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Research paper

Structure of copper(I) and silver(I) complexes with zwitterionic ligands derived from *N*-Heterocyclic Carbenes

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ABSTRACT

N-Heterocyclic Carbene (NHC) ligands have been instrumental in the synthesis of novel metal and main group-containing compounds, as well as their subsequent reactivity. Here, the coordination chemistry of CS_2 and PhNCS derivatives of the sterically encumbering 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) are studied. The reaction of IPr•CS_2 with Cu(I) and Ag(I) salts results in the isolation of dinuclear complexes, $[(\text{IPr•CS}_2)_2M_2(\text{THF})_n][X]_2$, M = Cu, X = PF_6, n = 4; M = Ag, X = OTf, n = 2. The 1:1 stoichiometric reaction of IPr•PhNCS with CuI results in to the formation of $([\text{IPr•PhNCS})_2\text{Cu}][\text{CuI}_2]$. All complexes were characterized by ^{1}H, ^{13}C, and IR spectroscopy and their solid-state structures determined by X-ray crystallography.

1. Introduction

Since their initial discovery [1–3], *N*-Heterocyclic Carbene (NHC) ligands have been transformational with respect to the coordination chemistry [4–6], reactivity [7,8], and catalysis[9–11] of main group and transition metal complexes. The steric and electronic properties of NHCs are readily tunable, and can be functionalized with other small molecules such as CS_2 and PhNCS [12–19]. These derivatives have been shown to bind to transition metals with varying coordination modes [20–26], such as monodentate, I [27–29], bidentate, II [30–34], and bridging, III [35–38], coordination modes, Fig. 1. However, the coordination chemistry of these zwitterionic ligands is limited [39].

Given the ability for these zwitterionic ligands to (Fig. 2) bridge metal ions, we were interested in examining their coordination chemistry with coinage metals. Our group's previous efforts have included investigation of ligands that form multimetallic Cu(I) complexes to study complexes featuring mode III in Fig. 1 more closely [40,41]. Since zwitterionic functionalized NHC ligands have been shown to display these coordination modes, we endeavored to study their coordination properties further. Given the interest in coinage metals for catalytic activity [42], photochemical [43] and anti-microbial properties [44], as well as the attention that NHC ligands have received [45,46], we investigated the coordination of these zwitterions with Cu(I) and Ag(I) salts. Herein, we describe the structures of four new compounds based on the IPr NHC ligand: two with the carbon disulfide and two with phenylisothiocyanate derivative. The Cu(I) and Ag(I) complexes are dinuclear with the IPr•CS_2 ligand, while the IPr•PhNCS complex features a two-coordinate Cu(I) metal center.

2. Results and discussion

The carbon disulfide functionalized NHC, 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-dithiocarboxylate (IPr•CS_2), **1**, was synthesized as previously reported [25]. Reaction of **1** with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in 1:1 stoichiometric ratio resulted in a dark brown colored solution, Scheme 1. The ^{1}H NMR spectrum showed conversion to a single product, which was collected in quantitative yield upon workup. Two resonances (in CD_3CN) are observed for the methyls of the isopropyl groups at 1.06 and 1.11 ppm while only one resonance, at 2.41 ppm, is seen for the methine proton. The quaternary carbon in the dithiocarboxylate moiety is located at 204.7 ppm in the ^{13}C{^{1}H} NMR spectrum. The IR spectrum showed absorptions at 1470 and 1065 cm^{-1} for the asymmetric imidazolium N_2C moiety and asymmetric C—S stretches [23], respectively. The strong absorption at 844 cm^{-1} is presumably the P-F asymmetric stretch. Crystals suitable for X-ray diffraction analysis were obtained from a saturated THF solution at −25 °C. The solid-state structure, Fig. 1, showed a dinuclear copper(I) complex with two IPr•CS_2 ligands, $\text{Cu}_2[\text{IPr•CS}_2]_2(\text{PF}_6)_2(\text{THF})_4$, **2**. The crystal had two unique molecules in the unit cell, one with a plane of symmetry making only one set of bond distances and angles. The structure is reminiscent of many dinuclear

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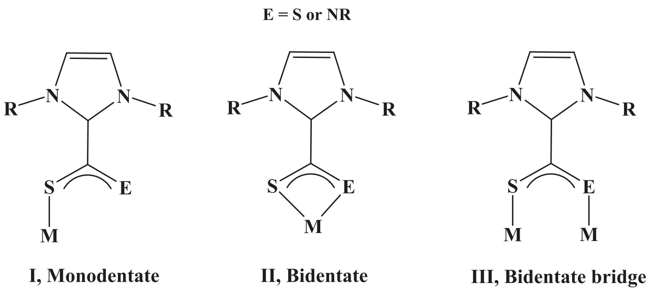


Fig. 1. Possible coordination modes of functionalized NHC ligands.

