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Article

Dinuclear Cu(I) Complexes of 1,2,4,5-Tetra(7-azaindolyl)benzene: Persistent 3-Coordinate Geometry, Luminescence, and Reactivity

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Five Cu(I) complexes $[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$ (**1**), $[Cu_2(ttab)(PPh_3)_2][BF_4]_2$ (**2**), $[Cu_2(ttab)I_2]$ (**3**), $[Cu_2(ttab)(I_3)_2]$ (**4**), and $[Cu_2(ttab)(I)BF_4]_n$ (**5**) with 1,2,4,5-tetra(7-azaindolyl)benzene (ttab) have been synthesized and characterized. The structures of compound **1**, **2**, **4**, and **5** have been determined by single-crystal X-ray diffraction analyses, which established that **1**, **2**, and **4** are discrete dinuclear Cu_2 compounds while compound **5** is a 1D coordination polymer with the I^- ligand bridging two dinuclear Cu_2 units. The ttab ligand in all four complexes adopts a 1,3-chelation mode. The Cu(I) center in all complexes is three-coordinate. Close contact between the Cu(I) center and the benzene ring in the ttab ligand was observed in all four structures, which is believed to play a role in stabilizing the three-coordinate geometry of the Cu(I) center. The crystals of **1**, **2**, and **5** contain channels in the lattice that host solvent molecules such as CH_2Cl_2 and toluene. Fluorescent measurements established that, in solution, compounds **1**–**3** display weak blue luminescence which originates from the ttab but is significantly red-shifted and has a much lower emission intensity, compared to the free ttab ligand. The application of compound **1** in C–N cross-coupling reactions was examined by using the reaction of phenyl halides with imidazole as a model system. For the reaction with phenyl iodide, **1** was found to be as effective a catalyst as the CuI/1,10-phenanthroline system. For the reaction with phenyl bromide, **1** is less effective than the CuI/1,10-phenanthroline system. Compound **1** reacts with O_2 gas, as established by UV–vis spectra, but the oxidized products have not been characterized.

Introduction

Cu(I) complexes with N,N-chelate ligands are a class of molecules that have been investigated extensively for their redox properties, their possible use as models for dioxygen activation by biological copper systems,[1] and their catalytic activity in C−N cross-coupling reactions.[2,3] Recently, a number of Cu(I) complexes containing either 1,10-phenanthroline (1,10-phen) chelate[4] or 2-(2′-pyridyl)benzimidazolyl chelate[5] and phosphine ancillary ligands have been found to be potentially useful phosphorescent emitters in organic light emitting diodes. These application prospects of Cu(I) complexes have motivated us to explore the chemistry of Cu(I) compounds with new N,N′-chelate ligands. One of the N,N′-

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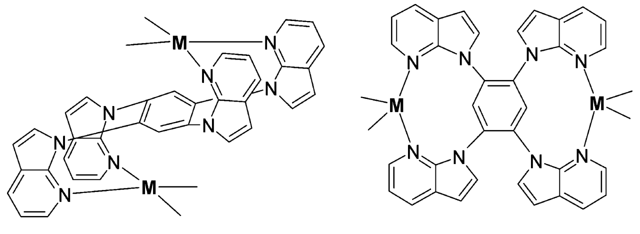
Chart 1



1,2-Chelation **1,3-Chelation**

chelate ligands selected for our investigation is 1,2,4,5-tetra(7-azaindolyl)benzene (ttab). The ttab ligand is a blue luminescent molecule and is capable of chelating to two metal centers.[6] Depending on the metal center, two bonding modes, namely the 1,2-chelate mode and the 1,3-chelate mode, as shown in Chart 1, are possible.[6] In the 1,2-chelate mode, we have observed that the geometrical constraint imposed by the ttab ligand forces the two metal centers to be in close proximity with the central benzene ring, which is responsible for the unusual reactivity of dinuclear Pt(II) complexes $Pt_2R_4(ttab)$ (R = CH_3, Ph) toward C−Cl bond and C−H bond activation.[7] Because of its potential to produce new phosphorescent and possibly reactive Cu(I) compounds, we have synthesized a number of Cu(I) coordination compounds with the ttab ligand and examined the properties of the new complexes. The results are presented herein.

Experimental Section

All reactions were performed under an inert atmosphere of dry N_2 with Schlenk techniques or in a drybox unless otherwise noted. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. CH_2Cl_2 was freshly distilled over P_2O_5. CH_3CN was freshly distilled over CaH_2. THF, DMF, and hexanes were purified using the solvent purification system (Innovation Technologies Co.). NMR spectra were recorded on Bruker Avance 300 or 500 MHz spectrometers. Elemental analyses were performed by Canadian Microanalytical Service, Ltd, Delta, BC. Thermogravimetric analysis for **1** was performed on a Perkin-Elmer TGA7 analyzer. Cyclic voltammetry (CV) was performed using a BAS CV-50W analyzer. The electrolytic cell used was a conventional three-compartment cell, in which a Pt working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode were employed. The CV measurements were performed at room temperature using 0.10 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte and dry DMF as the solvent. The ferrocenium/ferrocene couple was used as the internal standard ($E_o = 0.57$ V vs Ag/AgCl). $[Cu(CH_3CN)_4][BF_4]$ and $[Cu(CH_3CN)_2(PPh_3)_2][BF_4]$ were synthesized according to literature procedures.[8]

Synthesis of $[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$ (1). ttab (0.109 g, 0.20 mmol) and $[Cu(CH_3CN)_4][BF_4]$ (0.126 g, 0.40 mmol) were mixed in 10 mL of CH_2Cl_2, and the solution was stirred for 3 h at room temperature. Addition of hexanes (10 mL) resulted in precipitation of the product. Separation of the solid and then washing with 5 mL of THF/hexanes (1:1) resulted in 0.178 g (96%) of complex **1** as white solid. Crystals of complex **1** were obtained by slow diffusion of a CH_2Cl_2/toluene (2:1) (2 mL) solution of ttab (0.016 g, 0.030 mmol) into a CH_2Cl_2 (3 mL) solution of $[Cu(CH_3CN)_4][BF_4]$ (0.019 g, 0.060 mmol). NMR in CD_2Cl_2 at 25 °C (δ, ppm), ^1H NMR: 8.81 (br, s, 4H, aza), 8.56 (s, 2H, phenyl), 8.35 (d, $^3J = 7.2$ Hz, 4H, aza), 7.57 (br, s, 4H, aza), 6.73 (br, s, 4H, aza), 6.70 (d, $^3J = 3.4$ Hz, 4H, aza), 2.06 (br, s, 6H, CH_3CN). ^{13}C NMR: aza, 145.83, 145.11, 132.92, 127.94, 127.92, 119.59, 104.55; phenyl of ttab, 132.96, 124.09; CH3CN, 118.82, 2.33 (aza = 7-azaindolyl). Anal. Calcd for the vacuum-dried sample, $C_{34}H_{22}B_2Cu_2F_8N_8$ (complex **1** without the two CH_3CN ligands): C 48.43, H 2.63, N 13.29. Found: C 48.19, H 2.49, N 13.37.

Synthesis of $[Cu_2(ttab)(PPh_3)_2][BF_4]_2$ (2). Method 1. ttab (0.054 g, 0.10 mmol) and $[Cu(CH_3CN)_4][BF_4]$ (0.063 g, 0.20 mmol) were mixed in 5 mL of CH_2Cl_2, and the solution was stirred for 3 h at room temperature. PPh_3 (0.053 g, 0.20 mmol) was added to the solution. The mixture was stirred for another 1 h. Addition of hexanes (8 mL) resulted in precipitation of the product. Separation of the solid followed by recrystallization with CH_2Cl_2/hexanes resulted in 0.115 g (84%) of complex **2**. Crystals of complex **2** were obtained by slow evaporation of the solvents when it was recrystallized with the CH_2Cl_2/toluene (1:1) mixed solvents.

