Title: Spectroscopic Evidence for a Monomeric Copper(I) Hydride, and Crystallographic Characterization of a Monomeric Silver(I) Hydride

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Spectroscopic Evidence for a Monomeric Copper(I) Hydride, and Crystallographic Characterization of a Monomeric Silver(I) Hydride

Erik A. Romero,[a] Pauline M. Olsen,[a] Rodolphe Jazzar,[a] Michele Soleilhavoup,[a] Milan Gembicky,[b] Guy Bertrand[a]*

Dedication

Abstract: (1,3-bis[2,6-bis[(4-tert-butylphenyl)methyl]-4-methylphenyl]imidazol-2-ylidene)CuOPh [(IPr**)CuOPh] reacts with poly(methylhydrosiloxane) as the hydride donor, to afford the monomeric (IPr**)CuH complex which has been spectroscopically characterized. The latter is in equilibrium in solution with [(IPr**)CuH]$_2$, the dimer being exclusively present in the solid state. These results support the hypothesis that copper hydride aggregates dissociate in solution. In contrast, addition of pinacol borane to [(IPr**)AgOPh] at -40 °C allows for the isolation of the monomeric (IPr**)AgH complex, which has been crystallographically characterized.

Although Wurtz discovered a polymeric copper hydride as early as 1844,[1] low nuclearity coinage metal hydrides have challenged the skills of synthetic chemists for decades. Copper hydrides[2] have the propensity to aggregate as evidenced by the widely studied Stryker's reagent [(Ph$_3$P)CuH]$_6$.[3] In 2004, using an *N*-heterocylic carbene (NHC) ligand,[4] Sadighi *et al.* reported the isolation of the first monoligated dimeric copper hydride **A**,[5,6] but noted slow decomposition even at -40 °C (Figure 1). Since then, using cyclic (alkyl)(amino)carbenes (CAACs),[7,8] and 6- and 7-membered NHCs, several dimers of type **A** have been found to be stable at room temperature.[9] These dimers feature the reactivity expected for the corresponding monomers.[10,11] However, the existence of an equilibrium between a mononuclear LCuH and its polynuclear form (LCuH)$_n$ has never been experimentally observed.[12] For silver hydrides, in 2010 Liu *et al.* isolated cationic [Ag$_8$(μ$_4$−H){Se$_2$P(OR)$_2$}$_6$]$^+$ clusters **B** containing Ag(I)-hydride bridges (Ag−μ-H−Ag),[13] and in 2013 Sadighi *et al.* described the dimeric silver hydride cation **C**.[14] The only crystallographically characterized monomeric coinage metal hydrides are gold complexes of type **D** first described by Sadighi *et al.* in 2008.[15,16]

Here we report the unprecedented spectroscopic characterization of a monomeric LCuH complex, which is in equilibrium in solution with its dimer [LCuH]$_2$, as well as the isolation and crystallographic characterization of the first monomeric LAgH complex.

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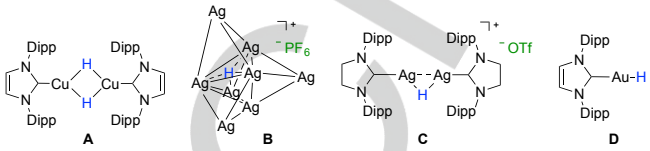
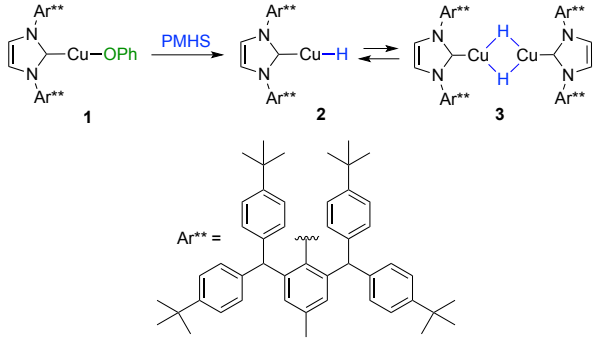


Figure 1. Previously reported coinage metal hydrides **A**-**D**.

We have recently shown the effectiveness of 2,6-bis[(4-tert-butylphenyl)methyl]-4-methylphenyl substituent (Ar**)[17] for the kinetic stabilization of species prone to dimerization.[18] Being involved in coinage metal chemistry,[19] we hypothesized that 1,3-bis[2,6-bis[(4-tert-butylphenyl)methyl]-4-methylphenyl]imidazol-2-ylidene (IPr**) reported by Straub *et al.*,[17] might provide sufficient kinetic protection to stabilize a monomeric copper hydride.

Addition at room temperature of one equivalent polymethylhydrosiloxane (PMHS) to a benzene solution of (IPr**)CuOPh **1** led after 4 hours to a yellow solution (Scheme 1). The ^{13}C{^{1}H} spectrum showed two carbene signals at 185.8 and 192.8 ppm. In the ^{13}C proton-coupled NMR, the signal at 192.8 ppm appeared as a triplet with a rather small coupling constant (3.6 Hz), indicative of the dimeric species **3**. In contrast, the signal at 185.8 ppm resolved as a doublet with a large coupling constant of 40 Hz consistent with a *trans*- $^2J(^{13}C\text{-}^1H)$ coupling, indicative of the desired monomeric copper hydride **2**.[20] The 2D-HMBC NMR spectrum correlated the ^{13}C NMR carbene signals to distinctive proton signals at 4.26 (**3**) and 2.14 ppm (**2**) (Figure 2). Evaporation of the solution afforded an oily residue that readily crystalized upon standing. The X-ray diffraction study showed the dimeric structure **3** (Figure 3).[21]



Scheme 1. Reaction of **1** with PMHS affords the monomeric copper hydride **2** in equilibrium in solution with its dimer **3**.

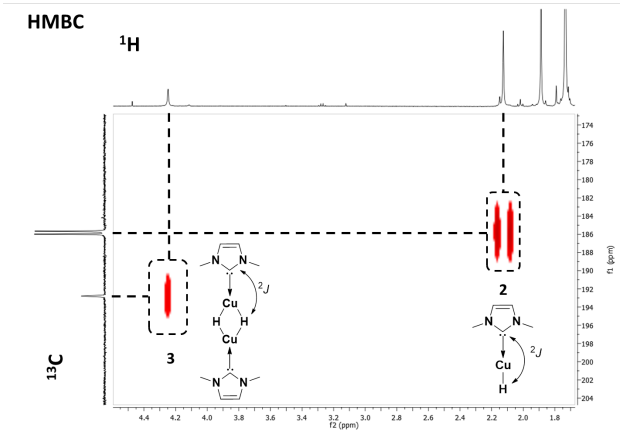


Figure 2. Hydride and carbene regions of the ^{1}H-^{13}C HMBC spectrum of **2** and **3** in C_6D_6.

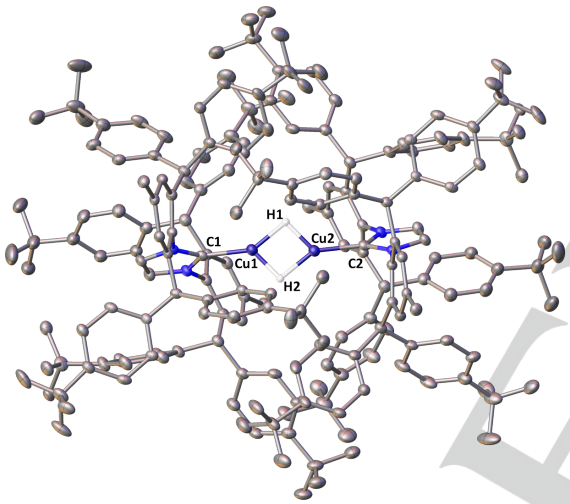


Figure 3. Molecular structure of **3** in the solid state. Hydrogen atoms other than the hydrides, and solvent molecules have been omitted for clarity. Thermal ellipsoids are set at 15% probability. Selected distances [Å]: C1-Cu1 1.89535(4); Cu1-H1 1.50400(6); Cu1-H2 1.63613(3); Cu1-Cu2 2.32432(4).

Importantly, when crystals of **3** were dissolved in C_6D_6 the original mixture **2/3** was observed by NMR, demonstrating the existence of an equilibrium between the dimer **3** and its monomer **2**. To further understand the nature of this equilibrium, a set of NMR experiments were performed (Figure 4). As expected, the monomer to dimer ratio depends on the temperature and the concentration. From these measurements we determined the equilibrium constant (K_{eq} = 4.04 ± 0.80 M^{-1}) as well as the enthalpy (ΔH = -6.15 ± 0.25 kcal.mol^{-1}), entropy (ΔS = -17.53 ± 1.36 cal.mol^{-1}.K^{-1}), and Gibbs free energy (ΔG = -0.84 ± 0.17 kcal.mol^{-1}) of the dimerization process at 30 °C.

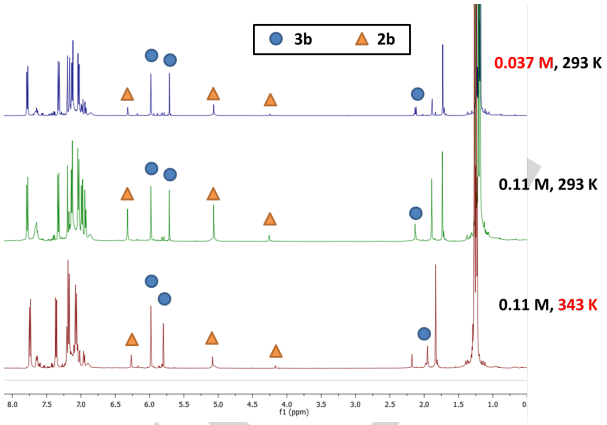
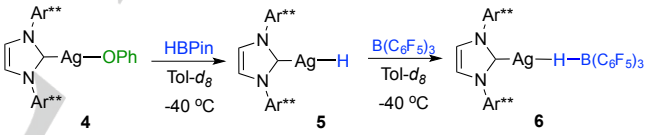


Figure 4. NMR study depicting the equilibrium between **2** and **3** in C_6D_6.

We then turned our attention to silver hydrides.[2b] The synthesis of (IPr**)AgOPh **4** was achieved using the same methodology as for **1**. Addition of one equivalent of pinacol borane at -40 °C to a toluene-d_8 solution of **4** immediately led to a colorless solution (Scheme 2). The ^{11}B{^{1}H} NMR spectrum of the crude mixture after 5 minutes revealed the formation of PhOBPin,[22] while the ^{1}H and ^{13}C{^{1}H} NMR spectra showed a pair doublets [^{1}H: 3.87 ppm, $^1J(^{107}Ag\text{-}^1H)$ = 224.6 Hz and $^1J(^{109}Ag\text{-}^1H)$ = 260.6 Hz; ^{13}C: 193.2 ppm, $^1J(^{107}Ag\text{-}^{13}C)$ = 113.2 Hz and $^1J(^{109}Ag\text{-}^{13}C)$ = 126.6 Hz], as expected for the monomeric silver(I) hydride **5** (Figure 5).



Scheme 2. Synthesis of the monomeric silver hydride **5** and its Lewis acid adduct **6**.

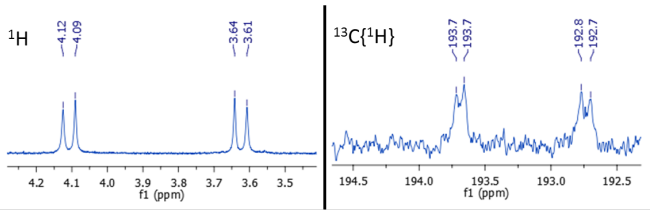


Figure 5. Hydride and carbene regions of ^{1}H and ^{13}C{^{1}H} NMR spectra of the monomeric silver hydride **5** at –40 °C.

Within 20 minutes at room temperature, the NMR resonances corresponding to the free NHC appeared and grew steadily over time. After 1 hour, the solution became deep dark purple with no signals other than those corresponding to the NHC. We were fortunate to obtain single crystals by keeping the solution at -40 °C overnight, and the X-ray diffraction study confirmed the monomeric nature of **5** (Figure 6).

Silver hydride **5** crystallizes in the chiral space group P^{-1} with 2 molecules in the asymmetric unit cell. Analysis of the unit cell

shows no interaction between molecules as the nearest neighboring atom is 3.74 Å away. Due to positional disorder of the silver atom, the hydride could not be located and was fixed in the molecular structure of **5**. However, addition of one equivalent tris(pentafluorophenyl)borane to a solution of **5** at -40 °C yields the corresponding LAgH[$B(C_6F_5)_3$] adduct **6**, for which the hydride could be located and isotropically refined by X-ray crystallography (Figure 7).[23]

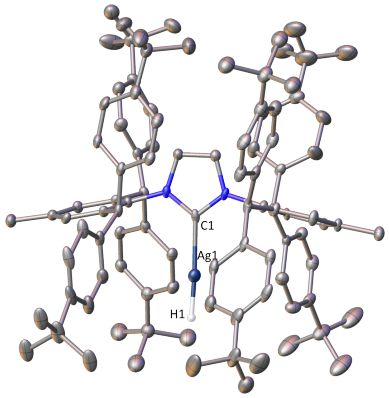


Figure 6. Molecular structure of **5** in the solid state. Hydrogen atoms other than the hydride, and solvent molecules are omitted for clarity. C1-Ag1 2.108(6) Å.

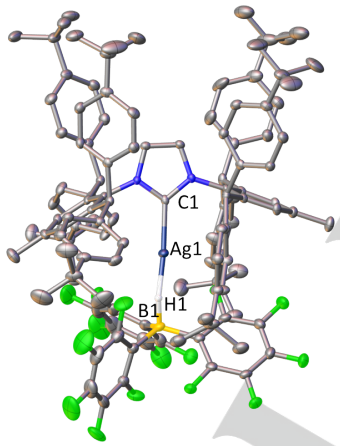


Figure 7. Molecular structure of **6** in the solid state. Hydrogen atoms other than the hydride, and solvent molecules have been omitted for clarity. Selected distances [Å] and angles [°]: C1-Ag1 2.095(2); Ag1-H1 1.81(3); H1-B1 1.21(3); C1-Ag1-H1 173.5(9); Ag1-H1-B1 159.7(13).

In conclusion the very bulky IPr** allows for the first spectroscopic characterization of a monomeric copper hydride [(IPr**)CuH, **2**], which is not isolable in the solid state, but is found to be in equilibrium in solution with its dimer $[(IPr^{**})CuH]_2$ **3**. These results support the hypothesis that copper hydride aggregates dissociate in solution.[12] On the other hand, our data suggest that silver hydrides do not have the tendency to aggregate in the solid state; however, the labile nature of the Ag – Carbene bond, which is typically used in carbene transmetallation reactions,[24] makes them prone to dissociation in solution.