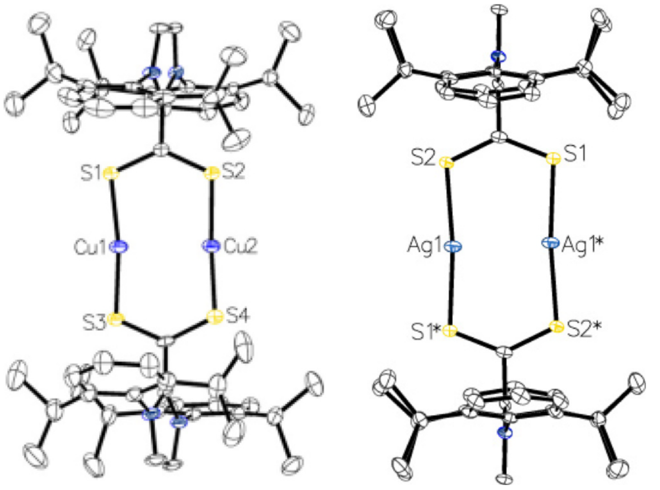


Fig. 2. Thermal ellipsoid plots of **2** (left) and **3** (right) shown at the 50% probability level. The outer sphere anions, coordinated THF molecules, and hydrogens have all been omitted for clarity.

copper dithiocarbamate complexes that have been crystallographically characterized [47–49]. Two IPr•CS_2 zwitterions and two THF molecules coordinate to each copper(I) center with one sulfur from each ligand bound to a different copper. Two PF_6 anions are outer sphere for charge balance. The Cu1-S1 and Cu1-S3 bond distances are 2.2078(15) and 2.2030(15) Å, respectively, while the Cu2-S2 and Cu2-S4 distances are 2.2065(15) and 2.2112(16) Å, respectively. These Cu-S distances are only slightly longer than observed with sterically encumbering terphenyl anionic ligated Cu(I) complexes. For example, the Cu-S distances in $Cu_2[S_2C(2,6\text{-}(Trip)_2C_6H_3)]_2(NCCH_3)$ range from 2.004(2) – 2.2205(5) Å [40]. The Cu1-O1(THF) bond distance is 2.161(5) Å, while the Cu1-O2(THF) distance is quite long at 2.585(5) Å. The Cu2-O3(THF) and Cu2-O4(THF) bond lengths are 2.095(4), and 2.321(5) Å. The O1-Cu1-O2 and O3-Cu2-O4 bond angles are 103.25(5) and 96.05(19)°. The Cu-Cu distance is 2.791(1) Å, which is far longer than the 2.24 Å for a single bond, and longer than most cuprophilic interactions [50]. Hence, no metallophilic interactions occur in **2**.

In a similar manner, **1** was reacted with AgOTf, OTf = trifluoromethanesulfonate, in THF. The ^{1}H and ^{13}C NMR spectra were nearly identical of **2**, and the product was collected in quantitative yield. Pale pink crystals suitable for X-ray diffraction analysis were obtained from a saturated THF solution at −25 °C. The solid-state structure, $Ag_2[IPr\bullet CS_2]_2(OTf)_2(THF)_2$, **3**, Fig. 1, is nearly identical to **2** except with two Ag(I) ions, and only one THF molecule bound to each metal. The Ag1-S1 and Ag1*-S2 bond distances are 2.4320(7) and 2.4303(7) Å, respectively, while the Ag-Ag distance is 2.8979(5) Å. This Ag-Ag distance is also much longer than those found in the dinuclear amidinate complexes, $Ag_2[(2,6\text{-}R_2C_6H_3N)_2C(H)]_2$, of 2.7527(3) Å (R = CH_3), and 2.7544(6) Å (R = ^{i}Pr) [40]. The Ag-O(THF) bond length is 2.478(2) Å. Interestingly, the two THF molecules in **2** are located nearly 90° apart, with a Ag1-Ag1*-O1 angle of 88.24(7)°. The S1-Cu1-Cu2 bond angle in **2** of 93.81(5)° is comparable with the S1-Ag1-Ag1* angle of 91.21(2)°, and the S1-Cu1-S3 bond angle is 156.39(7)° in **2**, is also similar to the S1-Ag1-S1* angle of 158.55(3)° in **3**.