Method 2. A CH_2Cl_2 (15 mL) solution of $[Cu(CH_3CN)_2(PPh_3)_2][BF_4]$ (0.303 g, 0.40 mmol) was added into a CH_2Cl_2 (15 mL) solution of ttab (0.109 g, 0.20 mmol) over 20 min, and the mixture was stirred for 3 h at room temperature. Then, the solution was concentrated into ~10 mL and hexanes (15 mL) were added. The solid was isolated and recrystallized with CH_2Cl_2/hexanes to afford 0.208 (76%) of white solid **2**. NMR in CD_2Cl_2 at 25 °C (δ, ppm), $^{31}P\{^1H\}$: −0.16. ^1H NMR: 8.94 (br, s, 4H, aza), 8.44 (d, $^3J = 7.6$ Hz, 4H, aza), 7.83 (br, s, 2H, phenyl of ttab), 7.71 (br, s, 4H, aza), 7.30 (br, m, 6H, phenyl of PPh_3), 7.11 (br, m, 12H, phenyl of PPh_3), 6.92 (br, m, 12H, phenyl of PPh_3), 6.77(d, $^3J = 3.4$ Hz, 4H, aza), 6.31 (d, $^3J = 3.4$ Hz, 4H, aza). ^{13}C NMR: aza, 145.30, 144.97, 131.43, 127.32, 120.84, 119.18, 105.57; phenyl of ttab, 133.70, 124.49; phenyl of PPh_3, 133.03, 132.92, 129.69, 129.61. Anal. Calcd for $C_{70}H_{52}B_2Cu_2F_8N_8P_2$: C 61.47, H 3.83, N 8.19. Found: C 61.46, H 3.71, N 8.13.

Synthesis of $[Cu_2(ttab)(I)_2]$ (3). ttab (0.054 g, 0.10 mmol) and CuI (0.038 g, 0.20 mmol) were dissolved in the CH_3CN (20 mL)/CH_2Cl_2 (10 mL) mixed solvents, and the solution was stirred for 1 h at room temperature. Separation of the yellow solid from the obtained suspension resulted in 0.085 g (92%) of complex **3**. NMR in DMSO/CD_3CN (3:1) at 25 °C (δ, ppm), ^1H NMR: 8.32 (s, 2H, phenyl of ttab), 8.30 (s, 4H, aza), 8.01 (b, s, $^3J = 7.2$ Hz, 4H, aza), 7.20 (br, s, 8H, aza), 6.50 (br, s, 4H, aza). ^{13}C NMR: 147.81, 143.91, 133.50, 130.10, 130.07, 121.36, 117.78. 102.79. Anal. Calcd for $C_{34}H_{22}Cu_2I_2N_8$: C 44.22, H 2.40, N 12.13. Found: C 44.04, H 2.34, N 11.95.

Syntheses of $[Cu_2(ttab)(I_3)_2]$ (4) and $[Cu_2(ttab)(\mu\text{-}I)(BF_4)]_n$ (5). ttab (0.054 g, 0.10 mmol) and $[Cu(CH_3CN)_4][BF_4]$ (0.063 g, 0.20 mmol) were mixed in 5 mL of CH_2Cl_2, and the solution was stirred for 3 h at room temperature. After a THF/toluene (4:1) (2.5 mL) solution of I_2 (0.051 g, 0.20 mmol) was added to the solution, the mixture was stirred overnight. After addition of CH_3CN (5 mL) and the slow evaporation of the solvent for several days, deep red crystals of complex **4** (~0.013 g, ~9% yield, based on ttab) were obtained. After the separation of complex **4**, further evaporation of the mother liquor afforded yellow crystals of **5**, along with trace amount of small deep red crystals of **4**. After being washed with 3 mL of CH_2Cl_2, the red crystals were separated manually from the mixture, and the yellow crystals of **5** were obtained (~0.041 g, 46% yield, based on ttab).

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Complexes **4** and **5** were also obtained by the following direct syntheses. For **4**, $[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$ (0.038 g, 0.040 mmol), Bu_4NI (0.030 g, 0.080 mmol), and I_2 (0.020 g, 0.080 mmol) were mixed in 5 mL of CH_2Cl_2, and the resulting brown solution was stirred overnight. After evaporation of the solvent and recrystallization of the residue with CH_3CN, deep red crystals of **4** were obtained (~40% yield). NMR in $CDCl_3/CD_3CN$ (1:5) at 25 °C (δ, ppm), ^1H NMR: 8.21(s, 2H, phenyl of ttab), 8.12 (s, 4H, aza), 7.90 (br, s, 4H, aza), 7.19 (br, s, 4H, aza), 7.09 (br, s, 4H, aza), 6.50 (br, s, 4H, aza).^{13}C NMR: 147.97, 143.81, 133.80, 129.69, 128.90 (×2), 121.38, 117.50, 102.56. Anal. Calcd for $C_{34}H_{22}Cu_2I_6N_8$: C 28.54, H 1.55, N 7.83. Found: C 28.38, H 1.46, N 8.06.

For **5**, $[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$ (**1**, 0.019 g, 0.020 mmol) and Bu_4NI (0.007 g, 0.020 mmol) were mixed in 2 mL of CH_2Cl_2, and the resulting clear yellow solution was stirred. The solution turned cloudy after a while, followed by the precipitation of light yellow solid. Separation and recrystallization of the solid with CH_3CN afforded 0.011 g (58%) of light yellow crystals of **5**. NMR data are not available due to its poor solubility. Anal. Calcd for $C_{34}H_{22}BCu_2F_4N_8I{\cdot}0.5CH_2Cl_2$: C 44.76, H 2.50, N 12.10. Found: C 44.47, H 1.98, N 11.44.

General Procedure for Cu(I)-Catalyzed Coupling Reactions of Phenyl Halide with Imidazole. CuI/1,10-Phenanthroline as the Catalyst. A 50 mL oven-dried Schlenk tube containing a stir bar was quickly charged with CuI (0.019 g, 0.10 mmol), 1,10-phenanthroline (1,10-phen) (0.036 g, 0.20 mmol), imidazole (0.068 g, 1.0 mmol), and the base Cs_2CO_3 (0.650 g, 2.0 mmol). The tube was sealed and evacuated and refilled with N_2. Predried phenyl halide (1.0 mL), after being bubbled with N_2, was transferred into the Schlenk tube via syringe. The mixture was heated in an oil bath under appropriate temperature for 19 or 48 h. After being cooled to room temperature, the reaction mixture was diluted with 20 mL of water and was extracted with CH_2Cl_2 (3 × 20 mL). After the solvent was removed, the residue was purified by chromatography on a silica gel column with ethyl acetate/hexanes (4:1) as the eluent. The organic product was characterized by ^1H NMR.

Complex 1 as the Catalyst. The same procedure as above was adopted, except that complex **1** (0.047 g, 0.050 mmol) was used as the catalyst instead of CuI/1,10-phen. No additional free ttab ligand was added to the complex **1** catalyst system except for entry 6 in Table 3 where 1 equiv of ttab was used.