Acknowledgements

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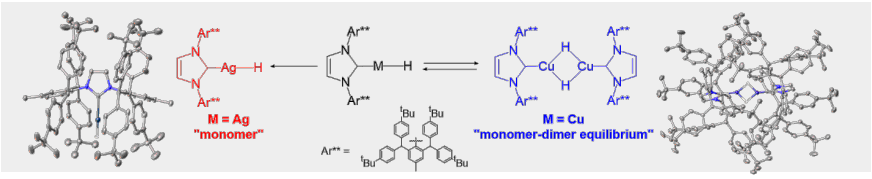
[1] A. Wurtz, *Ann. Chem. Phys.* **1844**, *11*, 250 – 251.
[2] For reviews on coinage metal hydrides, see: a) C. Deutsch, N. Krause, B. H. Lipshutz, *Chem. Rev.* **2008**, *108*, 2916 – 2927; b) A. J. Jordan, G. Lalic, J. P. Sadighi, *Chem. Rev.* **2016**, *116*, 8318 – 8372; c) N. Cox, H. Dang, A. M. Whittaker, G. Lalic, *Tetrahedron* **2014**, *27 – 28*, 4219 – 4231; d) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896 – 7936; *Angew. Chem.* **2006**, *118*, 8064 – 8105.
[3] a) W. S. Mahoney, D. M. Brestensky, J. M. Stryker, *J. Am. Chem. Soc.* **1988**, *110*, 291 – 293; b) C. F. Albert, P. C. Healy, J. D. Kildea, C. L. Raston, B. W. Skelton, A. H. White, A. H. *Inorg. Chem.* **1989**, *28*, 1300 – 1306; c) S. A. Bezman, M. R. Churchill, J. A. Osborn, J. Wormald, *J. Am. Chem. Soc.* **1971**, *93*, 2063 – 2065.
[4] For recent thematic issues and books on stable carbenes, see: a) T. Rovis, S. P. Nolan, *Synlett* **2013**, *24*, 1188 – 1189; b) A. J. Arduengo, G. Bertrand, *Chem. Rev.* **2009**, *109*, 3209 – 3210. c) *N-Heterocyclic Carbene in Transition Metal Catalysis and Organocatalysis*, (Ed.: C. S. J. Cazin), Springer, London, **2011**; d) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, (Ed.: S. Díez-González), Royal Society of Chemistry Publishing, Cambridge, **2017;** e) *N-Heterocyclic Carbenes–Effective Tools for Organometallic Synthesis*, (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2014**.
[5] N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369 – 3371.
[6] A di-ligated dimeric copper-hydride have also been reported: G. V. Goeden, J. C. Huffman, K. G. Caulton, *Inorg. Chem.* **1986**, *25*, 2484 – 2485.
[7] For reviews on CAACs, see: a) D. Martin, M. Soleilhavoup, Bertrand, G. *Chem. Sci.* **2011**, *2*, 389 – 399; b) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020 – 3030; c) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2015**, *48*, 256 – 266; d) S. Roy, K. C. Mondal, H. W. Roesky, *Acc. Chem. Res.* **2016**, *49*, 357 – 369.
[8] For the synthesis of CAACs, see: a) V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705 – 5709; *Angew. Chem.* **2005**, *117*, 5851 – 5855; b) R. Jazzar, R. D. Dewhurst, J. B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, *46*, 2899 – 2902; *Angew. Chem.* **2007**, *119*, 2957 – 2960; c) R. Jazzar, J. B. Bourg, R. D. Dewhurst, B. Donnadieu, G. Bertrand, *J. Org. Chem.* **2007**, *72*, 3492 – 3499; d) X. Zeng, G. D. Frey, R. Kinjo, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2009**, *131*, 8690 – 8696.
[9] a) G. D. Frey, B. Donnadieu, M. Soleilhavoup, G. Bertrand, *Chem. Asian J.* **2011**, *6*, 402 – 405; b) A. J. Jordan, C. M. Wyss, J. Bacsa, J. P. Sadighi, *Organometallics* **2016**, *35*, 613 – 616.
[10] Using DTBM-Segphos (DTBM = 3,5-di-tert-butyl-4-methoxyphenyl) as a ligand, Lipshutz *et al.* reported that the corresponding tricoordinated copper(I) hydride was stable in solution at ambient temperature: B. H. Lipshutz, B. A. Frieman, *Angew. Chem. Int. Ed.* **2005**, *44*, 6345 – 6348; *Angew. Chem.* **2005**, *117*, 6409; however, Sadighi *et al.* wrote in 2016,[2b] "The nuclearity of this complex remains unknown, and for practical purposes the complex is typically depicted as a monomer, although a dimeric hydride-bridged structure appears plausible."
[11] a) C. M. Wyss, B. T. Tate, J. Bacsa, T. G. Gray, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2013,** *52,* 12920 – 12923; *Angew. Chem.* **2013**, *125*, 13158 – 13161; b) L. R. Collins, I. M. Riddlestone, M. F. Mahon, M. K. Whittlesey, *Chem. -Eur. J.* **2015**, *21*, 14075 – 14084; c) A. M. Suess, G. Lalic, *Synlett* **2016**, *27*, 1165 – 1174; d) M. R. Uehling, R. P. Rucker, G. Lalic, *J. Am. Chem. Soc.* **2014**, *136*, 8799 – 8803.
[12] a) T. Vergote, F. Nahra, A. Merschaert, O. Riant, D. Peeters, T. Leyssens, *Organometallics* **2014**, *33*, 1953 – 1963; b) S. C. Schmid, R. Van Hoveln, J. W. Rigoli, J. M. Schomaker, *Organometallics* **2015**, *34*, 4164 – 4173; c) G. Dey, S. D. Elliott, *Theor. Chem. Acc.* **2014**, *133*, 1 – 7.
[13] C. W. Liu, H. W. Chang, B. Sarkar, J. Y. Saillard, S. Kahlal, Y. Y. Wu, *Inorg. Chem.* **2010,** *49*, 468 – 475.
[14] B. K. Tate, C. M. Wyss, J. Bacsa, K. Kluge, L. Gelbaum, J. P. Sadighi, *Chem. Sci.* **2013,** *4*, 3068 – 3074; b) B. K. Tate, A. J. Jordan, J. Bacsa, J. P. Sadighi, *Organometallics* **2016**, online, DOI: 10.1021/acs.organomet.6b00771.

[15] E. Y. Tsui, P. Müller, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2008,** *47*, 8937 – 8940; *Angew. Chem.* **2008**, *120*, 9069 – 9072.
[16] a) D. Rosca, D. Smith, D. Hughes, D. Bochmann, *Angew. Chem. Int. Ed.* **2012**, *51*, 10643 – 10646; *Angew. Chem.* **2012**, *124*, 10795 – 10798; b) G. Klienhans, M. M. Hansmann, G. Guisado-Barrios, D. C. Liles, G. Bertrand, D. I. Bezuidenhout, *J. Am. Chem. Soc.* **2016**, *138*, 15873 – 15876; c) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12935 – 12936; *Angew. Chem.* **2012**, *124*, 13109 – 13110.
[17] a) S. G. Weber, C. Loos, F. Rominger, B. F. Straub, *ARKIVOC* **2012**, *iii*, 226 – 242; b) M. W. Hussong, W. T. Hoffmeister, F. Rominger, B. F. Straub, *Angew. Chem. Int. Ed.* **2015**, *54*, 10331 – 10335; *Angew. Chem.* **2015**, *127*, 10472 – 10476.
[18] a) L. Liu, D. A. Ruiz, D. Munz**,** G. Bertrand, *Chem* **2016**, *1*, 27 – 29; b) M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356 – 8359.
[19] See for recent examples: a) D. S. Weinberger, N. Amin SK, K. C. Mondal, M. Melaimi, G. Bertrand, A. C. Stückl, H. W. Roesky, B. Dittrich, S. Demeshko, B. Schwederski, W. Kaim, P. Jerabek, G. Frenking, *J. Am. Chem. Soc.* **2014***, 136,* 6235 – 6238; b) L. Jin, D. R. Tolentino, M. Melaimi, G. Bertrand, *Sci. Adv.* **2015**, *1***,** e1500304; c) L. Jin, E. A. Romero, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2015**, *137*, 15696 – 15698; d) J. L. Peltier, R. Jazzar, M. Melaimi, G. Bertrand,. *Chem. Commun.* **2016**, *52*, 2733 – 2735; e) E. A. Romero, R. Jazzar, G. Bertrand, *Chem. Sci.* **2017**, *8*, 165 – 168; f) E. A. Romero, R. Jazzar, G. Bertrand, *J. Organomet. Chem.* **2016**, DOI 10.1016/ j.jorganchem.2016.09.025. g) Y. D. Bidal, O. Santoro, M. Melaimi, D. B. Cordes, A. M. Z. Slawin, G. Bertrand, C. S. J. Cazin, *Chem. –Eur. J.* **2016**, *22*, 9404 – 9409; h) Y. D. Bidal, M. Lesieur, M. Melaimi, F. Nahra, D. B.Cordes, K. S. A. Arachchige, A. M. Z. Slawin, G. Bertrand, C. S. J. Cazin, *Adv. Synth. Catal.* **2015**, *357*, 3155 – 3161.
[20] G. M. Whitesides, G. Maglio, *J. Am. Chem. Soc.* **1969**, 91, 4980 – 4986.
[21] CCDC 1523194 (**3**), 1529272 (**5**) and 1528927 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[22] E. A. Romero, J. L. Peltier, R. Jazzar, G. Bertrand, *Chem. Commun.* **2016**, *52*, 10563 – 10565.
[23] A similar copper hydride boron adduct has recently been described: Collins, L. R.; Rajabi, N. A.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. *Angew. Chem. Int. Ed.* **2016**, *55*, 15539 – 15543; *Angew. Chem.* **2016**, *128*, 15768 – 15772.
[24] a) H. M. J. Wang, I. B. J. Lin, *Organometallics* **1998**, *17*, 972 – 975; b) I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev*. **2007**, *251*, 642 – 670.

COMMUNICATION



Copper hydrides like to aggregate but a silver analogue can stay alone. The monomeric (IPr**)CuH complex is in equilibrium in solution with $[(IPr^{**})CuH]_2$ and does not exist in the solid state. In contrast, (IPr**)AgH complex can be crystallographically characterized.

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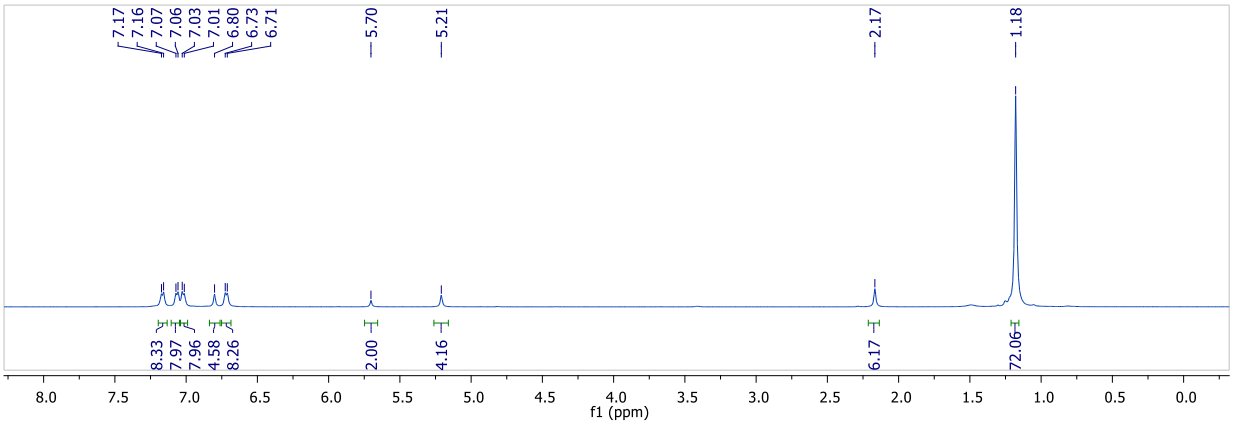
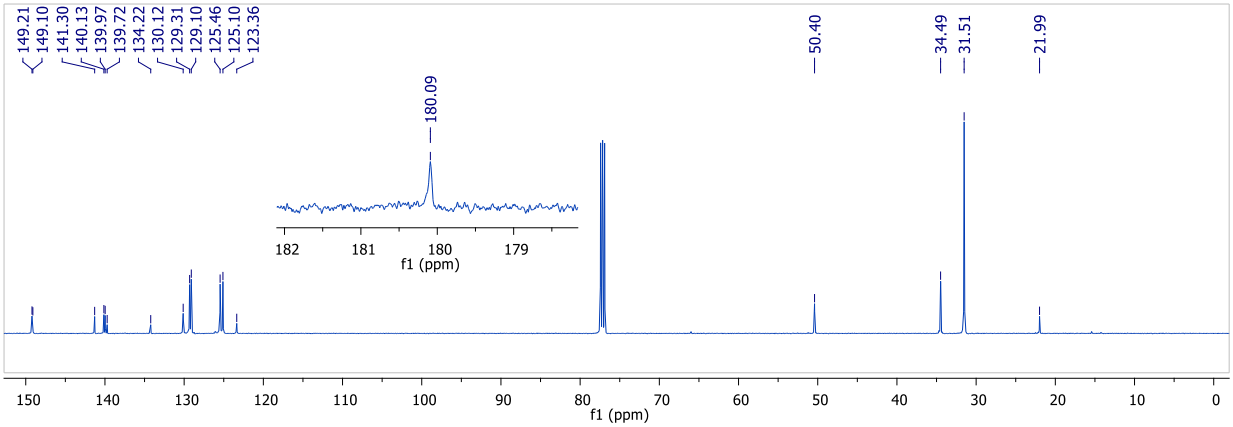
A. General Considerations

All reactions were performed under an atmosphere of argon using standard Schlenk or dry box techniques; all solvents were dried and degassed using standard procedures. Toluene, benzene, hexane, pentane, THF, and diethyl ether were distilled from sodium. C_6D_6 was distilled from sodium benzophenone and stored over a potassium mirror. Dichloromethane and chloroform were dried by distillation from CaH_2. Reagents of analytical grade were obtained from commercial suppliers, dried over 4Å molecular sieves and degassed before use. $B(C_6F_5)_3$ was sublimated before use. ^{1}H, ^{13}C, ^{11}B and Variable temperature NMR spectra were obtained using a Varian Inova 500 MHz and ECA JEOL 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, quin = quintet, sextet, dd = doublet of doublets, dt = doublet of triplets, qt = quartet of triplets, m = multiplet, br = broad signal. IPr**HCl[1] imidazolium precursor was prepared according to literature procedures.

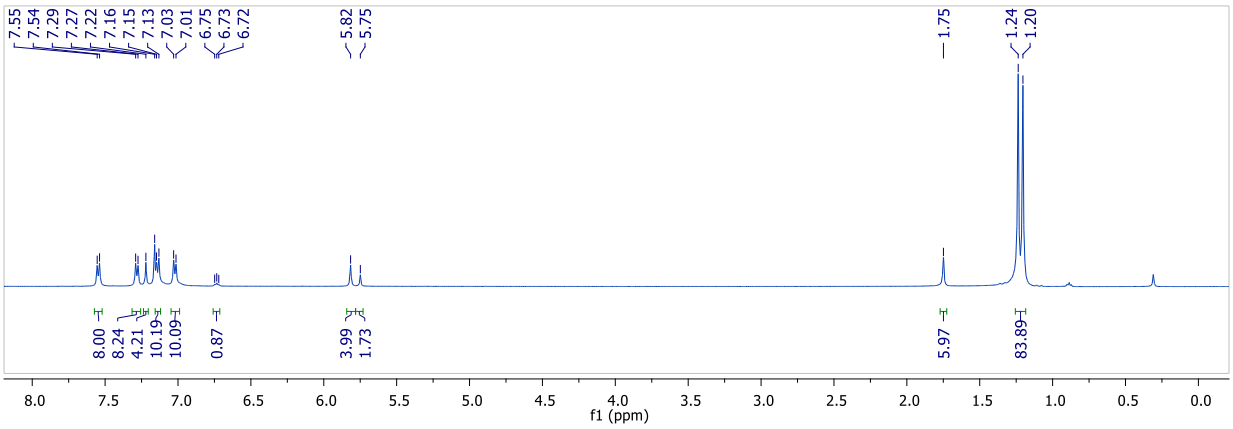
B. Preparation of Copper/Silver Phenoxide Complexes (1/4)

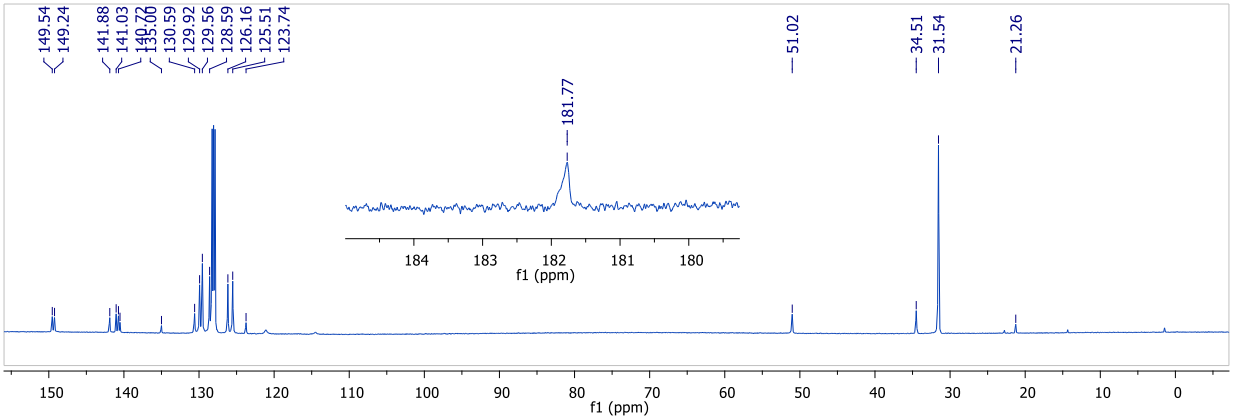
Synthesis of (IPr)CuCl**: A Schlenk tube was charged with IPr**HCl imidazolium (2.21 g, 1.58 mmol, 1 eq.), KOtBu (0.19 g, 1.66 mmol, 1.05 eq.), and CuCl (0.19 g, 1.90 mmol, 1.2 eq.). 10 mL anhydrous toluene was added and the resulting solution was stirred for 24 hours at room temperature. The reaction was filtered over celite and the volatiles were evaporated under vacuum. The residue was washed with 3 x 5 mL portions of cold diethyl ether, and dried under vacuum thus yielding (IPr**)CuCl in 2.10 g (91%) as an off white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18 (s, 72 H), 2.17 (s, 6 H), 5.21 (s, 4 H), 5.70 (s, 2 H) 6.72 (d, J = 7.0 Hz, 8 H), 6.80 (s, 4 H), 7.02 (d, J = 7.5 Hz, 8 H), 7.28 (d, J = 7.9 Hz, 8 H), 7.17 (d, J = 7.4 Hz, 8 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 180.1 (C_{carb}), 149.2, 149.1, 141.3, 140.1, 140.0, 139.7, 134.2, 130.1, 129.3, 129.1, 125.5, 125.1, 123.4, 50.4 ($CHAr_2$), 34.5 ($ArCH_3$), 31.5 ($C(CH_3)_3$), 22.0 ($C(CH_3)_3$).