Reaction of IPr with PhNCS results in a neon yellow colored solution at room temperature, Scheme 2. The ^{1}H and ^{13}C NMR spectra indicated clean conversion of the starting material to zwitterionic product, IPr•SCNPh, **4**, which was isolated in 87% yield. While the ^{13}C NMR resonance for the *ipso* carbon of CS_2 fragment in **2** and **3** was located ∼ 200 ppm, the *ipso* carbon of the PhNCS fragment is ∼ 40 ppm upfield at 166 ppm. Although the ^{13}C NMR spectrum of the mesityl-substituted ligand, IMes•SCNPh, was not reported, the gold complex, $[(Ph_3P)Au(SCNPh\bullet IMes)]PF_6$, shows an *ipso* carbon resonance at 153.4 ppm [17]. Crystals suitable for X-ray crystallographic analysis were grown from a saturated toluene solution at −25 °C, Fig. 3. While no isolable product could be obtained from reaction of **4** with $[Cu(NCMe)_4]PF_6$, reaction with CuI in THF, Scheme 2, resulted in a yellow colored solution from which yellow crystals suitable for X-ray diffraction were obtained, revealing the cation–anion pair, $[(IPr\bullet SCNPh)_2Cu][CuI_2]$, **5**, Fig. 3, which exhibits no metallophilic interactions. In addition, no isolable product could be obtained from reaction of **4** and AgI for comparison.

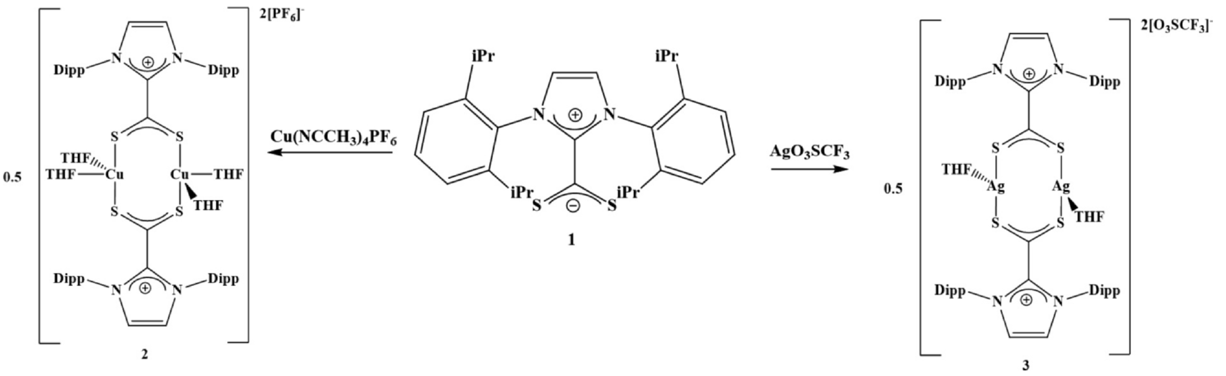
The structure of **5** is reminiscent of mesityl-substituted NHC ligand, IMes•SCNPh, with Au that has been previously reported, $[Au(SCNPh\bullet IMes)_2]PF_6$ [17]. In both complexes, there is a linear geometry about the coinage metal. In **5**, both S-Cu-S and I-Cu-I bond angles are 180°. The C—N bond distance of 1.291(3) Å in **4** is longer than the 1.277(2) Å in **5**, indicating a more localized structure in **5**. This is also observed in the C—S bond of 1.697(3) Å in **4**, which is shorter than the 1.733(2) Å in **5**. The Cu-S bond distances of 2.166(4) Å are similar to the Cu-S distances of 2.1671(8) Å, R = Me; 2.1813(10) Å; R = Et; and 2.2027(7) Å; R = ^{i}Pr, in R_3tacnCu(S = $SbPPh_3$), R_3tacn = 1,4,7-trialkyltriazacyclonones [51].