Monitoring the Dioxygen Reaction with Compound 1. In a drybox, compound **1** was dissolved in dry THF to make a colorless solution of $\sim 1.0 \times 10^{-5}$ M. Then, 2.5 mL of this solution was transferred to a UV−vis cell and the cell was sealed by a rubber stopper. A UV−vis spectrum of the solution was recorded at ambient temperature. Eight portions of 2 mL of O_2 gas at 1 atm was introduced to the UV−vis cell via a syringe at ~3 min intervals. The spectra were recorded at an ~1 min interval. After the addition of about 10 mL of O_2, no further spectral change was observed. No obvious color change of the solution was observed during and after the O_2 addition. White precipitation was observed during the O_2 addition.

X-ray Diffraction Analysis. Single crystals of the complexes **1**, **2**, **4**, and **5** were obtained and characterized by X-ray diffraction analysis. Crystals were mounted on glass fibers for data collection. Data were collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo Kα radiation, operating at 50 kV and 35 mA at 180 K. No significant decay was observed for all of the samples. Data were processed on a PC using the Bruker SHELXTL software package[9] (version 5.10) and were corrected for Lorentz and polarization effects. Crystals of **1**, **4**, and **5** belong to the monoclinic space groups $P2_1/n$, $P2_1/c$, and $C2/m$, respectively, while the crystals of **2** belong to the triclinic space group $P\bar{1}$. All four molecules possess a crystallographically imposed inversion center. Toluene solvent molecules are located in the lattice of **1** and refined successfully. CH_2Cl_2 solvent molecules are located in the lattice of **2** and refined successfully. The crystal of **5** is small and diffracts weakly. As a result, less than 20% of the independent reflections collected have the intensity greater than $2\sigma(I)$. Disordered toluene and THF solvent molecules are found in the lattice of **5**, and they are partially located, modeled, and refined due to the limitation of data. In addition, the BF_4^- is disordered, which along with the poor quality of data and the disordered solvent molecules and the missing solvent molecules contributes to the relatively poor structural parameters of **5**. All non-hydrogen atoms except the disordered solvent molecules were refined anisotropically. All hydrogen atoms except those of the disordered solvent molecules were calculated, and their contributions in structural factor calculations were included. The crystallographic data are given in Table 1. Selected bond lengths and angles for complexes **1**, **2**, **4**, and **5** are listed in Table 2.

Results and Discussion

Synthesis of the ttab Ligand. Synthesis of the ttab ligand was initially achieved in ~30% yield as previously reported,[7a] by the reaction of excess 7-azaindole and 1,2,4,5-tetrabromobenzene in the presence of $CuSO_4$ and KOH as catalyst and HBr scavenger, respectively. However, because this procedure requires a high temperature (260 °C) and the use of a large excessive amount of 7-azaindole, unreacted starting material, multiple byproducts, and decomposed species are all present in the reaction mixture, making the separation and purification of the product very difficult. To improve the synthesis of ttab, we used the modified homogeneous C−N coupling method developed by the Buchwald group.[3b] In the new procedure, 7-azaindole was reacted with 1,2,4,5-tetrabromobenzene in a 5:1 ratio in DMF in the presence of CuI, 1,10-phen, and Cs_2CO_3 at 155 °C. This new procedure increased the yield of ttab to ~70% without the use of a large excessive amount of 7-azaindole, and only trace amount of di- and trisubstituted byproducts were observed.

Syntheses of Dinuclear Cu(I) Complexes of 1−5. The air-sensitive colorless dinuclear Cu(I) complex **1** was obtained nearly quantitatively by the reaction of $[Cu(CH_3CN)_4]BF_4$ with ttab in a 2:1 ratio. This new complex is moderately stable toward air in acetonitrile but highly air-sensitive in other common organic solvents, which may be attributed to the known stabilization effect of acetonitrile to Cu(I) complexes.[10] On the other hand, the ^1H NMR of **1** in CH_3CN changes with concentration (at low concentration, the spectrum of **1** is identical to that of free ttab in CH_3CN) and time, an indication that some degree of ttab dissociation from the Cu(I) center in **1** occurs in CD_3CN, presumably due to the formation of the $[Cu(CH_3CN)_4][BF_4]$. In solvents such as CH_2Cl_2 compound **1** remains intact, as confirmed by

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Table 1. Crystal Data for Complexes **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
formula	$C_{38}H_{28}N_{10}B_2F_8Cu_2\cdot C_7H_8$	$C_{70}H_{52}N_8B_2F_8Cu_2\cdot 4CH_2Cl_2$	$C_{34}H_{22}N_8I_6Cu_2$	$C_{34}H_{22}N_8BF_4ICu_2\cdot 2C_7H_8\cdot C_4H_8O$
fw	1017.54	1707.54	1431.08	1139.75
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/m$
a/Å	8.3948(19)	12.323(4)	8.997(1)	24.954(5)
b/Å	14.034(3)	13.386(4)	23.441(4)	14.712(3)
c/Å	18.518(4)	13.496(4)	9.4998(16)	14.377(3)
α/deg	90	93.117(6)	90	90
β/deg	99.223(5)	102.741(5)	108.838(3)	112.475(3)
γ/deg	90	116.504(5)	90	90
V/Å^3	2153.4(9)	1913.2(10)	1896.1(5)	4877.1(3)
Z	2	1	2	4
D_c/g cm^{-3}	1.563	1.482	2.507	1.552
μ/mm^{-1}	1.070	0.945	6.044	1.568
$2\theta_{max}$/deg	56.76	56.70	56.64	56.74
no. of rflns measured	11 772	13 374	12 569	17 687
no. of rflns used (R_{int})	4925 (0.0443)	8589 (0.0242)	4473 (0.1048)	6077 (0.1993)
no. of params	331	469	230	286
final R [$I > 2\sigma(I)$]				
R1^a	0.0621	0.0772	0.0610	0.1055
wR2^b	0.1340	0.2064	0.0974	0.2516
R (all data)				
R1^a	0.1229	0.1129	0.1585	0.3546
wR2^b	0.1586	0.2303	0.1135	0.3296
GOF on F^2	1.019	1.054	0.847	0.811

[a] $R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma(wF_o^2)\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angels (deg)