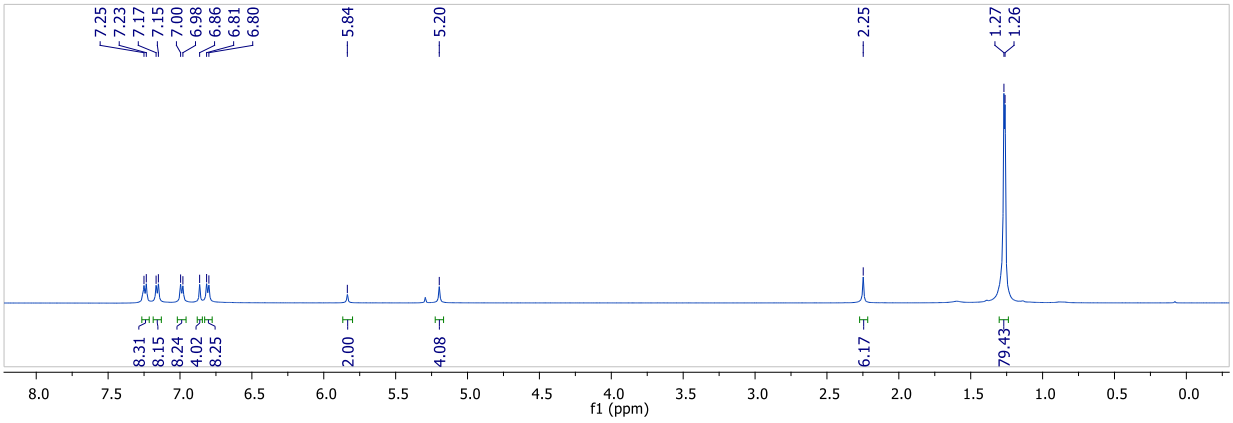


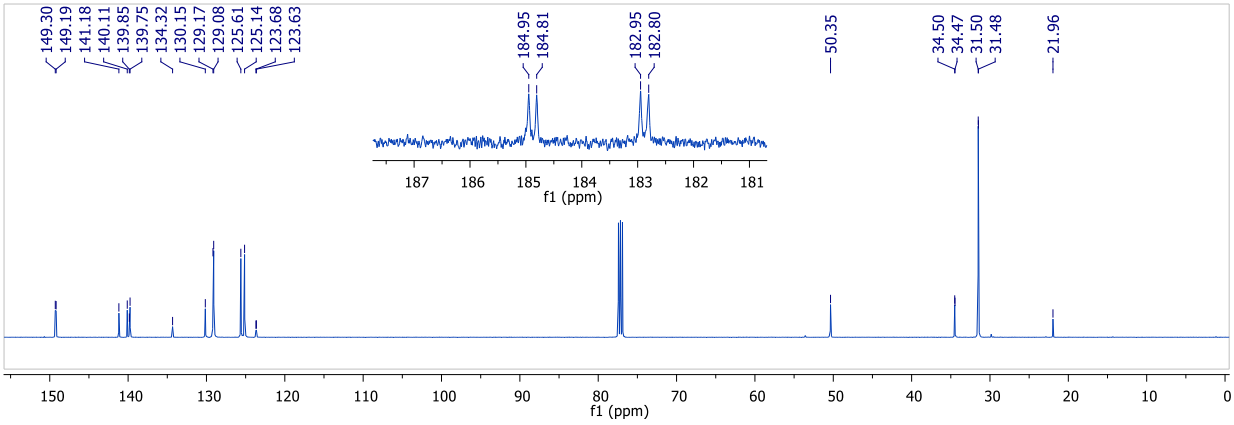
Synthesis of (IPr)CuOPh (1)**: To a Schlenk tube charged with IPr**CuCl (3.18 g, 2.18 mmol, 1 eq.) was added KOPh (0.35 g, 2.61 mmol, 1.2 eq.). 10 mL anhydrous dichloromethane was added and the resulting solution was stirred overnight at room temperature. The reaction was filtered over celite. The celite was washed with 2 x 5 mL DCM and the combined organic extracts were evaporated under vacuum yielding 2.71 g of **1** as a white solid (82% yield). M. P.: 299.3 ^{o}C dec. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.20 (s, 36 H), 1.24 (s, 36 H), 1.75 (s, 6 H), 5.75 (s, 2 H), 5.82 (s, 4 H) 6.73 (t, J = 6.6 Hz, 1 H), 7.02 (d, J = 8.5 Hz, 10 H), 7.10 (d, J = 8.0 Hz, 8 H), 7.22 (s, 4 H), 7.28 (d, J = 8.4 Hz, 8 H), 7.55 (d, J = 8.0 Hz, 8 H). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 181.8 (C_{carb}), 149.5, 149.2, 141.9, 141.0, 140.7, 135.0, 130.6, 129.9, 129.6, 128.6, 126.2, 125.5, 123.7, 51.0 ($CHAr_2$), 34.5 ($ArCH_3$), 31.5 ($C(CH_3)_3$), 21.2 ($C(CH_3)_3$). HRMS ESI-TOF+ found m/z 1423.8734, $[M - OPh]^+$ calculated for $[C_{101}H_{120}CuN_2]^+$ 1423.8742.



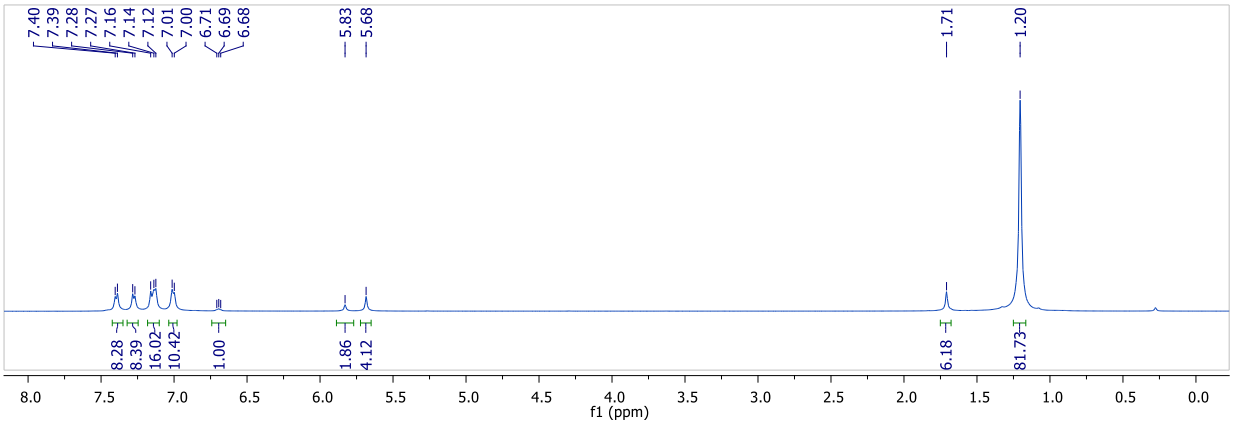


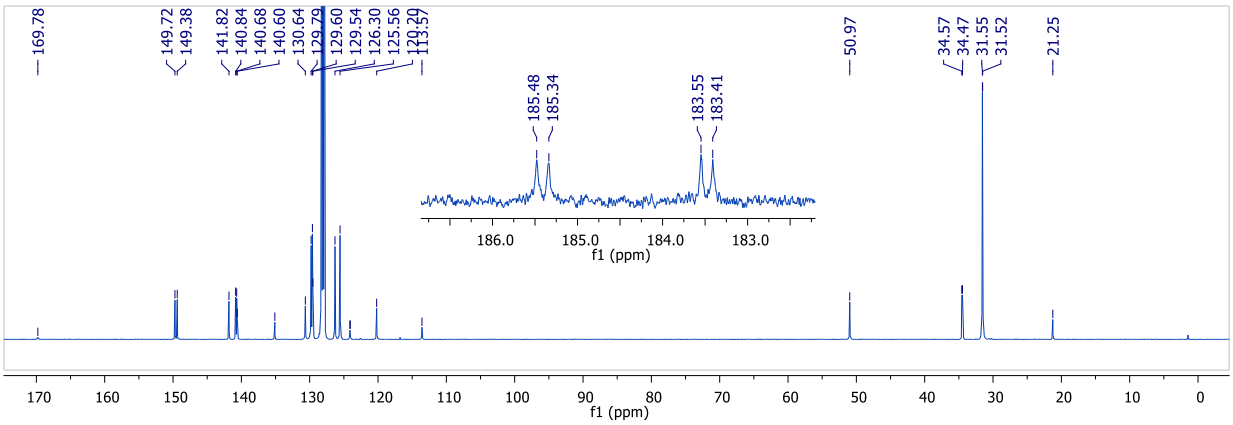
Synthesis of (IPr)AgCl**: A Schlenk tube was charged with IPr**HCl imidazolium (1.00 g, 0.65 mmol, 2 eq.), Ag_2O (0.075 g, 0.325 mmol, 1 eq.), and MgSO4 (0.325 g, 1 eq w/w). 10 mL anhydrous DCM was added and the resulting solution was stirred for 24 hours at 40 ^{o}C. The reaction was filtered over a short pad of silica and the silica was washed with 3 x15 mL DCM. The volatiles were evaporated under vacuum yielding (IPr**)AgCl in 0.85 g (87%) as a white solid. M. P.: > 300 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 (pseudo-d, 72 H), 2.25 (s, 6 H), 5.20 (s, 4 H), 5.84 (s, 2 H), 6.80 (d, J = 7.8 Hz, 8 H), 6.86 (s, 4 H), 6.99 (d, J = 8.0 Hz, 8 H), 7.16 (d, J = 7.8 Hz, 8 H), 7.24 (d, J = 8.1 Hz, 8 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 183.9 (pseudo-dd, $^{1}J(^{13}C\text{-}^{107}Ag)$ = 232.3 Hz, $^{1}J(^{13}C\text{-}^{109}Ag)$ = 268.4 Hz, $C_{carbene}$-Ag), 149.3, 149.2, 141.2, 140.1, 139.8, 134.3, 130.2, 129.2, 129.1, 125.6, 125.1, 123.7, 123.6, 50.4 (CHAr$_2$), 34.50 (ArCH$_3$), 34.47 (ArCH$_3$), 31.50 (C(CH$_3$)$_3$), 31.48 (C(CH$_3$)$_3$), 22.0 (C(CH$_3$)$_3$). HRMS ESI-TOF+ found m/z 1467.8476, $[M - Cl]^+$ calculated for $[C_{101}H_{120}AgN_2]^+$ 1423.8742.





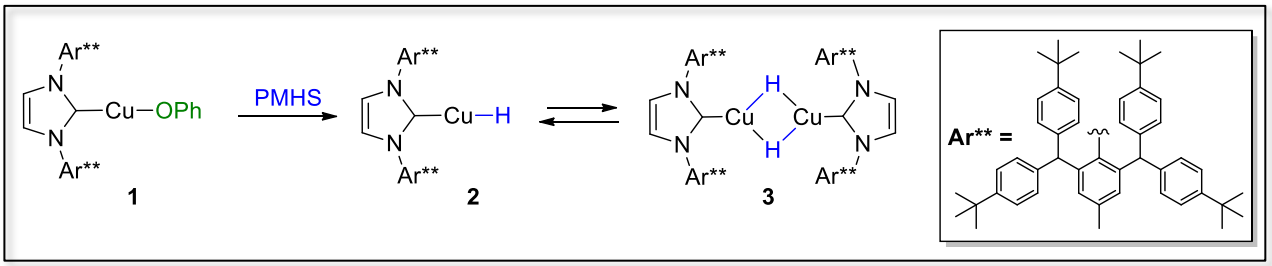
Synthesis of (IPr)AgOPh (4)**: To a Schlenk tube charged with IPr**AgCl (0.300 g, 0.199 mmol, 1 eq.) was added KOPh (0.029 g, 0.259 mmol, 1.3 eq.). 5 mL anhydrous DCM was added and the solution was stirred overnight at room temperature. The reaction was filtered over celite. The celite was washed with 3 x 5 mL DCM and the combined organic extracts were evaporated under vacuum yielding 0.286 g of **4** as an off white solid (92% yield). M. P.: 175.6 – 182.5 ^{o}C ^{1}H NMR (C_6D_6, 500 MHz): δ 1.20 (s, 72 H), 1.71 (s, 6 H), 5.68 (s, 4 H), 5.83 (s, 2 H), 6.69 (t, J = 6.8 Hz, 1 H), 7.00 (d, J = 7.4 Hz, 10 H), 7.14 (m, 15 H), 7.27 (d, J = 7.8 Hz, 8 H), 7.39 (d, J = 7.8 Hz, 8 H). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 184.4 (pseudo-dd, $^{1}J(^{13}C\text{-}^{107}Ag)$ = 223.3 Hz, $^{1}J(^{13}C\text{-}^{109}Ag)$ = 243.4 Hz, $C_{carbene}$-Ag), 169.8 ($C_{carbene}$AgO*C*), 149.7, 149.4, 141.8, 140.8, 140.7, 140.6, 135.1, 130.6, 129.8, 129.6, 129.5, 126.3, 125.6, 124.12, 124.07, 120.2, 113.6, 51.0 (*C*HAr$_2$), 34.6 (Ar*C*H$_3$), 34.5 (Ar*C*H$_3$), 31.6 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 21.3 (*C*(CH$_3$)$_3$). HRMS ESI-TOF+ found m/z 1467.8483, $[M - OPh]^+$ calculated for $[C_{101}H_{120}AgN_2]^+$ 1467.8497.





C. Reaction Procedures

(IPr)CuH Monomer/Dimer (2/3)**: IPr**CuOPh (60 mg, 39.6 µmol, 1 eq.) was added to a J-Young NMR tube, followed by 500 µL C_6D_6 and PMHS (2.50 µL, 39.6 µmol, 1 eq.). The solution was shaken and left overnight at room temperature. Over time, an intense yellow solution appeared, however, no precipitate formed. The crude solution was then analyzed by NMR. Evaporation of the solution afforded an oily residue that readily crystalized upon standing thus affording bright yellow crystals of **3**.