3. Conclusions

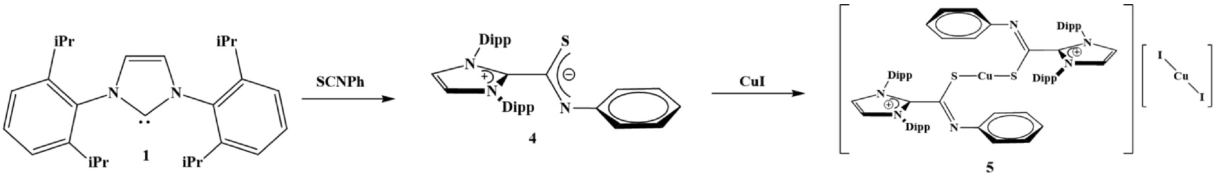
The coordination chemistry of zwitterionic ligands derived from NHCs with carbon disulfide and isothiocyanate has been expanded to the coinage metals, Cu and Ag. Despite the larger steric properties of the diisopropyl groups, no significant structural deviations from the mesityl derivative were observed. Two novel dinuclear copper(I) and silver(I) complexes, which feature long metal–metal distances of over 0.1 Å longer than those found in other dinuclear Cu(I) and Ag(I) complexes, were characterized. Finally, a new ligand, IPr•PhNCS, was synthesized as well as a copper(I) complex formed from ligand redistribution. This report adds to the family of complexes derived from NHC derivatives.

4. Experimental section

General Considerations. The syntheses and manipulations described were conducted under anaerobic (N_2 atmosphere) and anhydrous conditions using Schlenk and glove box techniques. Organic solvents were sparged with N_2 and dried over molecular sieves before use. $[Cu(CH_3CN)_4]PF_6$ (Strem), AgOTf, iodine, and phenylisothiocyanate (Aldrich) were degassed prior to use. 1,3-Bis-(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr) [52] and 1,3-Bis(2,6-diisopropylphenyl)imidazolium-2-dithiocarboxylate (IPr•CS_2), **1** [25], were made as previously described from reaction of IPr with CS_2 in toluene. Acetonitrile-*d*$_3$ (Cambridge Isotope Laboratories) was dried over molecular sieves and degassed with three freeze–evacuate–thaw cycles. ^{1}H and ^{13}C{^{1}H} NMR were recorded on a 300 MHz, 500 MHz, or 600 MHz DRX Bruker spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given relative to the residual solvent peak at δ 1.94 (CD_2HCN) and δ 118.26 ($^{13}CD_3CN$). Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross,



Scheme 1. Synthesis of **2** and **3** from **1**.



Scheme 2. Synthesis of **4** and **5**.

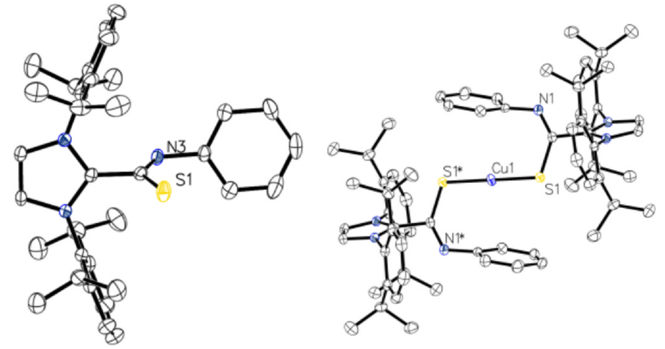


Fig. 3. Thermal ellipsoid plots of **4** (left) and **5** (right) shown at the 50% probability level. The hydrogens, as well as the CuI_2^- counteranion in **5**, have been omitted for clarity.

GA).