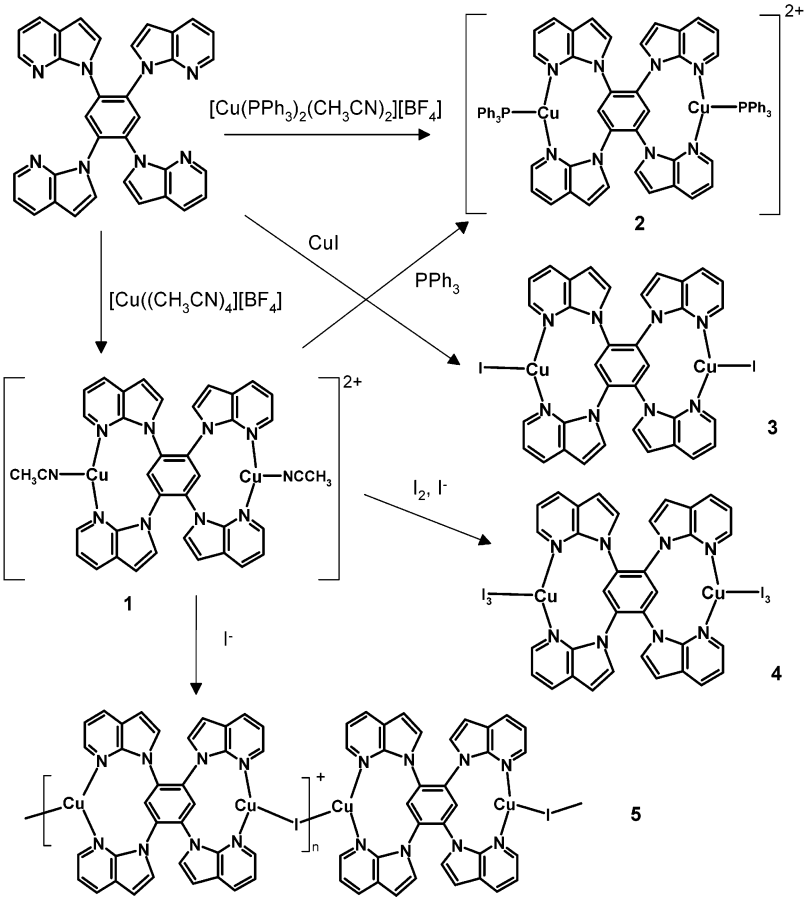
1		**2**		**4**		**5**	
Cu(1)−N(1)	2.005(3)	Cu(1)−N(1)	2.034(4)	Cu(1)−N(2)	2.027(9)	I(1)−Cu(1)	2.537(2)
Cu(1)−N(3)	2.001(4)	Cu(1)−N(3)	2.061(4)	Cu(1)−N(3)	1.994(9)	Cu(1)−N(1)	1.960(13)
Cu(1)−N(5)	1.971(4)	Cu(1)−P(1)	2.2189(14)	Cu(1)−I(1)	2.5123(17)	Cu(1)−N(3)	1.996(13)
N(5)−Cu(1)−N(3)	109.68(15)	N(1)−Cu(1)−N(3)	113.90(17)	I(1)−I(2)	3.0605(12)	Cu(1)−I(1)−Cu(1′)	96.82(9)
N(5)−Cu(1)−N(1)	113.46(16)	N(1)−Cu(1)−P(1)	129.76(13)	I(2)−I(3)	2.8014(12)	N(1)−Cu(1)−N(3)	126.3(5)
N(3)−Cu(1)−N(1)	133.72(13)	N(3)−Cu(1)−P(1)	111.12(12)	N(3)−Cu(1)−N(2)	118.9(4)	N(1)−Cu(1)−I(1)	113.9(4)
				N(3)−Cu(1)−I(1)	129.3(3)	N(3)−Cu(1)−I(1)	118.3(4)
				N(2)−Cu(1)−I(1)	110.8(3)		
				Cu(1)−I(1)−I(2)	106.95(5)		
				I(1)−I(2)−I(3)	179.41(4)		

NMR. The coordinated CH_3CN in **1** can be readily exchanged by phosphine ligands, as evidenced by the isolation of the colorless complex **2** in 84% yield from the reaction of 2 equiv of PPh_3 with **1**. Complex **2** is relatively stable due to the coordination of the bulky PPh_3 ligand to the Cu(I) center, as evidenced by the fact that its ^{1}H NMR spectrum does not show any obvious change after being kept for several days under air. Complex **2** was also obtained in good yield by the direct reaction of ttab with 2 equiv of $[Cu(CH_3CN)_2(PPh_3)_2][BF_4]_2$. The loss of one PPh_3 ligand from the Cu(I) center is likely caused by the steric interaction between PPh_3 and the 7-azaindolyl groups of ttab in **2**, as revealed by the crystal structure of **2**. The air-stable light yellow complex **3**, which has poor solubility in most organic solvents, was synthesized by the direct reaction of CuI with ttab. The reaction of $LiCH_3$ with complex **3** was carried out in an attempt to synthesize $[Cu_2(ttab)(CH_3)_2]$. The treatment of the suspension of **3** in dry Et_2O by $LiCH_3$ at 0 °C yielded a colorless solution. However, attempts to isolate the product were unsuccessful due to its rapid decomposition at ambient temperature.

The dark red complex **4** and the yellow complex **5** were initially isolated from the reaction mixture of complex **1** with I_2, and their structures were determined by X-ray crystallography analyses. The presence of the I_3^- anion in **4** or the I^- anion in **5** indicates the occurrence of a redox reaction involving I_2. We believe that a small amount of Cu(I) reacted with I_2 to produce I^- which in turn reacted with I_2 to form the I_3^- anion. The syntheses of complex **4** and **5** were also achieved by direct preparative methods. The reaction of **1** with 2 equiv of NBu_4I and 2 equiv of I_2 produced **4** in ~40% yield. The reaction of **1** with 1 equiv of NBu_4I afforded **5** in 58% yield. The synthetic procedures for complexes **1**−**5** are summarized in Scheme 1.

Attempts to synthesize the mononuclear complexes $[Cu(ttab)(CH_3CN)][BF_4]$ and $[Cu(ttab)(PPh_3)][BF_4]$ were also carried out with the intention to use these complexes as starting materials for heterobimetallic compounds. However, all our attempts for the mononuclear complexes by adjusting the ratio of ttab versus Cu(I) led to the isolation of the dinuclear complexes. These results demonstrate the high preference of ttab to the formation of dinuclear complexes. This may be caused by the relative orientation of the 7-azaindolyl groups in the coordinated ttab ligand, which upon the coordination of the first Cu(I) ion can cause the reorientation of the remaining two 7-azaindolyl groups such that it leads to a faster nucleophilic attack toward the next Cu(I) ion, resulting in the isolation of its dinuclear complex.

Scheme 1



The preference by the ttab ligand to coordinate to two metal centers is consistent with our previous findings in ttab complexes[6] of Pd(II), Pt(II), and Zn(II).

Complexes **1**−**5** were fully characterized by NMR spectroscopy and elemental analyses. The vacuum-dried complex **1** shows no peaks between 2250 and 2350 cm^{-1} in the IR spectrum, indicating the loss of the coordinated CH_3CN, as further confirmed by elemental analyses. Thermogravimetric analysis indicated that the loss of CH_3CN in **1** occurs at ∼40 °C and is complete at ∼105 °C (see Supporting Information). The chemical shift of $^{31}P\{^1H\}$ of **2** in CD_2Cl_2 is −0.16 ppm at room temperature, comparable with previously reported Cu(I) PPh_3 complexes.[5] To establish the bonding mode of the ttab ligand in the complexes, the structures of **1**, **2**, **4**, and **5** were determined by single-crystal X-ray diffraction analyses. The structure of complex **3** was not analyzed by X-ray diffraction analysis due to the lack of suitable crystals.

Structures of Complexes 1, 2, 4, and 5. The structures of the cations in compounds **1**, **2**, and **5**, and the molecular structure of **4** are shown in Figures 1−4, respectively. The BF_4^- anion is omitted for clarity for **1**, **2**, and **5**. The dinuclear units of all four structures possess a crystallographically imposed inversion center. The common feature among the four compounds is that the Cu(I) center is three-coordinate with an approximate trigonal planar geometry and the ttab ligand is chelated to the Cu(I) center in the 1,3-chelation mode in all four structures with CH_3CN, Ph_3P, I_3^-, or I^- occupying the third coordination site. The four Cu−N$_{aza}$ bond lengths in the four complexes are nearly identical, as shown in Table 2, and are close to those in $[Cu(H_2CPz'_2)(CH_3CN)]ClO_4$ (1.997 Å),[10] $[Cu(dmp)(CH_3CN)]PF_6$ (2.027 Å),[11] and $[Cu(Phen)(CH_3CN)]BF_4$ (2.014 Å).[12]