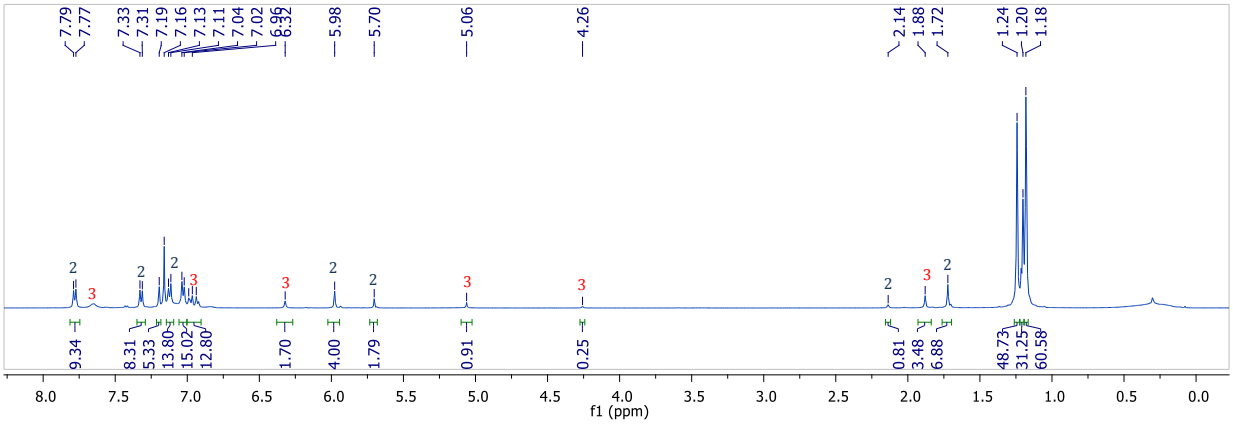


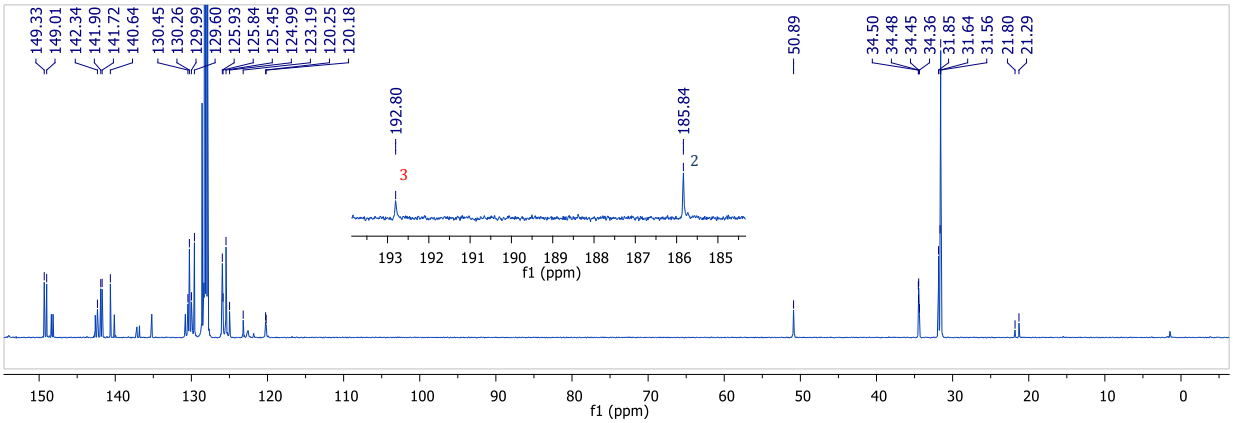
Spectra reported for a 1:2 mixture of 2:3 at 25 °C and 0.089 M solution in C_6D_6:

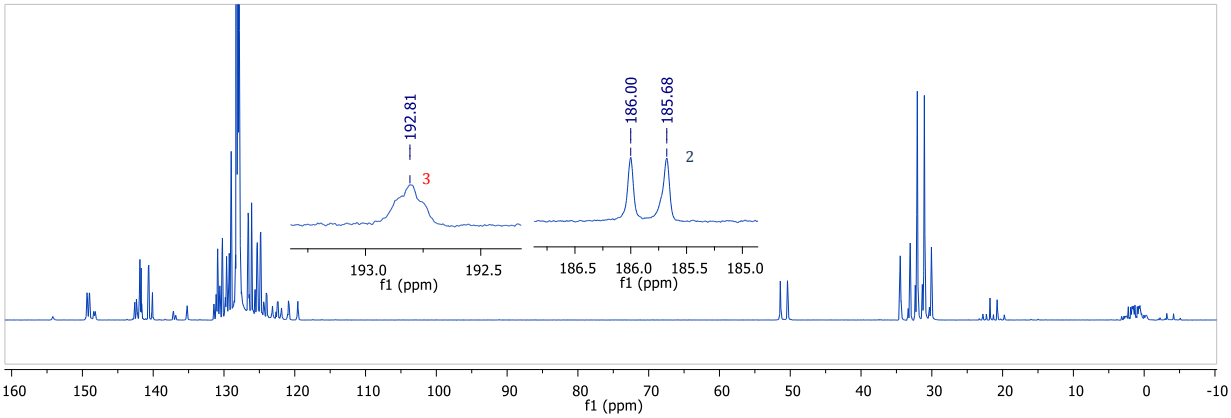
2. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.18 (s, 36 H), 1.24 (s, 36 H), 1.72 (s, 6 H), 2.14 (s, 1 H, Cu*H*), 5.70 (s, 2 H), 5.98 (s, 4 H), 7.03 (d, J = 7.8 Hz, 8 H), 7.12 (d, J = 8.4 Hz, 8 H), 7.19 (s, 4 H), 7.32 (d, J = 7.8 Hz, 8 H), 7.78 (d, J = 8.4 Hz, 8 H). ^{13}C{^{1}H}(C_6D_6, 125 MHz): δ 185.8 (C_{carb}), 149.3, 149.0, 141.9, 141.7, 140.6, 130.5, 129.6, 128.6, 125.9, 125.5, 123.2, 122.5, 120.3, 50.9, 34.50, 34.45, 31.6, 21.3. ^{13}C (C_6D_6, 125 MHz): δ 185.8 (d, J = 40.0 Hz, C_{carb}), 149.3 (m), 149.0 (m), 141.9 (d, J = 7.7 Hz), 141.7 (q, J = 6.9 Hz), 140.6 (q, J = 8.5 Hz), 130.5 (m), 129.5 (m), 128.6 (m) 126.3 (dd, J = 6.8 Hz, 61.0 Hz), 125.1 (dd, J = 6.2 Hz, 61.0 Hz), 123.2 (t, J = 6.8 Hz), 122. 4 (d, 11.5 Hz), 120.2 (dd, J = 8.1 Hz, 159.9 Hz), 50.9 (d, J = 129.6 Hz), 35.5 (m), 31.5 (qm, J = 124.4 Hz), 21.3 (qt, J = 4.6 Hz, 125.9 Hz). HRMS ESI-TOF+ shows only $[M - H]^+$.

3. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.18 (s, 72 H), 1.20 (s, 72 H), 1.88 (s, 12 H), 4.26 (s, 2 H, Cu*H*), 5.06 (s, 4 H), 6.32 (s, 8 H), 6.93 (d, J = 7.7 Hz, 16 H), 6.97 (d, J = 8.3 Hz, 16 H), 6.99 (s, 8 H), 7.65 (s, br, 16 H). ^{13}C{^{1}H}(C_6D_6, 125 MHz): δ 192.8 (C_{carb}), 148.4, 148.2, 142.6, 142.3, 140.1,

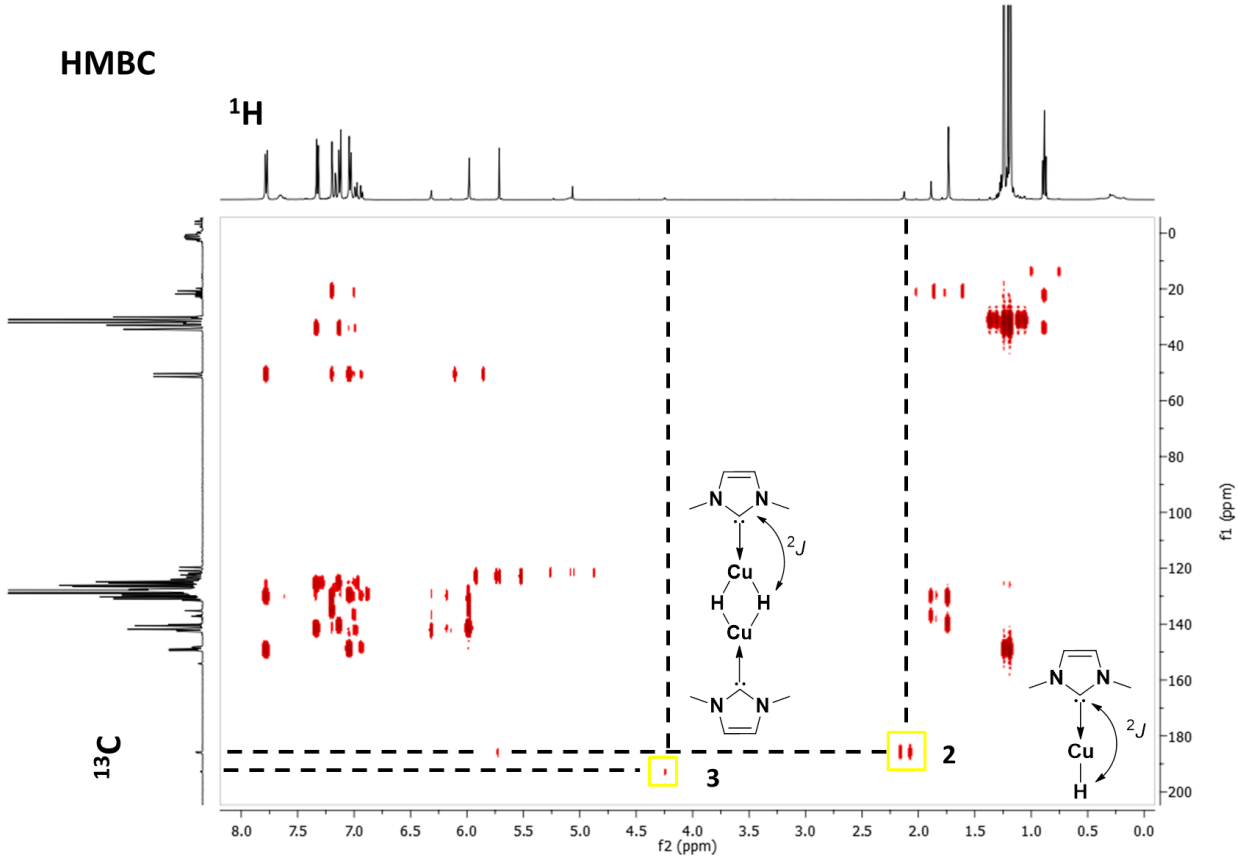
137.2, 136.8, 135.2, 130.8, 130.5, 130.0, 125.8, 125.0, 122.7, 121.8, 120.2, 50.9, 34.5, 34.4, 31.9, 31.6, 21.8. ^{13}C (C_6D_6, 125 MHz): δ 192.8 (t, J = 6.4 Hz, C_{carb}), 148.4 (m), 148.2 (m), 142.6 (d, J = 7.7 Hz), 142.3 (q, J = 6.6 Hz), 140.1 (q, J = 6.2 Hz), 137.2 (q, J = 6.0 Hz), 136.8 (sept, J = 3.7 Hz), 135.2 (sept, J = 4.3 Hz), 130.8 (dd, J = 4.1 Hz, 6.9 Hz), 130.5 (m), 130.0 (dd, J = 4.3 Hz, 7.0 Hz), 125.9 (dd, J = 6.9 Hz, 107.5 Hz), 125.3 (m), 122.6 (d, J = 12.7 Hz), 122.6, 121.8 (m), 120.2 (dd, J = 8.1 Hz, 159.9 Hz), 50.9 (d, J = 129.6 Hz), 35.5 (m), 31.8 (qpent, J = 5.0 Hz, 124.8 Hz), 21.8 (qt, J = 4.7 Hz, 126.2 Hz).



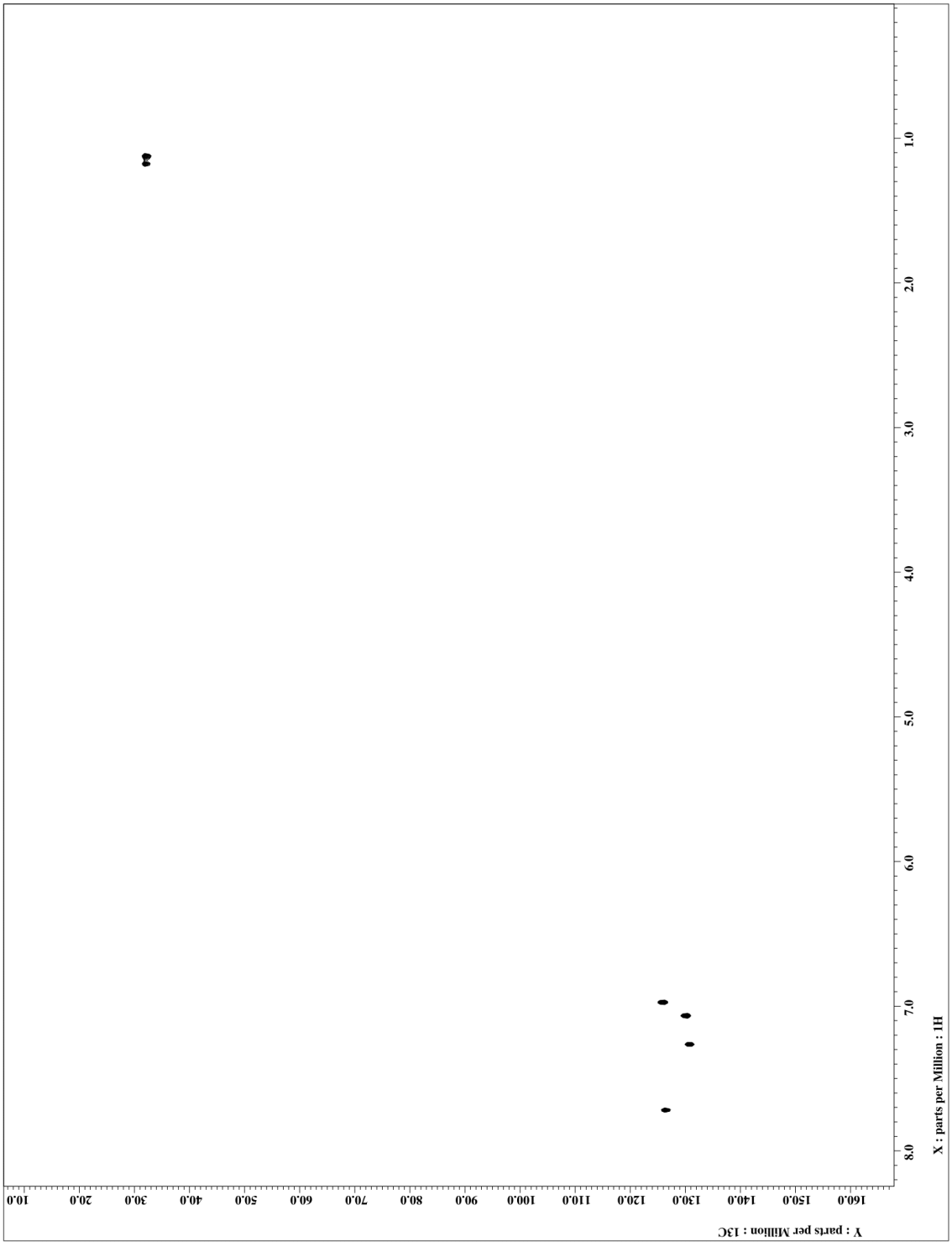




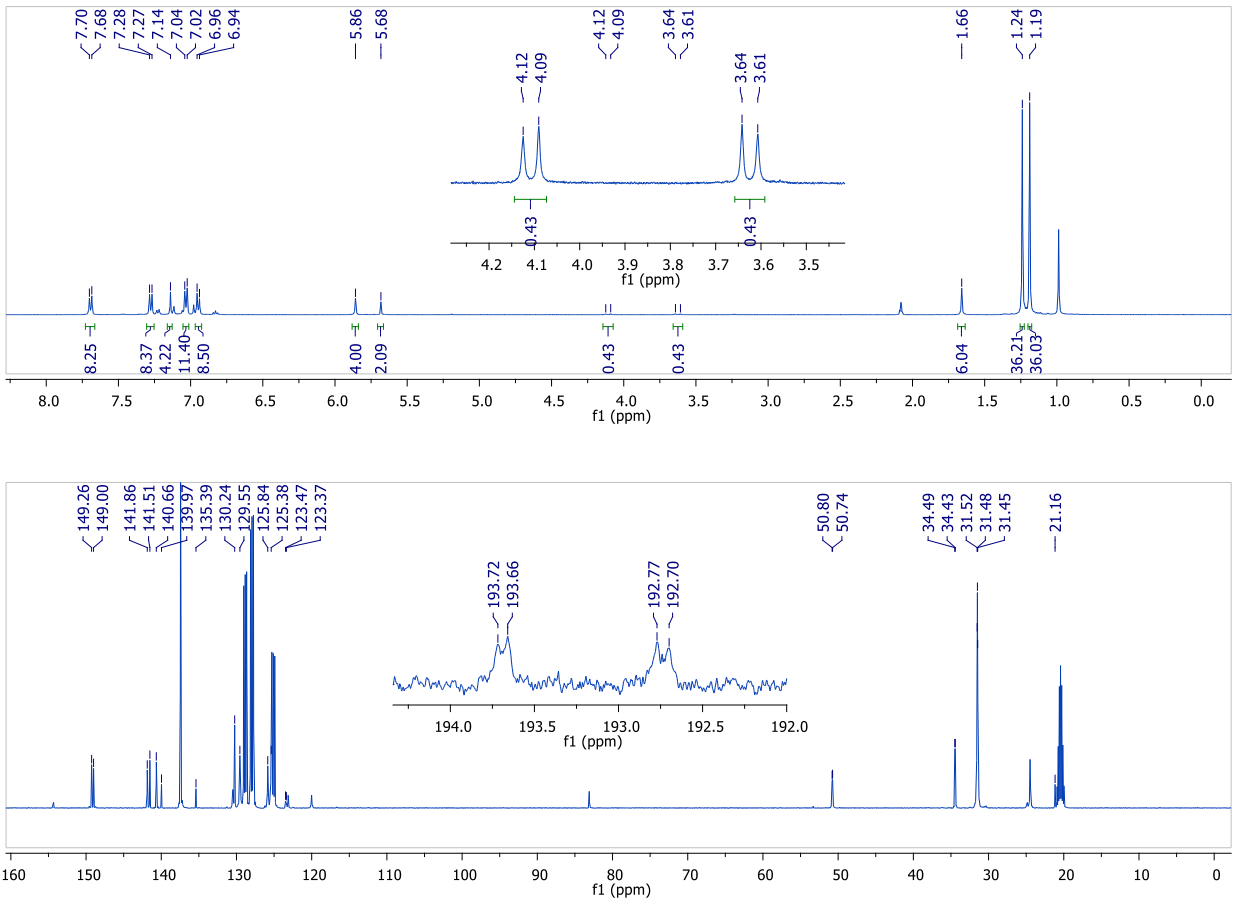
HMBC (C_6D_6, 500 MHz, 40 Hz HMBC coupling):