$Cu_2[IPr\cdot CS_2]_2(PF_6)_2(THF)_4$, 2. IPr•CS$_2$ (100 mg, 0.22 mmol) was dissolved in THF (10 mL), and 5 mL of $[Cu(CH_3CN)_4]PF_6$ (80 mg, 0.21 mmol) in THF was added to yield a dark brown solution. After stirring at room temperature overnight, the solvent was removed *in vacuo* to yield $Cu_2(IPr\cdot CS_2)_2(PF_6)_2(THF)_3$ in quantitative yield. X-ray quality crystals were obtained from a concentrated THF solution at −25 °C. We note the ^1H and ^{13}C NMR spectra were taken in CD_3CN which displaces the THF, thus no coordinated THF was observed. ^1H NMR (500 MHz, CD_3CN): δ 1.06 (d, 24H, $^3J_{H\text{-}H}$ = 7 Hz, *o*-CH(*Me*)Me), 1.11 (d, 24H, $^3J_{H\text{-}H}$ = 6.5 Hz, *o*-CH(*Me*)Me), 2.41 (sept, 8H, $^3J_{H\text{-}H}$ = 6.5 Hz, *o*-C*H*Me$_2$), 7.26 (d, 8H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-CH), 7.50 (t, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *p*-CH), 7.57 (s, 4H, Im-C*H$_{4,5}$*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 23.6 (CH*Me$_2$*), 25.2 (CH*Me$_2$*), 30.2 (*C*HMe$_2$), 125.5 (*C*$_6$H$_2$), 125.9 (*C*$_6$H$_2$), 132.4 (*C*$_6$H$_2$), 132.5 (*C*$_6$H$_2$), 146.3 (*C*$_6$H$_2$), 147.7 (*C*$_6$H$_2$), 204.7 (N*C*N). IR (KBr, cm^{-1}): 2966(s), 2931(m), 2872(w), 1557(w), 1470(s), 1388(w), 1366(w), 1209(s), 1065(m), 844(s), 558(m). Anal. Calcd for $C_{68}H_{96}Cu_2F_{12}N_4O_4P_2S_4$: C, 51.75; H, 6.13; N, 3.55. Found: C, 51.35; H, 6.43; N, 3.53.

$Ag_2[IPr\cdot CS_2]_2(OTf)_2(THF)_2$, 3. The synthesis was carried out in a similar manner to $Cu_2(IPr\cdot CS_2)_2(PF_6)_2(THF)_3$ with IPr•CS$_2$ (100 mg, 0.22 mmol) and AgOTf (55 mg, 0.21 mmol) to yield $Ag_2(IPr\cdot CS_2)_2(OTf)_2(THF)_2$ in quantitative yield. We note the ^1H and ^{13}C NMR spectra were taken in CD_3CN which displaces the THF, thus no coordinated THF was observed. ^1H NMR (500 MHz, CD_3CN): δ 1.12 (d, 24H, $^3J_{H\text{-}H}$ = 6.5 Hz, *o*-CH(*Me*)Me), 1.15 (d, 24H, $^3J_{H\text{-}H}$ = 6.5 Hz, *o*-CH(*Me*)Me), 2.50 (sept, 8H, $^3J_{H\text{-}H}$ = 6.5 Hz, *o*-C*H*Me$_2$), 7.30 (d, 8H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-CH), 7.54 (t, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *p*-CH), 7.62 (s, 4H, Im-C*H$_{4,5}$*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 22.9 (CH*Me$_2$*), 25.6 (CH*Me$_2$*), 29.0 (*C*HMe$_2$), 124.9 (*C*$_6$H$_2$), 130.6 (*C*$_6$H$_2$), 130.7 (*C*$_6$H$_2$), 147.5 (*C*$_6$H$_2$), 163.4 (*C*$_6$H$_2$), 165.3 (*C*$_6$H$_2$), 219.7 (N*C*N). IR (KBr, cm^{-1}): 3087(w), 2966(s), 2930(m), 2871(m), 1556(w), 1471(s), 1388(w), 1366(w), 1280(s), 1259(s), 1159(s), 1065(m), 1029(s), 805(m), 758(m), 637(s). Anal. Calcd for $C_{66}H_{88}Ag_2F_6N_4O_8S_6$: C, 49.95; H, 5.59; N, 3.53. Found: C, 49.48; H, 5.20; N, 4.11.