For metal ions that have a square planar geometry, the 1,2-chelation mode of ttab has been observed exclusively.[6,7] For d^{10} metal ions that prefer a tetrahedral geometry, the preferred bonding mode is 1,3-chelation because it minimizes the interactions between the ligands on the metal center and the ttab ligand. The 1,3-bonding mode has been observed for a dinuclear Ag(I) complex where two $Ag(NO_3)(DMSO)$ groups are chelated to the ttab ligand.[6] An exception to the 1,3-chelation mode by a d^{10} metal ion was observed in the dinuclear complex Zn_2Cl_4(ttab) where the two $ZnCl_2$ units are chelated to the ttab ligand in a 1,2-chelation mode with a highly distorted tetrahedral geometry.[6] The preferential formation of the 1,3-chelation mode by the complexes **1**, **2**, **4**, and **5** can be attributed to the geometrical constraint imposed by the three-coordinate Cu(I) center which requires the N−Cu−N chelate ligand to be near 120°, which is difficult to achieve with the 1,2-chelating mode (the largest N−M−N bond angle we have observed in the 1,2-chelation mode is 97° in the dinuclear Zn(II) complex). The N(1)−Cu(1)−N(3) chelate angle in **1** was in fact determined to be

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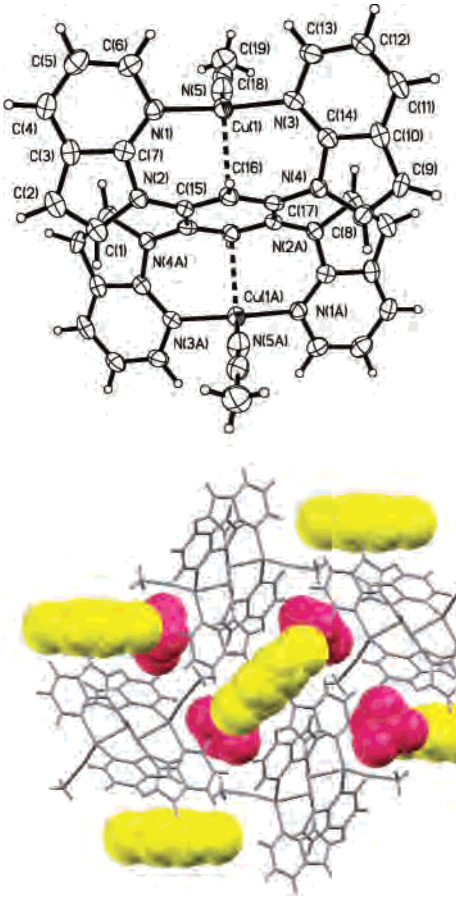

Figure 1. Top: Diagram showing the structure of the dinuclear unit in **1**. Bottom: Unit cell packing diagram projected down the *a* axis, showing the solvent channels in the lattice. The BF_4^- (red) and toluene (yellow) are shown in space-filling style.

133.72(13)°. In contrast, the same angle in **2** is much smaller, 113.90(17)°, which is clearly caused by the bulky PPh_3 group. For **4** and **5**, the N−Cu−N chelate angle is close to an ideal trigonal planar geometry (118.9(4)° and 126.3(5)°, respectively).

An important feature revealed by the structure of **1** is that, despite the relative small size of the CH_3CN ligand and its abundance in solution when **1** is produced, the Cu(I) center in **1** is only coordinated to one CH_3CN ligand. Cu(I) ions are known to have the tendency to form four-coordinate compounds. Three-coordinate Cu(I) compounds, albeit becoming increasingly abundant, are still less common than four-coordinate ones.[1] A close examination of the structure of **1** revealed the presence of a short separation distance between the Cu(I) center and one of the carbon atoms (C(16)) in the central benzene ring, as evidenced by the Cu(1)···C(16) distance of 2.383(4) Å. Although this distance is much longer than a typical Cu−C bond length, it is close to the previously reported weak d−π interaction distances between a Cu(I) center and an aryl ring[1d,13,14] and much shorter compared to the sum of van der Waals radii 3.10 Å of Cu and carbon atoms; a weak interaction between the central benzene ring and the Cu center is therefore likely present in **1**. If we consider C(16) as a weakly bound donor atom, the Cu(I) center has an approximate tetrahedral geometry (the angles of C(16)···Cu(1)−N range from 87.99(14)° to 114.63(16)°). Hence, the three-coordinate geometry of the Cu(I) center in **1** may be attributed to the interaction between the Cu center and the central ring which effectively blocks the fourth coordination site. In other words, the geometry constraint imposed by the ttab ligand appears to stabilize or favor the formation of three-coordinate Cu(I) centers. In the structure of **2**, a similar interaction between the Cu center and the central phenyl ring is also evident, as shown in Figure 2, although the separation distance between the Cu atom and the carbon atom (C(2)) is considerably longer (2.454(4) Å) than that in **1**, clearly due to the presence of the bulky PPh_3 ligand. For **4** and **5**, short separation distances between the Cu center and the central benzene ring (C(16)) are also present (Cu(1)···C(16) = 2.361(12) Å in **4**, Cu(1)···C(16) = 2.377(12) in **5**), which are much shorter than that in **2** but similar to that in **1**. The persistent three-coordinate

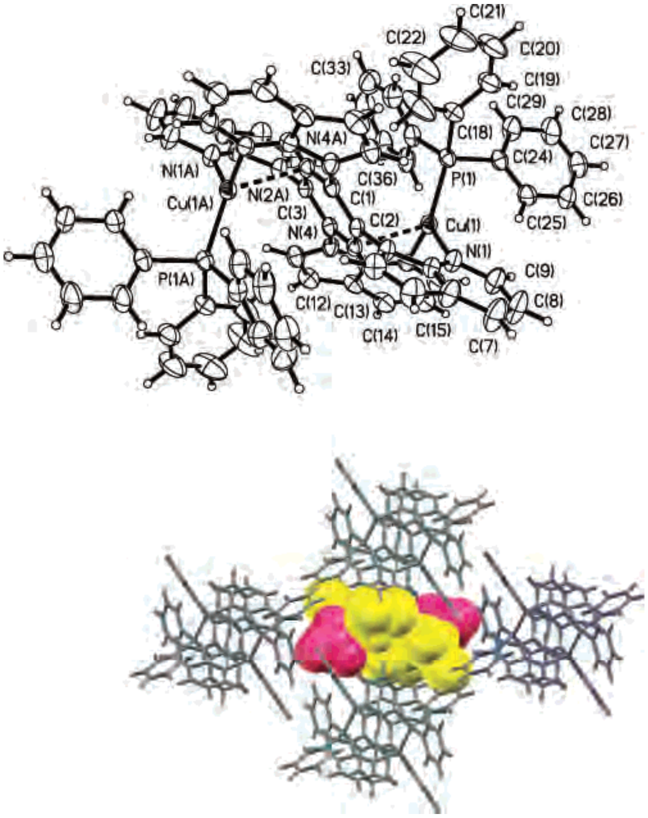

Figure 2. Top: Diagram showing the structure of the dinuclear unit in **2**. Bottom: Unit cell packing diagram projected down the *a* axis, showing the solvent channels in the lattice. The BF_4^- (red) and CH_2Cl_2 (yellow) are shown in space-filling style.