H2BC

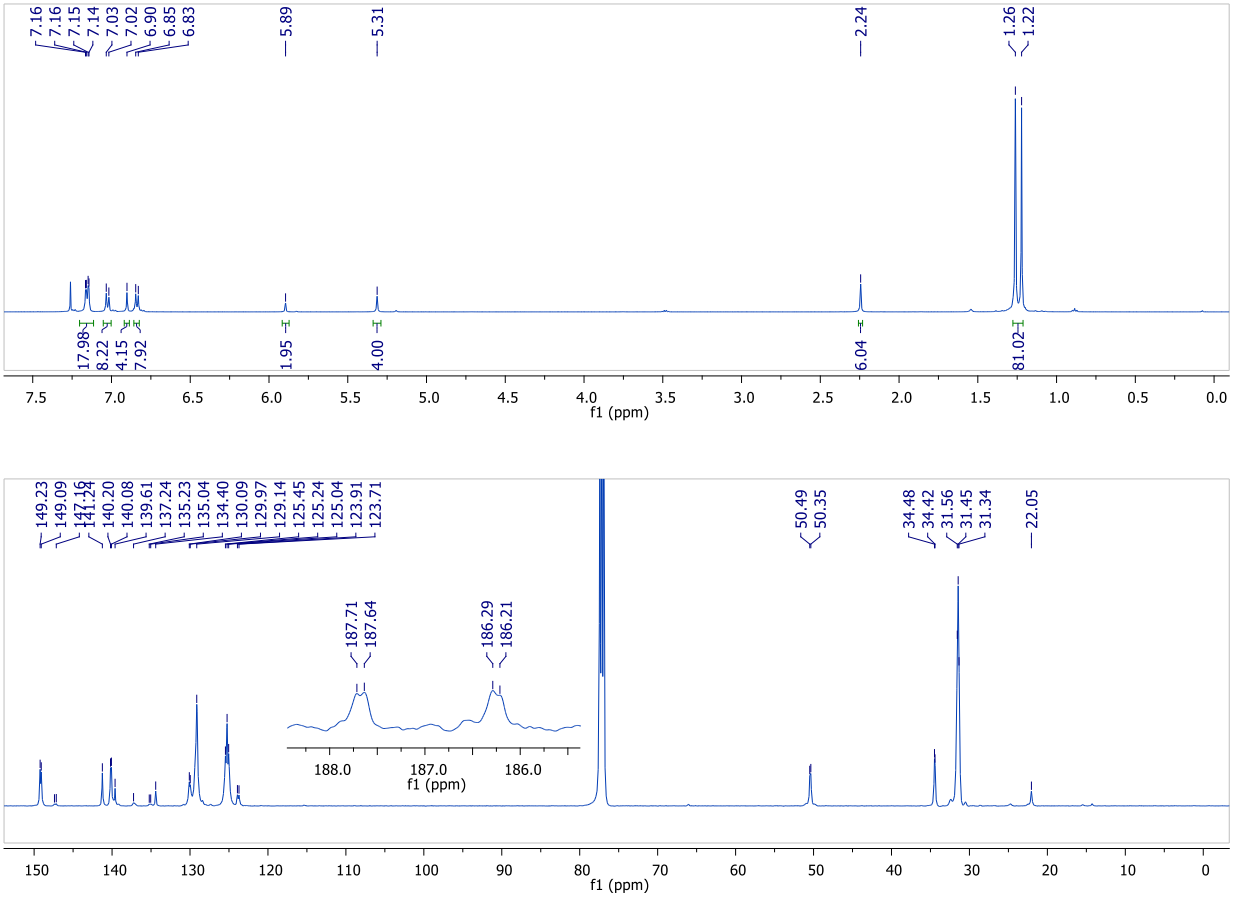


Synthesis of (IPr)AgH (5)**: A J-Young NMR tube charged with IPr**AgOPh (0.030 g, 0.019 mmol, 1 eq.) and 500 µL toluene-d_8 was cooled to -40 °C. Pinacol borane (2.8 µL, 0.019 mmol, 1 eq.) was added thus resulting in an immediate color change. The sample was taken to a pre-cooled NMR spectrometer at -40 °C. After collection of $^{1}H/^{13}C$ spectra, the sample was returned to the freezer overnight for crystallization. Clear colorless needles of **3** grew overnight, which were suitable for X-ray crystallography. M. P.: >-10 °C dec. ^{1}H NMR (tol-d_8, 500 MHz): δ 1.19 (s, 36 H), 1.24 (s, 36 H), 1.66 (s, 6 H), 3.87 (pseudo-dd, $^{1}J(^{1}H\text{-}^{107}Ag)$ = 224.6 Hz, $^{1}J(^{1}H\text{-}^{109}Ag)$ = 260.6 Hz, Ag-*H*), 5.68 (s, 2 H), 5.86 (s, 4 H), 6.95 (d, J = 8.1 Hz, 8 H), 7.03 (d, J = 8.2 Hz, 8 H), 7.14 (s, 4 H), 7.27 (d, J = 7.5 Hz, 8 H) , 7.69 (d, J = 7.0 Hz, 8 H). $^{13}C\{^{1}H\}$ NMR (tol-d_8, 125 MHz): δ 193.2 (pseudo-dd, $^{1}J(^{13}C\text{-}^{107}Ag)$ = 113.2 Hz, $^{1}J(^{13}C\text{-}^{109}Ag)$ = 126.6 Hz, $C_{carbene}$-Ag), 149.3, 149.0, 141.9, 141.5, 140.7, 140.0, 135.4, 130.2, 129.6, 125.8, 125.4, 123.5, 123.4, 50.8 ($CHAr_2$), 50.7 ($CHAr_2$), 34.5 ($ArCH_3$), 34.4 ($ArCH_3$), 31.52 ($C(CH_3)_3$), 31.48 ($C(CH_3)_3$), 31.45 ($C(CH_3)_3$), 21.2 ($C(CH_3)_3$). HRMS ESI-TOF+ shows only $[M - H]^+$.



Synthesis of (IPr)AgHBCF (6)**: To a J-Young NMR tube charged with IPr**AgOPh (0.060 g, 0.038 mmol, 1 eq.) and 600 µL tol-d_8 was added pinacol borane (5.6 µL, 0.038 mmol, 1 eq.) at -40 °C. After 15 minutes, solid BCF (0.020 g, 0.038 mmol, 1 eq.) was added in one portion and allowed to sit at -40 °C for 1 hour before being allowed to warm to room temperature. The solution was concentrated under vacuum until ~ 50 µL toluene remained. Pentane was added to the NMR tube and left at room temperature overnight, during which time, X-ray quality crystals

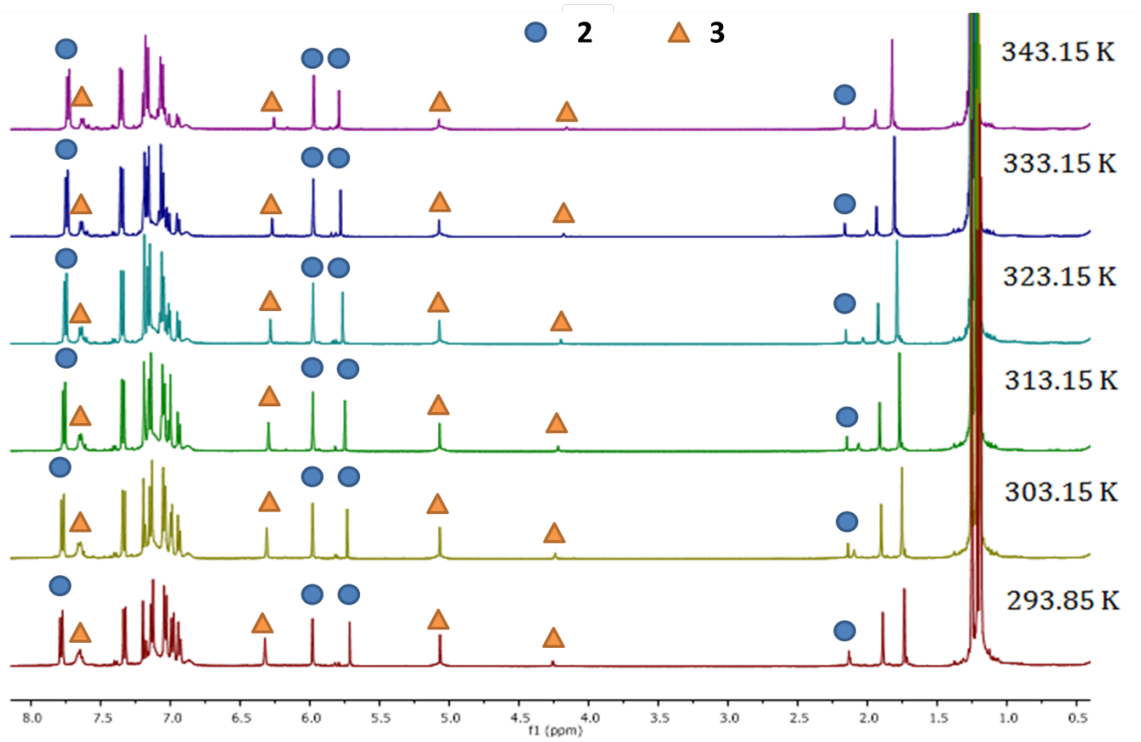
of **6** grew as colorless blocks. The white crystals were filtrated and dried under vacuum yielding 0.073 g (96 %) of **6**. M. P.: 271.8 °C dec. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 (s, 36 H), 1.26 (s, 36 H), 2.24 (s, 6 H), 5.31 (s, 4 H), 5.89 (s, 2 H), 6.84 (d, J = 8.1 Hz, 8 H), 6.90 (s, 4 H), 7.02 (d, J = 8.1 Hz, 8 H), 7.15 (d, J = 8.5 Hz, 8 H) , 7.16 (d, J = 8.5 Hz, 8 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 187.0 (pseudo-dd, $^{1}J(^{13}C\text{-}^{107}Ag)$ = 168.8 Hz, $^{1}J(^{13}C\text{-}^{109}Ag)$ = 189.0 Hz, $C_{carbene}$-Ag), 149.2, 149.1, 147.4, 147.2, 141.3, 140.2, 140.1, 139.6, 137.2, 135.2, 135.0, 134.4, 130.1, 130.0, 129.1, 125.5, 125.2, 125.0, 123.9, 123.7, 50.5 (*C*HAr$_2$), 50.4 (*C*HAr$_2$), 34.5 (Ar*C*H$_3$), 34.4 (Ar*C*H$_3$), 31.6 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 22.1 (*C*(CH$_3$)$_3$). ^{11}B NMR ($CDCl_3$, 96 MHz): δ -22.7 ppm.



D. Determining ΔG, ΔH, and ΔS for Dimerization of 2

(IPr)CuH Dimer – Monomer Equilibrium Variable Temperature NMR Experiment (2/3)**: IPr**CuOPh (67 mg, 44.0 µmol, 1 eq.) was added to a J-Young NMR tube. 400 µL C_6D_6 was added to the NMR tube followed by PMHS (2.8 µL, 44.0 µmol, 1 eq.) to give a 0.11 M solution. The tube was shaken and left overnight at room temperature. Over time, an intense yellow solution appeared, however without any precipitate formed. All volatiles were evaporated under vacuum. 0.2 mL of pentane was added to the residue and set in the freezer at -40 °C, at which temperature, a yellow powder formed. The solid was filtered and washed with 1 mL pentane and dried under vacuum. 400 µL C_6D_6 was then added to re-dissolve the solid **3** for VT

analysis at 10 °C intervals between 20.7 °C and 70 °C on a Varian Inova 500 MHz spectrometer. Upon reaching each temperature, the tube was allowed to equilibrate at this temperature for 10 minutes before data collection. After the first collection, 10 additional minutes elapsed before collection of a second spectrum at the same temperature. This process was repeated for each temperature point collected and again when returning to room temperature for a total of 4 collections at each temperature. The integration values were averaged before use in subsequent calculations.



Relevent Equations:

1) $\Delta G = -RTln(K_{eq})$

2) $\frac{\Delta G}{T} = -Rln(K_{eq})$

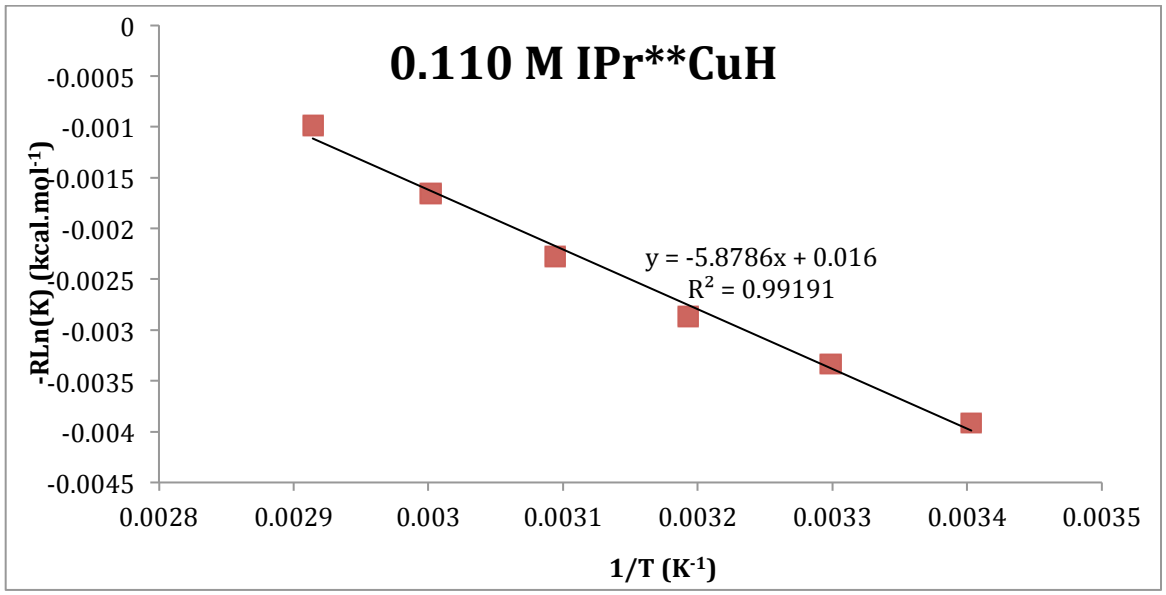
3) $\Delta G = \Delta H - T\Delta S$

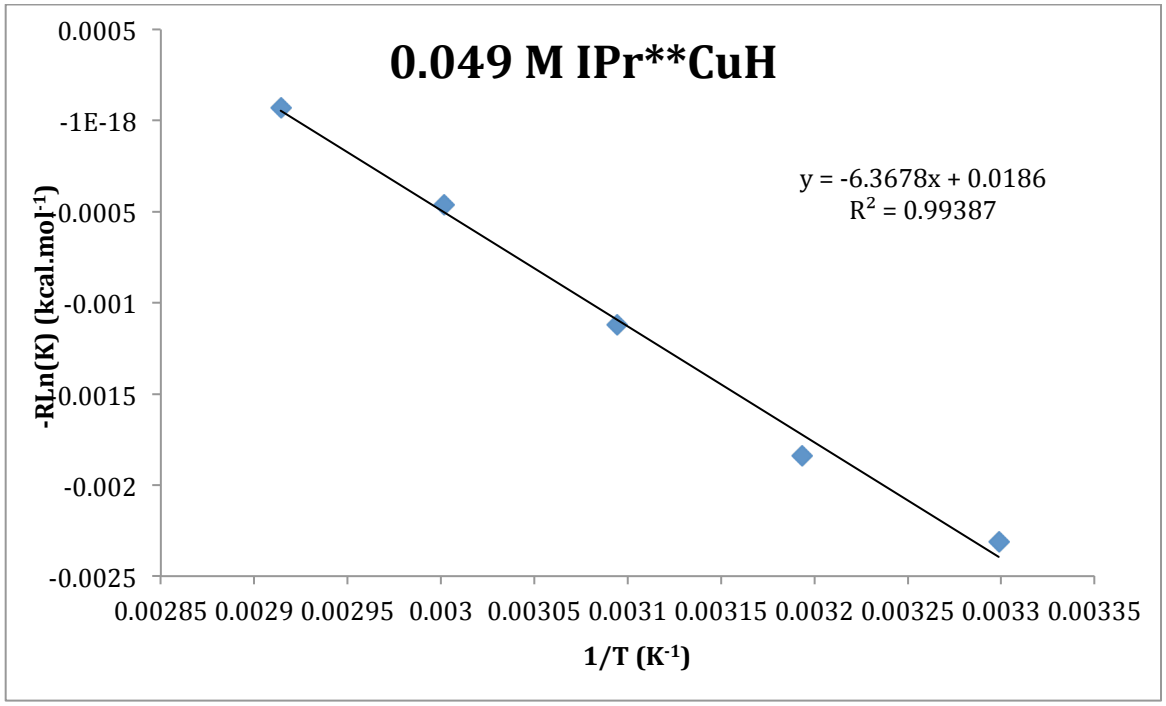
4) $\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$