IPr•PhNCS, 4. IPr (300 mg, 0.77 mmol) was suspended in hexane (10 mL), and a minimal amount THF was added to the suspension to dissolve the suspension. Phenylisothiocyanate was added to the solution and a neon yellow solid immediately precipitated. The suspension was stirred at ambient temperature for 30 min. The product was then collected by centrifugation, and the solvent was removed under vacuum to yield IPr•PhNCS as a yellow powder (352 mg, 87%). X-ray quality crystals were obtained from a concentrated toluene solution at −25 °C. ^1H NMR (600 MHz, CD_3CN): δ 1.30 (d, 12H, $^3J_{H\text{-}H}$ = 6.6 Hz, *o*-CH(*Me*)Me), 1.37 (d, 12H, $^3J_{H\text{-}H}$ = 6.6 Hz, *o*-CH(*Me*)Me), 3.5 (sept, 4H, $^3J_{H\text{-}H}$ = 6.6 Hz, *o*-C*H*Me$_2$), 6.32 (m, 2H, *m*-NPh), 6.75 (m,1H, *p*-NPh), 6.98 (m, 2H, *o*-NPh), 7.30 (d, 4H, $^3J_{H\text{-}H}$ = 7.8 Hz, *m*-CH), 7.34 (s, 2H, Im-C*H$_{4,5}$*), 7.40 (t, 2H, $^3J_{H\text{-}H}$ = 7.8 Hz, *p*-CH). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 23.1 (CH*Me$_2$*), 25.5 (CH*Me$_2$*), 30.1 (*C*HMe$_2$), 122.3 (*m*-*C*$_6$H$_5$), 122.8 (*p*-*C*$_6$H$_2$), 122.9 (Im-*C*H), 125.0 (*m*-*C*$_6$H$_2$), 128.8 (*o*-*C*$_6$H$_5$), 131.9 (*p*-*C*$_6$H$_2$), 147.4 (*ipso*-*C*$_6$H$_2$), 148.0 (*ipso*-*C*$_6$H$_2$), 153.4 (*ipso*-*C*$_6$H$_5$), 166.3 (N*C*S). IR (KBr, cm^{-1}): 3069(w), 2962(s), 2928(m), 2868(m), 1590(m), 1560(w), 1517(s), 1479(s), 1383(w), 1362(w), 1213(m), 1023(m), 944(s), 801(m), 757(s). Anal. Calcd for $C_{34}H_{41}N_3S_1$: C, 77.98; H, 7.89; N, 8.02. Found: C, 77.66; H, 7.71; N, 8.27.

[(IPr•PhNCS)$_2$Cu] [CuI$_2$], 5. CuI (36.4 mg, 0.191 mmol) was suspended in THF (10 mL) and **4** (100. mg, 0.191 mmol) was added at room temperature. The yellow solution was allowed to stir overnight, was filtered, and concentrated, whereby the product precipitated as X-ray quality crystals upon cooling to −25 °C, (128 mg, 94%). ^1H NMR (600 MHz, CD_3CN): δ 1.18 (d, 24H, $^3J_{H\text{-}H}$ = 7.2 Hz, *o*-CH(*Me*)Me), 1.23 (d, 24H, $^3J_{H\text{-}H}$ = 7.2 Hz, *o*-CH(*Me*)Me), 2.63 (sept, 8H, $^3J_{H\text{-}H}$ = 7.2 Hz, *o*-C*H*Me$_2$), 5.78 (d, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *o*-NPh), 6.67 (t, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, *p*-NPh), 6.94 (t, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-NPh), 7.39 (d, 8H, $^3J_{H\text{-}H}$ = 7.8 Hz, *m*-CH), 7.48 (t, 4H, $^3J_{H\text{-}H}$ = 7.8 Hz, *p*-CH), 7.68 (s, 4H,

Table 1
Crystallography parameters from complexes **2**–**5**.

