silver salts that may be used as oxidants and provide potential anionic ligands or counterions.

The use of excess Cu(0) was not a necessity for the success of this reaction, rather the small scale of these reactions would have required measuring inconveniently small quantities of Cu(0). One can imagine that on an industrial scale, this reaction could be performed in an environmentally friendly manner, producing no waste: Cu(0) could be used stoichiometrically and Ag(0) and solvent could be recovered, with the former used for the regeneration of AgY starting material.

The size and composition of the anion plays an important role in the structure of the resulting complex: specifically, whether the anion will bind to the Cu(I) center. The complexes $\text{Cu}(\text{dtbp})(\text{O}_3\text{SCF}_3)$ (**1**) and $\text{Cu}(\text{dtbp})(\text{BF}_4)$ (**2**) contain bound anions. In (**2**), the relatively small BF_4^- anion sits comfortably in the cleft created by the *tert*-butyl groups. The larger CF_3SO_3^- anion sits in a similar position but is more substantially displaced above the phenanthroline plane. In these complexes, electronic and steric effects are in competition. As oxygen is a better σ -donor than fluorine, complex **1** may be considered to contain the strongest ion-

(38) The reduction potentials of Ag(I), Cu(II), and Cu(I) in acetone were not found in the literature, but the standard reduction potentials do offer some explanation. The standard one-electron reduction potentials of Ag(I), Cu(II), and Cu(I) are 0.799 V, 0.159 V, and 0.520 V, respectively. See ref 31.

pair, despite the larger size of the O_3SCF_3^- . This conclusion is borne out in the structures of **1** and **2**: the Cu–O distance is 1.927(2) Å, while the Cu–F distance in **2** is 2.012(2) Å. For a larger anion, such as SbF_6^- , the open coordination site on the Cu(I)(**dtbp**) center is not large enough, and the complex contains a noncoordinating ion pair. Presumably, as the distance between the metal center and the counterion increases, the stability of the ion pair decreases, allowing solvent molecules to remain coordinated to the metal. The solvato complex **3**, which was obtained from a CH_2Cl_2 /hexanes solution in poor yield, shows an acetone molecule filling the third coordination site. Since acetone is a ligand to the Cu center, isolation from acetone/hexanes resulted in significant improvement in the yield of **3**.

Large anions facilitate the synthesis of $[\text{Cu}(\text{dtbp})_2]^+$, a complex previously reported to be impossible to prepare.¹¹ As the size of the counterion is increased from SbF_6^- in **3** to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in **4** and **4**• CH_2Cl_2 , the distance between the $[\text{Cu}(\text{dtbp})]^+$ and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counterion becomes so great that a second **dtbp** ligand binds to the metal center (Figure 6). The weak ion pairing, and the fact that the anion is unable to closely approach the metal to satisfy its coordination requirements, enables formation of the sterically encumbered bis-**dtbp** complex $[\text{Cu}(\text{dtbp})_2]^+$. Notably, complex **4** was the sole product even when only 1 equiv of **dtbp** was added relative to $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$. In this reaction the product was 1/2 of an equiv of the bis-**dtbp** complex, $[\text{Cu}(\text{dtbp})_2]\text{-}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**).

At first glance, it may seem that an extraordinarily large counterion like $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ is necessary to prepare the $[\text{Cu}(\text{dtbp})_2]^+$ complex. However, once **4** was synthesized, simple adjustments to the stoichiometry of the reaction, i.e., addition of 2 equiv of **dtbp** relative to AgBF_4 or AgSbF_6 in reaction 5, allowed for the preparation of complexes **5**• CH_2Cl_2 and **6**• CH_2Cl_2 , using smaller counterions and inexpensive, commercially available materials. Though considerably smaller than the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion. The SbF_6^- anion is sufficiently large to behave in a similar manner to the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion. SbF_6^- is too large to fit into the cleft created by the two *tert*-butyl groups of the $[\text{Cu}(\text{dtbp})]^+$ moiety, as evidenced by the molecular structure of complex **3**. The smaller size of BF_4^- allows it to compete with free **dtbp** ligands during reactions for the synthesis of **2**. However, when a second equiv of **dtbp** ligand is present, there is no competition between the two; **dtbp** is the better ligand due to the chelate effect and the $[\text{Cu}(\text{dtbp})_2][\text{BF}_4]$ complex is easily prepared.