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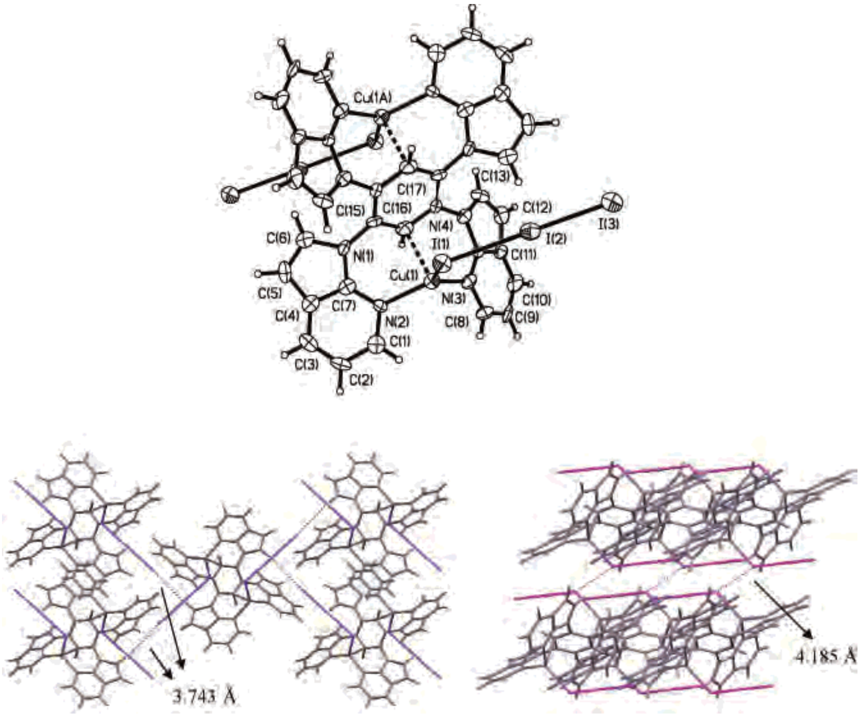

Figure 3. Top: Diagram showing the structure of the dinuclear unit in **4**. Bottom: Unit cell packing diagram projected down the *a* axis (left) and *b* axis (right), showing the intermolecular interactions between the I_3^- ligands.

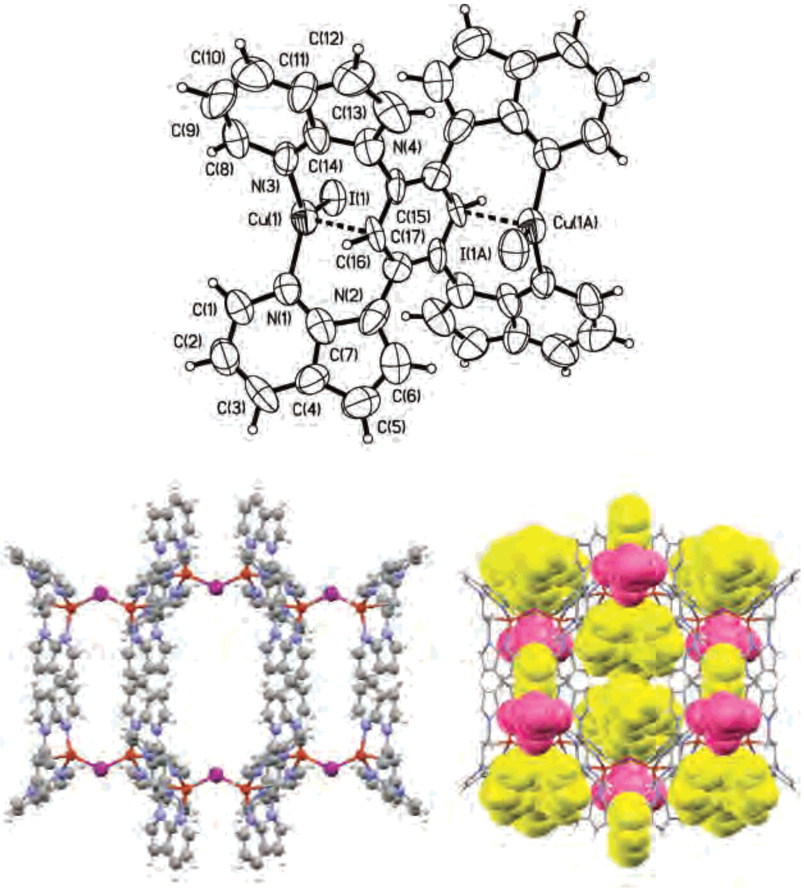

Figure 4. Top: Diagram showing the structure of the dinuclear unit in **5**. Bottom, left: Unit cell packing diagram projected down the *c* axis, showing the iodide-bridged 1D polymer chains without the BF_4^- and solvent molecules removed. Bottom, right: The same unit cell packing diagram with the BF_4^- (red) and the disordered solvent molecules (yellow) being shown in space-filling style.

geometry of Cu(I) in all four complexes is therefore consistent with the presence of weak interaction between the central benzene ring and the copper center, imposed by the geometry of the ttab ligand. The Cu···Cu separation distance within the dinuclear unit is 6.133, 6.313, 6.064, and 6.045 Å for **1**, **2**, **4**, and **5**, respectively.

The Cu−N (CH_3CN) bond distance in **1**,1.971(4) Å, is comparable to those reported in the four-coordinate Cu(I) complexes containing the CH_3CN ligand[15] but significantly longer than the Cu−$NCCH_3$ bond lengths in the three-coordinate Cu(I) complexes containing 1,10-phen chelate[11] (1.852(7) Å), bis(3,5-dimethylpyrazol-1-yl)methane chelate[10] (1.879(4) Å), and Tolman's *β*-diketiminate chelate[1a−1c] (1.859(4)−1.862(4) Å) and the two-coordinate complex[16] $[Cu^I(CH_3CN)_2][B(C_6F_5)_4]$ (1.844(2) Å). The relatively long Cu−N (CH_3CN) bond distance in **1** may account for the facile dissociation of the coordinated CH_3CN ligand in **1**. The Cu−P bond distance in **2** (2.219(2) Å) is similar to previously known Cu−P distances.[5]

Each Cu(I) center in **4** is bound by one I_3^- anion. Although Cu(I) complexes that contain a I_3^- ligand were reported previously,[17] to the best of our knowledge, complex **4** is the first reported example of three-coordinate Cu(I) complexes with a I_3^- ligand. The Cu−I bond length in **4** is 2.5123(17) Å, the I(1)−I(2) bond length, 3.0605(12) Å, is considerably longer than that of I(2)−I(3), 2.8014(12) Å, but similar to those reported in the literature.[18] The I_3^- anion has a nearly perfect linear geometry with the I(1)−I(2)−I(3) bond angle being 179.41(4)°. In the crystal lattice, the molecules of **4** have wavelike layered structures with the dinuclear Cu_2 units being sandwiched by the I_3^- anions. The I_3^- form layered structures with weak intermolecular I···I interactions. Within each layer, the neighboring I_3^- anions have a T-shaped arrangement with the I···I contact distance being 3.743(1) Å, as shown by the unit cell packing diagram projected down the *a* axis in Figure 3. Between two neighboring layers, the I_3^- anions interact in a zigzag manner with the I···I contact distance being 4.185(1) Å, as shown by the unit cell packing diagram shown projected down the *b* axis in Figure 3. Both T-shaped and zigzag-style I···I interactions between I_3^- anions have been observed previously.[18].

In the dinuclear unit of **5**, each Cu center is bound by a I^- ligand with a Cu−I bond length of 2.537(2) Å, similar to that observed in **4**. The iodide ligand in **5** acts as a bridging ligand by coordinating to two Cu(I) centers with a Cu−I−Cu bond angle of 96.82(9)°, thus linking two neighboring Cu_2 units together to form a 1D zigzag coordination polymer, as shown in Figure 5. The Cu−Cu separation distance bridged by the I^- ligand is 3.795(2) Å, much shorter than that within the dinuclear unit, but longer than the sum (3.40 Å) of van der Waals radii of two Cu atoms, indicating no Cu−Cu interaction. Cu(I) coordination polymers that contain an iodide bridge are known previously.[19] However, all previous reported examples involving iodide bridging ligands are all four-coordinate Cu(I) compounds.[19]

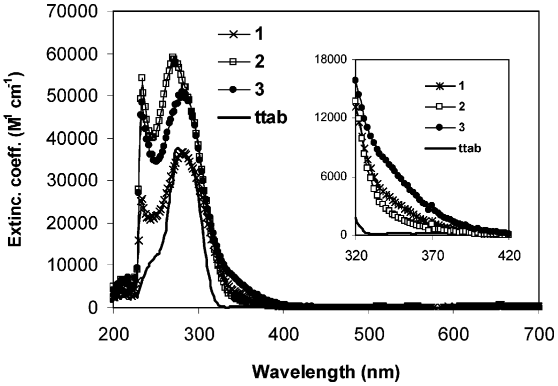

Figure 5. UV−vis absorption spectra of **1**−**3** and ttab in CH_2Cl_2 (∼10^{-5} M).