	2	**3**	**4**	**5**
CCDC deposit number	2012491	2011486	2011489	2011487
Empirical formula	$C_{68}H_{96}N_4O_4P_2F_{12}S_4Cu_2$	$C_{74}H_{104}N_4O_{10}F_6S_6Ag_2$	$C_{34}H_{41}N_3S$	$C_{68}H_{82}N_6S_2I_2Cu_2$
Formula weight (g/mol)	5048.74	1587.54	523.76	1428.39
Crystal habit, color	Prism, brown	Plate, pink	Needle, yellow	Prism, yellow
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Space group	$P2_1/n$	P-1	$P2_1/n$	P-1
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Volume (Å^3)	12618.8(7)	2018.12(14)	6135.1(17)	1667.91
a (Å)	12.8689(4)	12.0074(5)	12.923(2)	11.028(2)
b (Å)	62.1509(17)	12.6737(5)	32.794(5)	12.374(2)
c (Å)	16.1560(5)	14.7243(5)	15.719(3)	14.057(3)
α (°)	90	67.117(2)	90	77.921(2)
β (°)	102.433(2)	75.503(2)	112.934(2)	76.618(2)
γ (°)	90	89.698(3)	90	64.255(2)
Z	2	1	8	1
Calculated density (mg/m^3)	1.329	1.425	1.134	1.422
Absorption coefficient (mm^{-1})	2.541	0.711	0.131	1.669
Final R indices [$I > 2\sigma(I)$]	R = 0.1069	R = 0.0420	R = 0.0514	R = 0.0298
	w$R2$ = 0.2420	w$R2$ = 0.1020	w$R2$ = 0.1184	w$R2$ = 0.0797

Im-C$H_{4,5}$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 23.0 (CHMe_2), 25.5 (CHMe_2), 30.2 (CHMe$_2$), 124.7 (*p*-C$_6$H$_5$), 124.8 (Im-CH), 125.3 (*m*-C$_6$H$_2$), 131.4 (*ipso*-C$_6$H$_2$), 131.7 (*m*-C$_6$H$_5$), 146.6 (*ipso*-C$_6$H$_2$), 148.9 (*ipso*-C$_6$H$_2$), 151.2 (*ipso*-C$_6$H$_5$), 159.8 (NCS). IR (KBr, cm^{-1}): 3075(w), 2963(s), 2928(m), 2868(m), 1590(w), 1550(s), 1477(s), 1445(m), 1387(m), 1210(m), 1181(m), 1060(m), 932(s), 802(m), 755(s). Anal. Calcd for $C_{68}H_{82}N_6S_2I_2Cu_2$: C, 57.18%; H, 5.79%; N, 5.88%. Found: C, 56.99%; H, 5.70%; N, 5.78%.

Crystallographic Data Collection and Structure Determination: The selected single crystal was mounted on a nylon cryoloop using viscous hydrocarbon oil. X-ray data collection was performed at 100(2) K. The X-ray data was collected on a Bruker X8 Prospector equipped with a CCD area detector and a Cu-K$_\alpha$ micorofocus source (λ = 1.54178 Å) for **2**, a Bruker D8 Venture diffractometer with a Photon 100 CMOS detector and a Mo-K$_a$ microfocus source (λ = 0.71073 Å) for **3**, and a Bruker SMART diffractometer with an Apex II CCD detector and a Mo-K$_\alpha$ sealed source with a focusing collimator. The data collection and processing utilized Bruker Apex2 suite of programs [53]. The structures were solved using an iterative dual space approach as implemented in SHELXT [54] and refined by full-matrix least-squares methods on F2 using Bruker SHELX-2014/7 program. All full-occupancy non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and included in the refinement using a riding model. Thermal ellipsoid plots were prepared by using Olex2 [55] with 50% of probability displacements for non-hydrogen atoms. Selected X-ray crystallographic details are provided in Table 1.

The structure of **2** contained disordered THF molecules located on special positions, all parts of which could be refined anisotropically but with unrealistic bond distances that represent averages for non-resolvable positions. Riding H-atoms were not calculated for these molecules although they were included in the formula. **2** also appears to contain disorder of the entire metal complex about a two-fold axis which reverses the direction in which the pyramidal Cu atoms are deflected from the basal planes. The minor component of this disorder is present in very small amounts and is highly overlapping and thus could not be modeled. This unmodeled disorder affects the ADPs of some of the ligand carbon atoms and leads to an unusually large number of outlying reflections where $I_{obs} < I_{calc}$, likely because I_{calc} contains contributions from full occupancy heavy atoms that are actually at slightly less than 100% occupancy.

CRediT authorship contribution statement

Pokpong Rungthanaphatsophon: Investigation, Visualization. **Alexander J. Gremillion:** Investigation, Visualization. **Yuzhong Wang:** Investigation, Visualization. **Steven P. Kelley:** Data curation. **Gregory H. Robinson:** Conceptualization. **Justin R. Walensky:** Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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