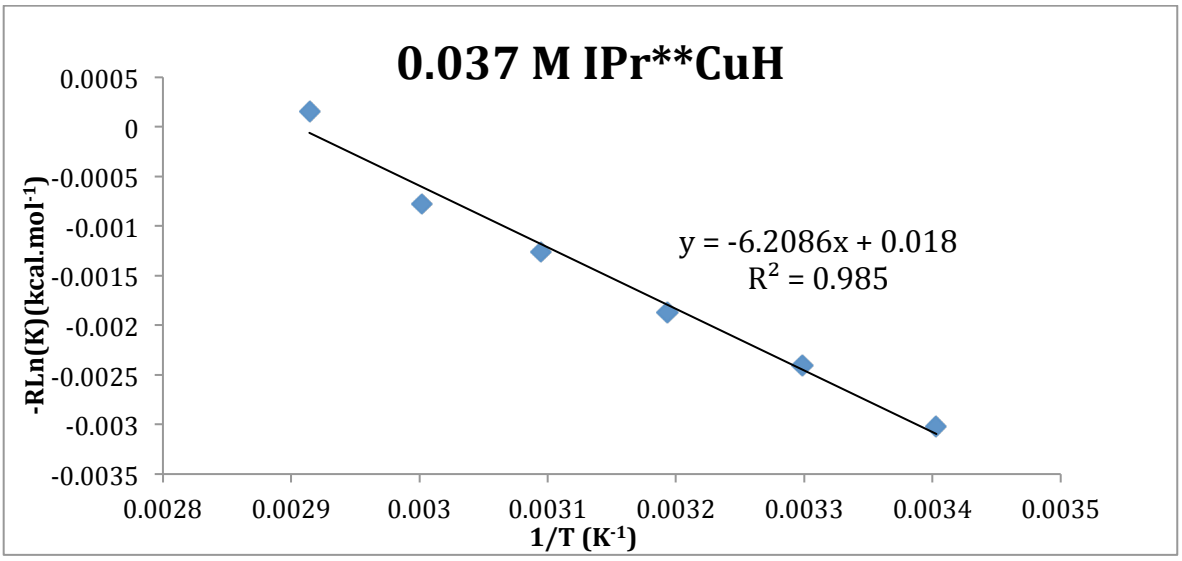
Plugging eq. 2 into eq. 4 gives the following:

5) $-Rln(K_{eq}) = \Delta H(\frac{1}{T}) - \Delta S$

Plotting –Rln(K_{eq}) vs. 1/T gives the linear plot shown below:







We can extract ΔH and ΔS from the m and b terms respectively, and use eq. 3 to solve for ΔG at 303 K. The values below correspond to the average of all three runs, 0.110 M 0.049 M, and 0.037 M.

ΔH	-6.15 ± 0.25	kcal.mol^{-1}
ΔS	-17.53 ± 1.36	cal.mol^{-1}.K^{-1}
$\Delta G_{(303K)}$	-0.84 ± 0.17	kcal.mol^{-1}

E. Crystal Structure Data For 3

Table 1 Crystal data and structure refinement for 3.

Identification code	P432121_sq
Empirical formula	C_{101} $H_{121}CuN_2$
Formula weight	1426.98
Temperature/K	100.0
Crystal system	tetragonal
Space group	$P4_32_12$
a/Å	30.1192(9)
b/Å	30.1192(9)
c/Å	21.0808(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	19123.8(14)
Z	8

ρ_{calc}g/cm^3	0.991
μ/mm^{-1}	0.627
F(000)	6162.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.148 to 114.466
Index ranges	-31 ≤ h ≤ 32, -18 ≤ k ≤ 32, -21 ≤ l ≤ 22
Reflections collected	87121
Independent reflections	12225 [R_{int} = 0.0316, R_{sigma} = 0.0222]
Data/restraints/parameters	12225/135/1155
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1615
Final R indexes [all data]	R_1 = 0.0648, wR_2 = 0.1685
Largest diff. peak/hole / e Å^{-3}	0.47/-0.35
Flack parameter	0.017(5)

Table 4 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu1[1]	2.3243(17)	C63	C66	1.491(9)
Cu1	C1	1.895(6)	C64	C65	1.396(9)
N1	C1	1.360(8)	C65	C98	1.534(8)
N1	C2	1.394(8)	C67	C68	1.525(8)
N1	C4	1.440(7)	C67	C88	1.480(11)
N2	C1	1.375(7)	C67	C78	1.72(2)
N2	C3	1.401(8)	C68	C69	1.380(8)
N2	C60	1.431(7)	C68	C73	1.385(8)
C2	C3	1.332(9)	C69	C70	1.393(9)
C4	C5	1.405(8)	C70	C71	1.374(9)
C4	C9	1.419(9)	C71	C72	1.407(9)
C5	C6	1.393(9)	C71	C74	1.534(9)
C5	C11	1.518(9)	C72	C73	1.361(9)
C6	C7	1.394(9)	C74	C75	1.530(11)
C7	C8	1.368(9)	C74	C76	1.488(10)
C7	C10	1.509(9)	C74	C77	1.534(10)
C8	C9	1.367(9)	C98	C99	1.518(8)
C9	C35	1.529(9)	C98	C113	1.530(9)
C11	C12	1.533(9)	C99	C100	1.364(9)
C11	C25	1.524(10)	C99	C104	1.378(9)
C12	C13	1.353(9)	C100	C101	1.360(10)
C12	C17	1.375(10)	C101	C102	1.380(11)
C13	C14	1.383(9)	C102	C103	1.377(11)
C14	C15	1.389(10)	C102	C105	1.48(2)

C15	C16	1.383(11)	C102	C106	1.66(2)
C15	C18	1.531(10)	C103	C104	1.399(9)
C16	C17	1.376(11)	C113	C114	1.387(10)
C18	C19	1.551(14)	C113	C118	1.364(9)
C18	C21	1.476(16)	C114	C115	1.385(11)
C18	C23	1.540(14)	C115	C116	1.386(12)
C18	C20	1.39(5)	C116	C117	1.399(11)
C18	C22	1.57(5)	C116	C119	1.543(11)
C18	C24	1.50(7)	C117	C118	1.381(10)
C25	C26	1.403(10)	C119	C120	1.551(16)
C25	C30	1.368(9)	C119	C121	1.533(13)
C26	C27	1.364(11)	C119	C122	1.518(15)
C27	C28	1.382(12)	C53	C56	1.48(4)
C28	C29	1.394(11)	C53	C57	1.52(4)
C28	C31	1.543(13)	C53	C59	1.57(4)
C29	C30	1.381(10)	C88	C89	1.391(13)
C31	C32	1.535(18)	C88	C93	1.387(16)
C31	C33	1.540(15)	C89	C90	1.393(17)
C31	C34	1.531(15)	C90	C91	1.423(19)
C35	C36	1.533(9)	C91	C92	1.40(2)
C35	C46	1.528(9)	C91	C94	1.51(2)
C36	C37	1.362(9)	C92	C93	1.385(16)
C36	C41	1.390(9)	C94	C95	1.53(2)
C37	C38	1.366(9)	C94	C96	1.519(19)
C38	C39	1.401(10)	C94	C97	1.51(3)
C39	C40	1.385(11)	C105	C108	1.62(4)
C39	C42	1.558(11)	C105	C110	1.46(4)
C40	C41	1.362(10)	C105	C112	1.46(4)
C42	C43	1.517(13)	C52	C54	1.61(5)
C42	C44	1.503(13)	C52	C55	1.42(5)
C42	C45	1.543(12)	C52	C58	1.55(5)
C46	C47	1.387(9)	C78	C83	1.3900
C46	C51	1.387(10)	C78	C79	1.3900
C47	C48	1.397(10)	C83	C82	1.3900
C48	C49	1.389(11)	C82	C81	1.3900
C49	C50	1.390(10)	C81	C80	1.3900
C49	C53	1.58(4)	C81	C84	1.61(5)
C49	C52	1.48(4)	C80	C79	1.3900
C50	C51	1.393(10)	C84	C85	1.50(6)
C60	C61	1.395(8)	C84	C86	1.52(6)
C60	C65	1.396(8)	C84	C87	1.64(5)
C61	C62	1.375(8)	C106	C107	1.51(4)

C61	C67	1.532(8)	C106	C109	1.55(3)
C62	C63	1.395(8)	C106	C111	1.59(4)
C63	C64	1.393(9)			

[1]+Y,+X,-Z

Table 5 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Cu1	Cu1[1]	170.41(18)	C60	C65	C98	122.9(5)
C1	N1	C2	112.7(5)	C64	C65	C98	119.4(5)
C1	N1	C4	122.9(5)	C61	C67	C78	105.2(11)
C2	N1	C4	124.3(5)	C68	C67	C61	107.7(5)
C1	N2	C3	111.4(5)	C68	C67	C78	113.6(14)
C1	N2	C60	129.2(5)	C88	C67	C61	117.9(6)
C3	N2	C60	119.3(5)	C88	C67	C68	113.4(6)
N1	C1	Cu1	124.8(4)	C69	C68	C67	123.7(5)
N1	C1	N2	102.5(5)	C69	C68	C73	116.8(6)
N2	C1	Cu1	132.6(4)	C73	C68	C67	119.5(5)
C3	C2	N1	106.3(6)	C68	C69	C70	121.4(6)
C2	C3	N2	107.0(5)	C71	C70	C69	121.9(6)
C5	C4	N1	118.2(5)	C70	C71	C72	115.9(6)
C5	C4	C9	121.5(6)	C70	C71	C74	123.3(6)
C9	C4	N1	120.3(5)	C72	C71	C74	120.7(6)
C4	C5	C11	120.5(6)	C73	C72	C71	122.0(6)
C6	C5	C4	117.5(5)	C72	C73	C68	121.9(6)
C6	C5	C11	121.9(6)	C75	C74	C71	110.1(6)
C5	C6	C7	121.4(6)	C75	C74	C77	108.9(6)
C6	C7	C10	119.2(6)	C76	C74	C71	111.8(6)
C8	C7	C6	119.2(6)	C76	C74	C75	106.5(7)
C8	C7	C10	121.6(6)	C76	C74	C77	111.3(7)
C7	C8	C9	122.9(6)	C77	C74	C71	108.2(6)
C4	C9	C35	118.4(5)	C99	C98	C65	108.7(5)
C8	C9	C4	117.6(6)	C99	C98	C113	113.6(5)
C8	C9	C35	123.9(5)	C113	C98	C65	115.6(5)
C5	C11	C12	112.7(5)	C100	C99	C98	118.7(5)
C5	C11	C25	109.8(5)	C100	C99	C104	117.5(6)
C25	C11	C12	111.9(5)	C104	C99	C98	123.8(6)
C13	C12	C11	120.5(6)	C101	C100	C99	122.2(7)
C13	C12	C17	117.9(6)	C100	C101	C102	121.7(7)
C17	C12	C11	121.6(6)	C101	C102	C105	112.9(13)
C12	C13	C14	121.8(6)	C101	C102	C106	129.0(11)
C13	C14	C15	121.4(7)	C103	C102	C101	116.9(7)

C14	C15	C18	122.6(7)	C103	C102	C105	128.6(13)
C16	C15	C14	115.6(7)	C103	C102	C106	113.6(11)
C16	C15	C18	121.9(7)	C102	C103	C104	121.2(7)
C17	C16	C15	122.6(7)	C99	C104	C103	120.5(6)
C12	C17	C16	120.6(8)	C114	C113	C98	117.4(6)
C15	C18	C19	111.3(7)	C118	C113	C98	125.1(6)
C15	C18	C23	109.3(7)	C118	C113	C114	117.5(7)
C15	C18	C22	107.7(19)	C115	C114	C113	120.8(8)
C21	C18	C15	109.2(8)	C114	C115	C116	122.6(8)
C21	C18	C19	109.1(10)	C115	C116	C117	115.3(7)
C21	C18	C23	112.2(10)	C115	C116	C119	121.3(8)
C23	C18	C19	105.7(9)	C117	C116	C119	123.4(9)
C20	C18	C15	108(2)	C118	C117	C116	122.0(8)
C20	C18	C22	115(4)	C113	C118	C117	121.8(7)
C20	C18	C24	112(4)	C116	C119	C120	107.6(9)
C24	C18	C15	110(2)	C121	C119	C116	107.9(8)
C24	C18	C22	103(4)	C121	C119	C120	110.6(9)
C26	C25	C11	119.9(6)	C122	C119	C116	113.5(8)
C30	C25	C11	123.0(6)	C122	C119	C120	107.7(8)
C30	C25	C26	117.1(7)	C122	C119	C121	109.5(11)
C27	C26	C25	121.2(7)	C56	C53	C49	111(2)
C26	C27	C28	122.0(8)	C56	C53	C57	109(3)
C27	C28	C29	116.7(7)	C56	C53	C59	110(3)
C27	C28	C31	121.1(8)	C57	C53	C49	107(2)
C29	C28	C31	122.2(8)	C57	C53	C59	108(2)
C30	C29	C28	121.3(8)	C59	C53	C49	111(3)
C25	C30	C29	121.7(7)	C89	C88	C67	121.7(8)
C32	C31	C28	109.3(11)	C93	C88	C67	122.8(9)
C32	C31	C33	109.2(10)	C93	C88	C89	115.5(10)
C33	C31	C28	108.3(8)	C88	C89	C90	122.6(11)
C34	C31	C28	112.5(8)	C89	C90	C91	120.7(11)
C34	C31	C32	110.8(9)	C90	C91	C94	117.4(18)
C34	C31	C33	106.6(11)	C92	C91	C90	116.8(12)
C9	C35	C36	113.2(5)	C92	C91	C94	125.8(17)
C46	C35	C9	110.0(5)	C93	C92	C91	120.2(14)
C46	C35	C36	112.4(5)	C92	C93	C88	124.2(16)
C37	C36	C35	119.8(5)	C91	C94	C95	114.8(13)
C37	C36	C41	116.6(6)	C91	C94	C96	108.6(11)
C41	C36	C35	123.5(6)	C91	C94	C97	109.7(18)
C36	C37	C38	122.8(6)	C96	C94	C95	105.7(14)
C37	C38	C39	120.6(7)	C97	C94	C95	106.3(13)
C38	C39	C42	119.3(7)	C97	C94	C96	111.7(14)