The crystals of **1**, **2**, and **5** all host solvent guest molecules inside the lattice. For **1**, the cationic dinuclear units are arranged in such a manner that 1D channels along the *a* axis are formed which host the BF_4^- and the toluene solvent molecules, as shown in Figure 1. For **2**, similar 1D channels are present in the lattice which host CH_2Cl_2 solvent molecules and BF_4^- (Figure 2). For **5**, 1D coordination polymer chains stack on top of each other in a parallel fashion that results in the formation of highly porous crystal lattice (∼35% of the volume of the unit cell is occupied by solvent molecules) with rectangular channels, as shown by the lattice packing diagram projected down the *c* axis (Figure 4). The larger channels appear to host disordered toluene and THF solvent molecules (not all solvent molecules were located due to the quality of the crystal), and the smaller channels host BF_4^- and toluene solvent molecules. The trapped solvent molecules escape from the crystal lattice readily at ambient temperature, as supported by the elemental analysis results of these compounds (crystalline samples were used). The tendency of the ttab copper(I) complexes to form porous crystal lattices that can host solvent molecules is consistent with our previous observation for the crystals of ttab Zn(II), Pd(II), and Pt(II) complexes.[6]

Electronic and Luminescent Properties. Compound **1** displays a broad irreversible oxidation peak at ∼1.1 V in the CV diagram in DMF (the $FeCp_2$ oxidation peak appears at 0.57 V under the same condition) which can be assigned to the oxidation of Cu(I) to Cu(II). Compound **2** displays two irreversible oxidation peaks at 0.80 and 1.10 V, respectively, which may be assigned to the oxidation of the two Cu(I) centers in **2**, indicative of the possible presence of electronic communication between the two Cu(I) centers in **2**. For compounds **3**−**5**, CV diagrams could not be obtained due to their poor solubility.

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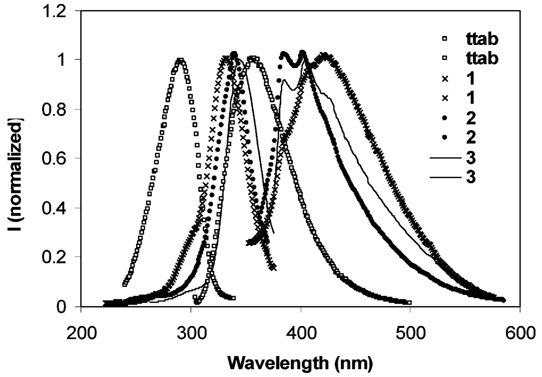


Figure 6. Normalized excitation and emission spectra of **1**−**3** and ttab in CH_2Cl_2 (~10^{-5} M) at ambient temperature.

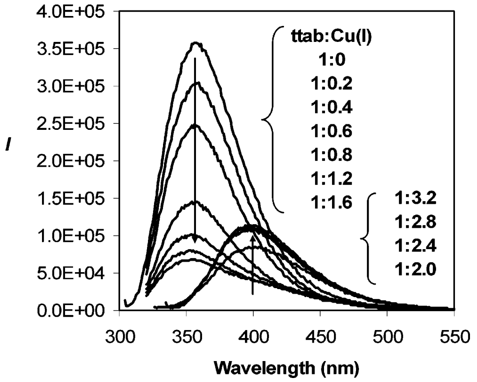
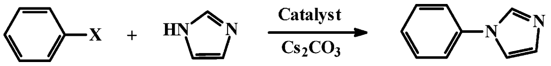


Figure 7. Emission spectral change of ttab in CH_2Cl_2 (1.0×10^{-5} M) with the addition of $[Cu(PPh_3)_2(CH_3CN)_2][BF_4]$ at ambient temperature.

The absorption spectra of complexes **1**−**3** have several intense absorption bands in the region of 200−350 nm which resemble those of the free ttab ligand as shown in Figure 5. For compounds **3**, a very weak and broad metal-to-ligand charge-transfer (MLCT) band in the 320−420 nm region was observed which accounts for its pale yellow color in solution (inset, Figure 5). The absorption spectra of **4** and **5** were not recorded due to their poor solubility. At ambient temperature, the solids of compounds **1**−**5** do not display any detectable emission when excited by UV light. In contrast, the free ttab ligand is a fairly bright blue emitter in the solid state.[6] In CH_2Cl_2 solution, complexes **1**−**3** emit a blue color with the emission wavelength being red-shifted significantly, compared to that of ttab (Figure 6). However, the emission intensity of the complexes is much weaker, compared to the free ligand in the same concentration. To demonstrate the impact of the Cu(I) coordination on the fluorescence of the ttab ligand, a titration experiment was carried out where an incremental amount of $[Cu(PPh_3)_2(CH_3CN)_2][BF_4]$ was added to the ttab solution (1.0×10^{-5} M) in CH_2Cl_2 while the excitation and emission spectra of the solution were monitored. As shown in Figure 7, in the low concentration range, the addition of the Cu(I) compound causes dramatic quenching of the ttab emission intensity without significantly altering the emission wavelength. After the addition of 1 equiv of Cu(I), the intensity change becomes less dramatic but significant red-shift of the emission wavelength occurs. After the addition of ~2.4 equiv of the Cu(I) compound, no further spectral change is observed. The emission spectrum of the ttab solution with 2.4 equiv of $[Cu(PPh_3)_2(CH_3CN)_2][BF_4]$ matches very well with that of **2** in CH_2Cl_2 (Figure 6), an indication that the emission spectrum is indeed from the ttab complex ($[Cu(PPh_3)_2(CH_3CN)_2][BF_4]$ has a very weak emission in the same region, but its intensity is less than 5% of that of **2** when recorded using the same concentration). The titration experiments using $[Cu(CH_3CN)_4][BF_4]$ or CuI were not performed due to the poor stability of the former and the poor solubility of the latter. Nonetheless, the intensity of the fluorescent spectra of **1** and **3** is $\leq$5% of that of ttab recorded using the same concentration. The emission spectra of **1**−**3** and the results of the titration experiments of ttab with $[Cu(PPh_3)_2(CH_3CN)_2][BF_4]$ established unequivocally that the coordination of the Cu(I) center to the ttab ligand causes drastic quenching of the emission intensity of the ttab ligand and shifts its emission energy to a longer wavelength. Similar fluorescent quenching of ttab by other d^{10} metal ions such as Ag(I) and Zn(II) has been observed previously.[6] At 77 K, using a time-resolved phosphorescent spectrometer, no MLCT emission band was observed for all three complexes but only the short-lived ligand-based emission was detected, a behavior that is in sharp contrast to the Cu(I) complexes of 2-(2′-pyridyl)-benzimidazolyl[5a−5b] and 2-phenylbenzimidazolyl[5c] derivative ligands where the ligand is either chelated to the Cu(I) center[6a−6ab] or bound to the Cu(I) center as a terminal ligand[5c] and the complexes display exclusively MLCT emission with a long decay lifetime. On the basis of the fluorescent titration data and the time-resolved spectral data, we conclude that the emission of the Cu(I) complexes is ligand-based.