The crystal structures of **4**, **4**• CH_2Cl_2 , **5**• CH_2Cl_2 , and **6**• CH_2Cl_2 demonstrate particularly long Cu(I)–N distances (Table 2) that are due to steric crowding imposed by the *tert*-butyl groups of the **dtbp** ligand. The long Cu(I)–N bond distances indicate the difficulty of positioning two **dtbp** ligands about the Cu center. The average Cu(I)–N distances of **4**, **4**• CH_2Cl_2 , **5**• CH_2Cl_2 , and **6**• CH_2Cl_2 (Table 2) are the longest in this class of compounds, longer than the average Cu(I)–N distance of all other bis(2,9-*R*₂-1,10-phenanthroline)Cu(I) complexes (2.045 Å) found in the Cambridge

Table 3. Average Cu–N Distances (in Å) of Other Bis-(2,9-*R*₂-1,10-phenanthroline)Cu(I) Complexes

complex	av Cu–N distance, Å	refs
$[\text{Cu}(\text{dmp})_2]\text{X}^a$	2.04	31, 40, 41, 13, 21
$[\text{Cu}(\text{dnpp})_2][\text{PF}_6]$	2.06	42
$[\text{Cu}(\text{dmp})(\text{dtbp})][\text{PF}_6]$	2.08	8
$[\text{Cu}(\text{dpp})_2]\text{X}^a$	2.06	43
$[\text{Cu}(2,9\text{-C}_6\text{F}_5\text{-1,10-phen})_2][\text{SbF}_6]\bullet\text{CH}_2\text{Cl}_2$	2.06	34
$[\text{Cu}(\text{xop})_2][\text{PF}_6]\bullet\text{CH}_3\text{OH}^b$	2.02	44

^a This complex has been crystallized with various counterions. The reported value is an average of all Cu–N distances found. ^b Most abbreviations are defined in footnote 17. xop, 2-(2-methylphenyl)-9-(2,6-dimethylphenyl)-1,10-phenanthroline.

Structural Database by more than three standard deviations.³⁹ The average Cu(I)–N distances of select bis(2,9-*R*₂-1,10-phenanthroline)Cu(I) complexes are listed in Table 3 for comparison.

When compared to other complexes of its class, $[\text{Cu}(\text{dtbp})_2]^+$ exhibits the least distortion from an idealized D_{2d} geometry. Bis complexes of 2,9-disubstituted phenanthroline ligands exhibit three different types of distortion: rocking, wagging, and flattening. Kovalevsky et al.²⁴ defined ζ_{CD} , which effectively combines these distinct structural deviations into a single parameter. A perfect D_{2d} structure would have a ζ_{CD} value of 1.00. For the $[\text{Cu}(\text{dtbp})_2]^+$ cation in complexes **4**, **4**• CH_2Cl_2 , **5**• CH_2Cl_2 (2 asymmetric units), and **6**• CH_2Cl_2 the ζ_{CD} values are 0.994, 0.980, 0.987 and 0.982, and 0.962, respectively (Table S2). Although there are examples of previously characterized complexes with similarly minimal distortions, the $[\text{Cu}(\text{dtbp})_2]^+$ cation exhibits the highest value of ζ_{CD} across multiple crystal forms. Another structural feature of the $[\text{Cu}(\text{dtbp})_2]^+$ cation is the minimal extent of π -stacking between the aromatic ring systems (Figure S7). This minimal π overlap is unlike that in the other complexes described herein; however, similarly minimal overlap was observed in multiple structures of the $\text{Cu}(\text{bfp})_2$ cation.²⁴