C40	C39	C38	116.8(7)	C102	C105	C108	106.4(17)
C40	C39	C42	123.9(6)	C110	C105	C102	112(2)
C41	C40	C39	121.2(6)	C110	C105	C108	107(3)
C40	C41	C36	121.9(7)	C110	C105	C112	105(2)
C43	C42	C39	109.6(6)	C112	C105	C102	118(2)
C43	C42	C45	108.4(8)	C112	C105	C108	108(2)
C44	C42	C39	109.9(7)	C49	C52	C54	110(3)
C44	C42	C43	109.5(8)	C49	C52	C58	111(3)
C44	C42	C45	108.6(7)	C55	C52	C49	111(3)
C45	C42	C39	110.8(7)	C55	C52	C54	107(3)
C47	C46	C35	120.9(6)	C55	C52	C58	110(3)
C51	C46	C35	121.3(6)	C58	C52	C54	107(3)
C51	C46	C47	117.8(6)	C83	C78	C67	121.1(19)
C46	C47	C48	120.7(7)	C83	C78	C79	120.0
C49	C48	C47	121.9(7)	C79	C78	C67	118.1(18)
C48	C49	C50	116.8(7)	C78	C83	C82	120.0
C48	C49	C53	125.6(13)	C83	C82	C81	120.0
C48	C49	C52	117.8(18)	C82	C81	C84	122(3)
C50	C49	C53	117.2(13)	C80	C81	C82	120.0
C50	C49	C52	125.3(19)	C80	C81	C84	118(3)
C49	C50	C51	121.6(7)	C81	C80	C79	120.0
C46	C51	C50	121.1(6)	C80	C79	C78	120.0
C61	C60	N2	119.3(5)	C81	C84	C87	103(2)
C61	C60	C65	121.3(5)	C85	C84	C81	111(5)
C65	C60	N2	119.1(5)	C85	C84	C86	117(3)
C60	C61	C67	121.0(5)	C85	C84	C87	107(3)
C62	C61	C60	118.6(5)	C86	C84	C81	109(2)
C62	C61	C67	120.0(5)	C86	C84	C87	108(4)
C61	C62	C63	122.3(5)	C107	C106	C102	109(2)
C62	C63	C66	122.2(6)	C107	C106	C109	112(3)
C64	C63	C62	117.1(5)	C107	C106	C111	107(2)
C64	C63	C66	120.6(5)	C109	C106	C102	113.3(16)
C63	C64	C65	122.5(5)	C109	C106	C111	113(3)
C60	C65	C64	117.4(5)	C111	C106	C102	101.5(19)

[1]+Y,+X,-Z

F. Crystal Structure Data For 5

Table 1 Crystal data and structure refinement for 5.

Identification code	ER_Final_sq
Empirical formula	$C_{101}H_{121}AgN_2$
Formula weight	1470.86

Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	17.8877(4)
b/Å	20.6603(5)
c/Å	29.4115(8)
α/°	88.331(2)
β/°	86.405(2)
γ/°	71.350(2)
Volume/Å^3	10278.0(5)
Z	4
ρ_{calc}g/cm^3	0.951
μ/mm^{-1}	1.857
F(000)	3152.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.514 to 109.018
Index ranges	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	89116
Independent reflections	25145 [R_{int} = 0.0861, R_{sigma} = 0.0916]
Data/restraints/parameters	25145/69/1930
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0782, wR_2 = 0.1924
Final R indexes [all data]	R_1 = 0.1105, wR_2 = 0.2133
Largest diff. peak/hole / e Å^{-3}	2.41/-0.89

Table 4 Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag1	C1	2.108(6)	N1'	C2'	1.374(7)
N1	C1	1.333(7)	N1'	C53'	1.461(7)
N1	C2	1.396(8)	N2'	C1'	1.354(7)
N1	C53	1.456(7)	N2'	C3'	1.391(8)
N2	C1	1.358(7)	N2'	C4'	1.419(7)
N2	C3	1.394(8)	C2'	C3'	1.357(8)
N2	C4	1.442(7)	C4'	C5'	1.407(8)
C2	C3	1.346(8)	C4'	C9'	1.398(8)
C4	C5	1.402(8)	C5'	C6'	1.400(8)
C4	C9	1.400(8)	C5'	C32'	1.521(8)
C5	C6	1.385(8)	C6'	C7'	1.395(8)
C5	C32	1.515(8)	C7'	C8'	1.382(8)
C6	C7	1.410(8)	C7'	C10'	1.496(8)
C7	C8	1.383(8)	C8'	C9'	1.388(8)

C7	C10	1.510(8)	C9'	C11'	1.545(8)
C8	C9	1.386(8)	C11'	C12'	1.509(10)
C9	C11	1.533(8)	C11'	C22'	1.536(9)
C11	C12	1.535(8)	C12'	C13'	1.389(11)
C11	C22	1.522(9)	C12'	C17'	1.381(10)
C12	C13	1.374(9)	C13'	C14'	1.393(13)
C12	C17	1.386(9)	C14'	C15'	1.388(14)
C13	C14	1.389(9)	C15'	C16'	1.404(14)
C14	C15	1.386(9)	C15'	C18'	1.526(14)
C15	C16	1.395(10)	C16'	C17'	1.398(13)
C15	C18	1.527(10)	C18'	C19'	1.581(14)
C16	C17	1.380(10)	C18'	C20'	1.543(14)
C18	C19	1.539(11)	C18'	C21'	1.511(14)
C18	C20	1.531(11)	C18'	C19C	1.506(18)
C18	C21	1.501(11)	C18'	C20C	1.547(19)
C22	C23	1.381(9)	C18'	C21C	1.544(19)
C22	C27	1.394(9)	C22'	C23'	1.363(9)
C23	C24	1.384(9)	C22'	C27'	1.388(10)
C24	C25	1.381(9)	C23'	C24'	1.407(10)
C25	C26	1.393(9)	C24'	C25'	1.373(10)
C25	C28	1.529(10)	C25'	C26'	1.382(9)
C26	C27	1.370(9)	C25'	C28'	1.526(10)
C28	C29A	1.529(12)	C26'	C27'	1.388(10)
C28	C30A	1.532(13)	C28'	C29'	1.594(15)
C28	C31A	1.556(13)	C28'	C30'	1.467(15)
C28	C29B	1.577(18)	C28'	C31'	1.484(15)
C28	C30B	1.540(18)	C28'	C29C	1.539(14)
C28	C31B	1.529(18)	C28'	C30C	1.641(15)
C32	C33	1.544(9)	C28'	C31C	1.479(13)
C32	C43	1.513(9)	C32'	C33'	1.520(8)
C33	C34	1.377(9)	C32'	C43'	1.526(8)
C33	C38	1.383(9)	C33'	C34'	1.386(8)
C34	C35	1.385(10)	C33'	C38'	1.392(9)
C35	C36	1.402(10)	C34'	C35'	1.391(9)
C36	C37	1.381(10)	C35'	C36'	1.371(9)
C36	C39	1.535(11)	C36'	C37'	1.382(10)
C37	C38	1.382(10)	C36'	C39'	1.537(11)
C39	C40	1.545(12)	C37'	C38'	1.395(10)
C39	C41	1.583(13)	C39'	C40'	1.592(16)
C39	C42	1.503(12)	C39'	C41'	1.480(16)
C43	C44	1.396(10)	C39'	C42'	1.486(14)
C43	C48	1.372(11)	C43'	C48'	1.393(8)

C44	C45	1.420(11)	C43'	C44'	1.378(8)
C45	C46	1.375(13)	C45'	C46'	1.424(10)
C46	C47	1.373(13)	C45'	C44'	1.367(10)
C46	C49A	1.61(2)	C46'	C47'	1.389(9)
C46	C49B	1.54(2)	C46'	C49'	1.515(10)
C47	C48	1.401(10)	C47'	C48'	1.382(9)
C53	C54	1.399(8)	C49'	C50'	1.509(11)
C53	C58	1.398(8)	C49'	C51'	1.525(12)
C54	C55	1.391(8)	C49'	C52'	1.550(11)
C54	C60	1.510(8)	C53'	C54'	1.390(8)
C55	C56	1.391(8)	C53'	C58'	1.399(8)
C56	C57	1.389(8)	C54'	C55'	1.401(8)
C56	C59	1.506(8)	C54'	C60'	1.529(8)
C57	C58	1.397(8)	C55'	C56'	1.391(8)
C58	C81	1.528(8)	C56'	C57'	1.390(8)
C60	C61	1.539(8)	C56'	C59'	1.499(8)
C60	C71	1.518(8)	C57'	C58'	1.387(8)
C61	C62	1.360(9)	C58'	C81'	1.537(8)
C61	C66	1.382(10)	C60'	C61'	1.529(9)
C62	C63	1.416(11)	C60'	C71'	1.509(8)
C63	C64	1.354(11)	C61'	C62'	1.381(14)
C64	C65	1.371(11)	C61'	C66'	1.37(2)
C64	C67	1.513(12)	C61'	C62C	1.451(19)
C65	C66	1.399(11)	C61'	C66C	1.29(2)
C67	C68	1.494(16)	C64'	C67'	1.544(11)
C67	C69	1.582(18)	C64'	C63'	1.391(17)
C67	C70	1.486(16)	C64'	C65'	1.361(19)
C71	C72	1.387(8)	C64'	C63C	1.36(2)
C71	C76	1.392(9)	C64'	C65C	1.38(2)
C72	C73	1.391(10)	C67'	C68'	1.520(15)
C73	C74	1.379(11)	C67'	C69'	1.520(13)
C74	C75	1.390(10)	C67'	C70'	1.524(13)
C74	C77	1.528(10)	C71'	C72'	1.387(8)
C75	C76	1.368(10)	C71'	C76'	1.384(8)
C77	C78A	1.573(15)	C72'	C73'	1.378(8)
C77	C79A	1.486(14)	C73'	C74'	1.396(8)
C77	C80A	1.536(14)	C74'	C75'	1.374(9)
C77	C78B	1.537(16)	C74'	C77'	1.537(9)
C77	C79B	1.549(16)	C75'	C76'	1.375(9)
C77	C80B	1.527(16)	C77'	C78'	1.552(10)
C81	C82	1.530(10)	C77'	C79'	1.539(11)
C81	C92	1.518(9)	C77'	C80'	1.503(11)

C82	C83	1.390(10)	C77'	C78C	1.511(16)
C82	C87	1.408(9)	C77'	C79C	1.556(16)
C83	C84	1.393(11)	C77'	C80C	1.564(16)
C84	C85	1.394(10)	C81'	C82'	1.516(8)
C85	C86	1.381(11)	C81'	C92'	1.540(8)
C85	C88	1.535(11)	C82'	C83'	1.391(9)
C86	C87	1.397(11)	C82'	C87'	1.374(8)
C88	C89A	1.538(12)	C83'	C84'	1.388(10)
C88	C90A	1.522(13)	C84'	C85'	1.395(10)
C88	C91A	1.539(12)	C85'	C86'	1.374(10)
C88	C89B	1.536(18)	C85'	C88'	1.544(10)
C88	C90B	1.556(19)	C86'	C87'	1.392(10)
C88	C91B	1.539(19)	C88'	C89'	1.518(9)
C92	C93	1.407(9)	C88'	C90'	1.522(10)
C92	C97	1.374(10)	C88'	C91'	1.573(9)
C93	C94	1.388(11)	C88'	C89C	1.567(18)
C94	C95	1.370(12)	C88'	C90C	1.558(18)
C95	C96	1.385(11)	C88'	C91C	1.526(17)
C95	C98	1.546(12)	C92'	C93'	1.372(9)
C96	C97	1.413(10)	C92'	C97'	1.384(9)
C98	C99	1.526(11)	C93'	C94'	1.382(9)
C98	C100	1.535(14)	C94'	C95'	1.391(9)
C98	C101	1.537(14)	C95'	C96'	1.370(10)
C5BA	C49A	1.537(16)	C95'	C98'	1.548(10)
C49A	C51A	1.521(17)	C96'	C97'	1.389(10)
C49A	C52A	1.531(16)	C98'	C99'	1.513(12)
C49B	C50B	1.558(17)	C98'	C200	1.529(10)
C49B	C51B	1.584(17)	C98'	C201	1.536(11)
C49B	C52B	1.542(16)	C62'	C63'	1.355(18)
Ag2	C1'	2.128(6)	C65'	C66'	1.44(3)
Ag2A	C1'	2.138(9)	C62C	C63C	1.40(2)
N1'	C1'	1.346(7)	C65C	C66C	1.40(3)

Table 5 Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	112.5(4)	C3'	N2'	C4'	122.5(5)
C1	N1	C53	126.2(5)	N1'	C1'	Ag2	128.1(4)
C2	N1	C53	121.3(5)	N1'	C1'	Ag2A	128.8(4)
C1	N2	C3	111.2(5)	N1'	C1'	N2'	104.7(5)
C1	N2	C4	125.4(5)	N2'	C1'	Ag2	127.2(4)

C3	N2	C4	123.4(5)	N2'	C1'	Ag2A	110.4(4)
N1	C1	Ag1	127.9(4)	C3'	C2'	N1'	106.4(5)
N1	C1	N2	104.1(5)	C2'	C3'	N2'	106.3(5)
N2	C1	Ag1	128.1(4)	C5'	C4'	N2'	118.6(5)
C3	C2	N1	105.7(5)	C9'	C4'	N2'	120.2(5)
C2	C3	N2	106.6(5)	C9'	C4'	C5'	121.2(5)
C5	C4	N2	118.2(5)	C4'	C5'	C32'	121.3(5)
C9	C4	N2	119.0(5)	C6'	C5'	C4'	117.6(5)
C9	C4	C5	122.6(5)	C6'	C5'	C32'	121.0(5)
C4	C5	C32	119.4(5)	C7'	C6'	C5'	122.3(5)
C6	C5	C4	117.7(5)	C6'	C7'	C10'	120.6(5)
C6	C5	C32	122.6(5)	C8'	C7'	C6'	117.6(5)
C5	C6	C7	121.4(5)	C8'	C7'	C10'	121.8(5)
C6	C7	C10	120.1(5)	C7'	C8'	C9'	122.8(5)
C8	C7	C6	118.2(5)	C4'	C9'	C11'	120.5(5)
C8	C7	C10	121.7(5)	C8'	C9'	C4'	118.2(5)
C7	C8	C9	122.8(5)	C8'	C9'	C11'	121.3(5)
C4	C9	C11	120.6(5)	C12'	C11'	C9'	114.2(5)
C8	C9	C4	117.1(5)	C12'	C11'	C22'	112.8(5)
C8	C9	C11	122.3(5)	C22'	C11'	C9'	110.6(5)
C9	C11	C12	112.6(5)	C13'	C12'	C11'	123.8(6)
C22	C11	C9	109.5(5)	C17'	C12'	C11'	117.2(7)
C22	C11	C12	116.0(5)	C17'	C12'	C13'	118.9(8)
C13	C12	C11	121.1(5)	C12'	C13'	C14'	120.9(8)
C13	C12	C17	117.5(6)	C15'	C14'	C13'	121.7(9)
C17	C12	C11	121.0(6)	C14'	C15'	C16'	116.3(9)
C12	C13	C14	121.6(6)	C14'	C15'	C18'	122.6(10)
C15	C14	C13	121.7(7)	C16'	C15'	C18'	121.1(10)
C14	C15	C16	116.0(6)	C17'	C16'	C15'	122.6(9)
C14	C15	C18	122.5(7)	C12'	C17'	C16'	119.6(9)
C16	C15	C18	121.5(6)	C15'	C18'	C19'	112.4(11)
C17	C16	C15	122.3(6)	C15'	C18'	C20'	110.3(10)
C16	C17	C12	120.9(7)	C15'	C18'	C20C	105(2)
C15	C18	C19	108.4(6)	C15'	C18'	C21C	102(2)
C15	C18	C20	112.7(6)	C20'	C18'	C19'	101.1(10)
C20	C18	C19	107.3(7)	C21'	C18'	C15'	111.0(9)
C21	C18	C15	109.5(6)	C21'	C18'	C19'	108.1(11)
C21	C18	C19	110.3(7)	C21'	C18'	C20'	113.6(12)
C21	C18	C20	108.7(7)	C19C	C18'	C15'	112(2)
C23	C22	C11	124.5(6)	C19C	C18'	C20C	113.0(17)
C23	C22	C27	116.8(6)	C19C	C18'	C21C	113.3(18)
C27	C22	C11	118.6(5)	C21C	C18'	C20C	110.0(17)