Reactivity of Complex 1. One of the important applications involving Cu(I) compounds is their use as catalysts in Ullmann condensation reactions for the formation of C−N bonds.[2,3] Although different forms of copper, including the metal itself, the Cu(I) or Cu(II) salts, and the oxides have been found to be able to catalyze the C−N coupling reactions, earlier mechanistic study revealed that the active species is the Cu(I) ion.[2] Traditional Ullmann condensation reactions require the use of high temperature and highly polar solvents, which greatly limits its scope of applications.[2] In 1999, Buchwald reported that the efficient Ullmann-type *N*-arylation of imidazoles can be achieved by using $(CuOTf)_2\cdot$benzene/1,10-phen as the catalyst and xylenes as the solvent at relatively low temperature.[3a] Since then, a variety of new ligand systems, along with different bases and solvents, have been examined to further improve the Ullmann condensation reactions.[3b−3j] However, all previous studies focused on mononuclear Cu(I) systems and no study on the use of dinuclear Cu(I) compounds as catalysts in Ullmann condensation reactions have been reported to date. We therefore decided to investigate if our dinuclear Cu(I) compound **1** can be used as an effective catalyst for C−N bond formation reactions. In our investigation, the condensation reaction of phenyl halides with imidazole was examined. The catalytic activity of complex **1** was compared with the CuI/1,10-phen system, reported by Buchwald's group in Ullmann condensation reactions.[3] Complex **2** was not investigated because the bulky PPh_3 ligand blocks the Cu(I) coordination site, making

Table 3. *N*-Arylation of Imidazole with Phenyl Halides



entry	Ph−X	catalyst	*T* (°C)/time	yield (%)[a]
1	Ph−I	CuI	145/19 h	<3
2	Ph−I	CuI/1,10-Phen (1:2)	145/19 h	95
3	Ph−I	$[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$	145/19 h	97
4	Ph−Br	CuI/1,10-Phen (1:2)	165/48 h	91
5	Ph−Br	$[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$	165/48 h	62
6	Ph−Br	$[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$/ttab (1:1)	165 /48 h	73
7	Ph−Cl	CuI/1,10-Phen (1:2)	165/72 h	trace[b]
8	Ph−Cl	$[Cu_2(ttab)(CH_3CN)_2][BF_4]_2$	165/72 h	trace[b]

[a] Isolated yield (±3%, average of two runs). [b] Based on TLC. All reactions were carried out with 1.0 mmol of imidazole, 2.0 mmol of Cs_2CO_3, 0.10 mmol of copper catalysts (based on copper) in 1.0 mL of phenyl halide, which was used both as the reagent and the solvent.

2 an unlikely candidate for Ullmann condensation reactions. Compounds **3**−**5** were also not examined for Ullmann condensation reactions because of their poor solubility in organic solvents. The results of our preliminary study are summarized in Table 3. The experimental data showed that the order of reactivity of the phenyl halides is PhI > PhBr > PhCl with the chlorobenzene being most inert toward coupling reactions with imidazole under the condition used, and that the *N*,*N*-chelate ligand is critical for the aryl C−N bond formation reactions (entry 1). These observations are in good agreement with the literature.[2,3] For the reaction of phenyl iodide, the performance of complex **1** is comparable to that of CuI and 2 equiv of 1,10-phen. The advantage for **1** here is that the addition of free ttab ligand is not necessary. For the reaction of phenyl bromide, the reaction has to be carried out at a temperature higher than that for phenyl iodide, and the reaction catalyzed by **1** has a lower yield than that catalyzed by CuI/1,10-phen, indicating that the simple CuI/1,10-phen system as a catalyst is better than the dinuclear compound **1**. To enhance the reactivity of **1**, 1 equiv of ttab ligand (relative to **1**) was added (entry 6 in Table 3), which led to an ∼10% increase of the yield, but still lower than the CuI/1,10-phen system. The relatively low activity of complex **1**, compared to that of CuI/1,10-phen, could be caused by its instability (ligand dissociation) at high temperature. Compared to 1,10-phen, which is an effective chelate ligand due to the formation of five-membered chelate ring, the ttab ligand forms a 10-membered chelate ring in the 1,3-bonding mode in **1**, which is clearly more prone to dissociation than the five-membered chelate ring formed by 1,10-phen.

Inspired by the work reported by Tolman and others on the reaction of O_2 with three-coordinate Cu(I) compounds[1] that have a coordination environment similar to that of complex **1**, we examined the reaction of complex **1** with O_2 by UV−vis spectroscopy. We monitored the dioxygen reaction with complex **1** at ambient temperature (currently we do not have the setup that allows accurate recording of UV−vis at low temperature.). As shown by the data in Figure 8, compound **1** in THF has two intense absorption bands with $\lambda = 262$ and 292 nm, respectively. The introduction of O_2 to the solution of **1** in THF led to the blue-shift of the absorption band at 262 nm to 244 nm. In addition to the blue-shift, the intensity of this band also increased substantially with the addition of O_2. After the addition of ∼16 mL of O_2 to a 2.5 mL solution of **1** (∼1.0×10^{-5} M), no further spectral change was observed. The colorless solution of **1** did not show any obvious color change during and after the addition of O_2. Colorless precipitation was observed. The spectral change was not caused by the dissociation of the ttab ligand, as shown by the free ttab UV−vis spectrum (Figure 8, inset). Our attempts to characterize and identify the oxidized products have not been successful.

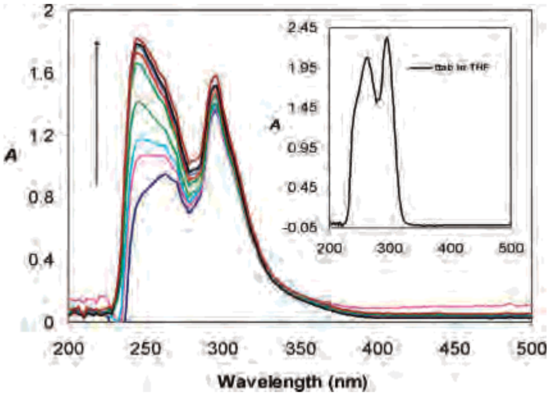


Figure 8. UV−vis spectra of compound **1** in THF, recorded at ambient temperature, with the addition of O_2 gas. (The concentration of **1** is ∼10^{-5} M. Eight portions of 2 mL of O_2 at 1 atm were introduced to the solution (2.5 mL) at an ∼3 min interval. The spectra were recorded at an ∼1 min interval, and not all the recorded spectra are shown.)

In summary, the ttab ligand has been shown to form dinuclear Cu(I) compounds readily, prefers the 1,3-chelation mode when bound to a Cu(I) center and favors the 3-coordinate geometry by Cu(I). In all dinuclear complexes, close contact between the central benzene ring and the Cu(I) center is present, which may play a role on the stability and reactivity of the complex. The ttab complexes have the tendency to trap solvent molecules in the crystal lattice. The coordination of the Cu(I) center to the ttab ligand partially quenches the emission of the ttab ligand and shifts the emission energy to a longer wavelength. The CH_3CN complex **1** displays a catalytic activity in the phenyl halide coupling reactions with imidazole, comparable to but not better than that of CuI/1,10-phen. In addition, preliminary UV−vis data indicate that compound **1** reacts with O_2 readily, but further research is needed to establish the detail of this oxidation reaction and the fate of the Cu(I) complex.

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Supporting Information Available: Complete X-ray diffraction data for **1**, **2**, **4**, and **5** including tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen parameters; TGA diagram for **1** and cyclic voltammetry diagrams for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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