When the orange complex **4** is dissolved in acetone, the resulting solution is yellow, suggesting that the solution-state structure is different from the solid-state structure. The yellow solution contains an acetone solvato complex, analogous to **3**, as confirmed by NMR. When an acetone solution of **4** is concentrated, the concentration of **dtbp** increases relative to the concentration of acetone, and the second **dtbp** is able to replace the coordinated acetone ligand. The resulting orange solid $[(\text{dtbp})_2\text{Cu}][\text{B}(\text{C}_6\text{F}_5)_4]$ forms an orange solution in CH_2Cl_2 , indicating that the connectivity of the complex

(39) A Cambridge Structural Database (updated November 2004) search for four-coordinate bis-phenanthroline-Cu(I) complexes found 79 matches. The Cu(I)–N distances for each complex were averaged, and the average of these distances was calculated to be 2.045 Å with a standard deviation of 0.017 Å.

(40) Pawlowski, V.; Kunkely, H.; Zabel, M.; Vogler, A. *Inorg. Chim. Acta* **2004**, *357*, 3, 824–826.

(41) Van Allen, D.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 11, 4590–4593.

(42) Eggleston, M. K.; Fanwick, P. E.; Pallenberg, A. J.; McMillin, D. R. *Inorg. Chem.* **1997**, *36*, 18, 4007–4010.

(43) Miller, M. T.; Karpishin, T. B. *Inorg. Chem.* **1999**, *38*, 23, 5246–5249.

(44) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *Inorg. Chem.* **1999**, *38*, 14, 3414–3422.

is preserved in a noncoordinating solvent. NMR spectral data confirm that both ligands are bound to the Cu(I) center in CD₂Cl₂ solution. Thus, a coordinated **dtbp** ligand of **4** is lost in the coordinating solvent acetone but is regained when the coordinating solvent is removed. This type of ligand-replacement reactivity may be of value in sensing applications.

Conclusion

We have designed an oxidation-based general synthetic route for the preparation of Cu(I) complexes, one which is particularly well-suited for the synthesis of complexes containing sterically bulky ligands. By a straightforward oxidation method we have prepared a series of three-coordinate Cu(I)-phenanthroline complexes containing weak ligands at the third coordination site, Cu(**dtbp**)Y (Y is SO₃CF₃⁻, BF₄⁻, or acetone), and a complex that was previously thought to be impossible to synthesize due to the steric bulk on the substituents of the phenanthroline ligand, [Cu(**dtbp**)₂]⁺. That a complex that is structurally unfavorable, with extraordinarily long Cu(I)–N distances, is the thermodynamically favored product exemplifies the simple beauty of this synthetic method. The photophysical properties and reactivity of these newly synthesized complexes will be reported elsewhere.

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Supporting Information Available: Crystallographic data for complex **4**, [Cu(**dtbp**)(CH₃CN)][PF₆], and [(Cu(**dtbp**))₂Cl][SbF₆], ζ_{CD} calculations of bis(2,9-R₂-1,10-phenanthroline)copper(I) complexes, molecular drawings of complexes **1**, **5•CH₂Cl₂**, **6•CH₂Cl₂**, [Cu(**dtbp**)(CH₃CN)][PF₆], and [(Cu(**dtbp**))₂Cl][SbF₆], packing diagrams of complex **1**, diagrams of π -stacking between the ligands of the various [Cu(**dtbp**)₂]⁺ complexes, and crystallographic data in CIF format of complexes **1**, **2**, **3**, **4**, **4•CH₂Cl₂**, **5•CH₂Cl₂**, **6•CH₂Cl₂**, [Cu(**dtbp**)(CH₃CN)][PF₆], and [(Cu(**dtbp**))₂Cl][SbF₆]. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 619999, CCDC 620000, CCDC 620001, CCDC 620002, CCDC 620003, CCDC 620004, CCDC 620005, CCDC 620006, and CCDC 620007 contain the supplementary crystallographic data for complexes **4**, **4•CH₂Cl₂**, **5•CH₂Cl₂**, **6•CH₂Cl₂**, [(Cu(**dtbp**))₂Cl](SbF₆), **2**, **1**, **3**, and [Cu(**dtbp**)(CH₃CN)](PF₆), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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