C22	C23	C24	121.2(6)	C23'	C22'	C11'	123.2(7)
C25	C24	C23	122.0(6)	C23'	C22'	C27'	117.3(6)
C24	C25	C26	116.8(6)	C27'	C22'	C11'	119.5(5)
C24	C25	C28	122.1(6)	C22'	C23'	C24'	120.7(7)
C26	C25	C28	121.1(6)	C25'	C24'	C23'	122.5(6)
C27	C26	C25	121.3(6)	C24'	C25'	C26'	116.3(6)
C26	C27	C22	121.9(6)	C24'	C25'	C28'	120.4(6)
C25	C28	C29A	109.2(7)	C26'	C25'	C28'	123.3(7)
C25	C28	C30A	113.7(7)	C25'	C26'	C27'	121.6(7)
C25	C28	C31A	107.9(7)	C22'	C27'	C26'	121.6(6)
C25	C28	C29B	105.7(13)	C25'	C28'	C29'	105.4(9)
C25	C28	C30B	109.9(14)	C25'	C28'	C29C	116.1(8)
C25	C28	C31B	114.0(12)	C25'	C28'	C30C	107.9(7)
C29A	C28	C30A	110.6(9)	C30'	C28'	C25'	108.5(9)
C29A	C28	C31A	109.9(9)	C30'	C28'	C29'	108.6(12)
C30A	C28	C31A	105.4(9)	C30'	C28'	C31'	119.8(14)
C30B	C28	C29B	106.9(18)	C31'	C28'	C25'	110.7(9)
C31B	C28	C29B	100.9(19)	C31'	C28'	C29'	102.9(12)
C31B	C28	C30B	118(2)	C29C	C28'	C30C	100.1(11)
C5	C32	C33	110.2(5)	C31C	C28'	C25'	114.5(8)
C43	C32	C5	113.5(5)	C31C	C28'	C29C	112.7(10)
C43	C32	C33	117.1(5)	C31C	C28'	C30C	103.6(11)
C34	C33	C32	119.8(5)	C5'	C32'	C43'	109.8(4)
C34	C33	C38	117.9(6)	C33'	C32'	C5'	115.2(5)
C38	C33	C32	121.9(5)	C33'	C32'	C43'	113.5(5)
C33	C34	C35	121.4(6)	C34'	C33'	C32'	120.5(5)
C34	C35	C36	120.7(7)	C34'	C33'	C38'	117.4(6)
C35	C36	C39	121.2(6)	C38'	C33'	C32'	121.8(5)
C37	C36	C35	117.0(7)	C33'	C34'	C35'	121.4(6)
C37	C36	C39	121.7(6)	C36'	C35'	C34'	122.0(6)
C36	C37	C38	121.7(6)	C35'	C36'	C37'	116.5(6)
C37	C38	C33	120.9(6)	C35'	C36'	C39'	121.6(7)
C36	C39	C40	108.5(7)	C37'	C36'	C39'	121.9(7)
C36	C39	C41	107.9(7)	C36'	C37'	C38'	122.8(7)
C40	C39	C41	108.4(8)	C33'	C38'	C37'	119.9(6)
C42	C39	C36	113.7(7)	C36'	C39'	C40'	108.7(8)
C42	C39	C40	109.2(8)	C41'	C39'	C36'	108.0(9)
C42	C39	C41	109.0(7)	C41'	C39'	C40'	115.1(9)
C44	C43	C32	123.3(7)	C41'	C39'	C42'	106.0(10)
C48	C43	C32	117.9(6)	C42'	C39'	C36'	114.3(8)
C48	C43	C44	118.6(6)	C42'	C39'	C40'	104.9(9)
C43	C44	C45	118.7(8)	C48'	C43'	C32'	122.9(5)

C46	C45	C44	121.9(8)	C44'	C43'	C32'	120.4(5)
C45	C46	C49A	129.4(11)	C44'	C43'	C48'	116.7(6)
C45	C46	C49B	108.4(12)	C44'	C45'	C46'	121.5(6)
C47	C46	C45	118.9(7)	C45'	C46'	C49'	122.2(6)
C47	C46	C49A	111.7(11)	C47'	C46'	C45'	115.4(6)
C47	C46	C49B	132.7(13)	C47'	C46'	C49'	122.3(6)
C46	C47	C48	119.8(9)	C48'	C47'	C46'	122.2(6)
C43	C48	C47	122.2(8)	C47'	C48'	C43'	121.6(5)
C54	C53	N1	118.5(5)	C46'	C49'	C51'	108.2(6)
C58	C53	N1	118.1(5)	C46'	C49'	C52'	109.6(6)
C58	C53	C54	123.4(5)	C50'	C49'	C46'	111.9(6)
C53	C54	C60	121.0(5)	C50'	C49'	C51'	113.3(8)
C55	C54	C53	116.8(5)	C50'	C49'	C52'	105.3(8)
C55	C54	C60	122.1(5)	C51'	C49'	C52'	108.5(7)
C56	C55	C54	122.3(5)	C54'	C53'	N1'	118.2(4)
C55	C56	C59	120.7(5)	C54'	C53'	C58'	123.2(5)
C57	C56	C55	118.3(5)	C58'	C53'	N1'	118.6(4)
C57	C56	C59	121.0(5)	C53'	C54'	C55'	116.6(5)
C56	C57	C58	122.4(5)	C53'	C54'	C60'	121.7(5)
C53	C58	C81	121.5(5)	C55'	C54'	C60'	121.6(5)
C57	C58	C53	116.6(5)	C56'	C55'	C54'	122.4(5)
C57	C58	C81	121.8(5)	C55'	C56'	C59'	120.3(5)
C54	C60	C61	110.8(5)	C57'	C56'	C55'	118.2(5)
C54	C60	C71	113.0(5)	C57'	C56'	C59'	121.4(5)
C71	C60	C61	113.3(4)	C58'	C57'	C56'	122.1(5)
C62	C61	C60	121.9(6)	C53'	C58'	C81'	120.5(5)
C62	C61	C66	116.9(6)	C57'	C58'	C53'	117.4(5)
C66	C61	C60	121.2(5)	C57'	C58'	C81'	122.1(5)
C61	C62	C63	120.6(7)	C54'	C60'	C61'	115.1(5)
C64	C63	C62	122.8(6)	C71'	C60'	C54'	111.5(5)
C63	C64	C65	116.6(7)	C71'	C60'	C61'	113.3(5)
C63	C64	C67	124.0(8)	C62'	C61'	C60'	116.0(7)
C65	C64	C67	119.4(9)	C66'	C61'	C60'	125.0(10)
C64	C65	C66	121.3(8)	C66'	C61'	C62'	118.9(11)
C61	C66	C65	121.8(7)	C62C	C61'	C60'	118.7(8)
C64	C67	C69	108.5(10)	C66C	C61'	C60'	126.2(11)
C68	C67	C64	109.3(9)	C66C	C61'	C62C	114.8(13)
C68	C67	C69	108.1(10)	C63'	C64'	C67'	122.3(8)
C70	C67	C64	114.5(9)	C65'	C64'	C67'	122.2(9)
C70	C67	C68	110.4(12)	C65'	C64'	C63'	115.5(10)
C70	C67	C69	105.8(10)	C63C	C64'	C67'	116.3(10)
C72	C71	C60	123.2(5)	C63C	C64'	C65C	119.0(13)

C72	C71	C76	116.2(6)	C65C	C64'	C67'	124.3(11)
C76	C71	C60	120.4(5)	C68'	C67'	C64'	109.2(8)
C71	C72	C73	121.5(6)	C68'	C67'	C69'	106.8(8)
C74	C73	C72	121.9(6)	C68'	C67'	C70'	110.3(9)
C73	C74	C75	116.2(6)	C69'	C67'	C64'	110.6(7)
C73	C74	C77	121.4(7)	C69'	C67'	C70'	109.8(8)
C75	C74	C77	122.5(7)	C70'	C67'	C64'	110.2(7)
C76	C75	C74	122.3(7)	C72'	C71'	C60'	119.7(5)
C75	C76	C71	121.9(6)	C76'	C71'	C60'	123.8(5)
C74	C77	C78A	110.8(8)	C76'	C71'	C72'	116.4(5)
C74	C77	C80A	113.4(7)	C73'	C72'	C71'	122.5(5)
C74	C77	C78B	107.6(12)	C72'	C73'	C74'	120.5(6)
C74	C77	C79B	106.4(13)	C73'	C74'	C77'	120.0(5)
C79A	C77	C74	110.1(8)	C75'	C74'	C73'	116.9(6)
C79A	C77	C78A	106.5(11)	C75'	C74'	C77'	123.1(5)
C79A	C77	C80A	111.3(11)	C74'	C75'	C76'	122.4(5)
C80A	C77	C78A	104.4(11)	C75'	C76'	C71'	121.3(6)
C78B	C77	C79B	110.6(13)	C74'	C77'	C78'	108.3(6)
C80B	C77	C74	107.6(12)	C74'	C77'	C79'	110.0(6)
C80B	C77	C78B	112.9(13)	C74'	C77'	C79C	106.5(12)
C80B	C77	C79B	111.5(13)	C74'	C77'	C80C	104.4(13)
C58	C81	C82	114.3(5)	C79'	C77'	C78'	108.1(7)
C92	C81	C58	110.1(5)	C80'	C77'	C74'	114.4(6)
C92	C81	C82	114.2(5)	C80'	C77'	C78'	108.7(7)
C83	C82	C81	122.2(6)	C80'	C77'	C79'	107.2(7)
C83	C82	C87	117.4(7)	C78C	C77'	C74'	114.6(13)
C87	C82	C81	119.8(6)	C78C	C77'	C79C	112.5(13)
C82	C83	C84	121.2(6)	C78C	C77'	C80C	110.3(13)
C83	C84	C85	122.0(7)	C79C	C77'	C80C	108.2(13)
C84	C85	C88	122.3(7)	C58'	C81'	C92'	111.3(4)
C86	C85	C84	116.4(7)	C82'	C81'	C58'	112.7(5)
C86	C85	C88	121.2(6)	C82'	C81'	C92'	113.8(5)
C85	C86	C87	122.9(6)	C83'	C82'	C81'	122.3(5)
C86	C87	C82	120.0(7)	C87'	C82'	C81'	120.1(5)
C85	C88	C89A	109.2(7)	C87'	C82'	C83'	117.5(6)
C85	C88	C91A	109.0(6)	C84'	C83'	C82'	121.3(6)
C85	C88	C89B	110(2)	C83'	C84'	C85'	121.1(7)
C85	C88	C90B	106(2)	C84'	C85'	C88'	118.8(7)
C85	C88	C91B	109(2)	C86'	C85'	C84'	117.0(6)
C89A	C88	C91A	108.7(7)	C86'	C85'	C88'	124.0(6)
C90A	C88	C85	112.7(7)	C85'	C86'	C87'	122.1(6)
C90A	C88	C89A	108.0(7)	C82'	C87'	C86'	121.1(6)

C90A	C88	C91A	109.2(8)	C85'	C88'	C91'	109.3(6)
C89B	C88	C90B	110.0(16)	C85'	C88'	C89C	95.2(17)
C89B	C88	C91B	112.4(17)	C85'	C88'	C90C	117.2(17)
C91B	C88	C90B	109.4(17)	C89'	C88'	C85'	111.8(7)
C93	C92	C81	122.7(6)	C89'	C88'	C90'	111.5(7)
C97	C92	C81	119.5(5)	C89'	C88'	C91'	106.0(6)
C97	C92	C93	117.8(6)	C90'	C88'	C85'	110.3(6)
C94	C93	C92	120.5(7)	C90'	C88'	C91'	107.7(7)
C95	C94	C93	121.8(6)	C90C	C88'	C89C	107.6(15)
C94	C95	C96	118.3(7)	C91C	C88'	C85'	114.8(18)
C94	C95	C98	122.2(7)	C91C	C88'	C89C	108.9(15)
C96	C95	C98	119.5(8)	C91C	C88'	C90C	111.3(15)
C95	C96	C97	120.5(8)	C93'	C92'	C81'	119.4(5)
C92	C97	C96	121.1(6)	C93'	C92'	C97'	117.5(6)
C99	C98	C95	109.9(7)	C97'	C92'	C81'	122.9(5)
C99	C98	C100	110.0(10)	C92'	C93'	C94'	122.4(6)
C99	C98	C101	107.9(8)	C93'	C94'	C95'	120.3(6)
C100	C98	C95	108.2(7)	C94'	C95'	C98'	122.6(6)
C100	C98	C101	109.2(7)	C96'	C95'	C94'	117.0(6)
C101	C98	C95	111.6(9)	C96'	C95'	C98'	120.4(6)
C5BA	C49A	C46	105.9(12)	C95'	C96'	C97'	122.8(6)
C51A	C49A	C46	107.2(13)	C92'	C97'	C96'	119.9(6)
C51A	C49A	C5BA	108.4(14)	C99'	C98'	C95'	112.5(6)
C51A	C49A	C52A	112.4(14)	C99'	C98'	C200	111.0(7)
C52A	C49A	C46	112.7(12)	C99'	C98'	C201	107.7(6)
C52A	C49A	C5BA	109.9(15)	C200	C98'	C95'	108.0(5)
C46	C49B	C50B	107.2(14)	C200	C98'	C201	108.3(6)
C46	C49B	C51B	121.3(15)	C201	C98'	C95'	109.2(7)
C50B	C49B	C51B	106.2(13)	C45'	C44'	C43'	122.5(6)
C52B	C49B	C46	105.0(12)	C63'	C62'	C61'	119.3(11)
C52B	C49B	C50B	109.8(14)	C62'	C63'	C64'	124.8(12)
C52B	C49B	C51B	107.1(13)	C64'	C65'	C66'	121.4(14)
C1'	N1'	C2'	111.8(4)	C61'	C66'	C65'	119.8(16)
C1'	N1'	C53'	126.0(4)	C63C	C62C	C61'	121.9(15)
C2'	N1'	C53'	122.0(5)	C64'	C63C	C62C	118.7(16)
C1'	N2'	C3'	110.7(5)	C64'	C65C	C66C	120.0(19)
C1'	N2'	C4'	126.7(5)	C61'	C66C	C65C	124(2)

G. Crystal Structure Data For 6

Table 1 Crystal data and structure refinement for 6.

Identification code	gb_ERAgHBCF_0m_sq
Empirical formula	$C_{128}H_{130}AgBF_{15}N_2$
Formula weight	2100.01
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.158(5)
b/Å	23.393(7)
c/Å	30.498(9)
α/°	90
β/°	95.659(7)
γ/°	90
Volume/Å^3	11472(6)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.249
F(000)	4396.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.868 to 50.05
Index ranges	-19 ≤ h ≤ 19, -23 ≤ k ≤ 27, -36 ≤ l ≤ 36
Reflections collected	152716
Independent reflections	20236 [R_{int} = 0.0566, R_{sigma} = 0.0314]
Data/restraints/parameters	20236/0/1386
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.0965
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1071
Largest diff. peak/hole / e Å^{-3}	0.83/-0.47

Table 4 Bond Lengths for 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag1	C1	2.095(2)	C21	C22	1.385(3)
F3	C106	1.339(3)	C70	C69	1.377(3)
F10	C111	1.345(4)	C70	C71	1.396(4)
F5	C108	1.354(3)	C98	C96	1.530(4)
F9	C115	1.354(3)	C106	C105	1.377(4)
F6	C112	1.347(4)	C12	C13	1.391(4)
F8	C114	1.347(4)	C3	C2	1.347(3)
F1	C104	1.356(3)	C90	C91	1.381(3)
F7	C113	1.345(4)	C90	C95	1.387(3)
F13	C119	1.345(3)	C90	C78	1.523(3)
F2	C105	1.342(3)	C69	C68	1.393(3)

F4	C107	1.346(3)	C100	C102	1.533(4)
F12	C118	1.347(3)	C100	C103	1.534(4)
F11	C117	1.352(3)	C100	C101	1.531(4)
F14	C120	1.344(5)	C110	C111	1.403(4)
F15	C121	1.347(7)	C110	B1	1.634(4)
F16	C122	1.35(4)	C15	C14	1.390(4)
F17	C123	1.38(3)	C92	C91	1.386(3)
N2	C1	1.349(3)	C17	C20	1.535(4)
N2	C4	1.440(3)	C17	C18	1.525(4)
N2	C2	1.390(3)	C17	C14	1.533(3)
N1	C52	1.446(3)	C58	C55	1.506(3)
N1	C1	1.348(3)	C34	C33	1.382(3)
N1	C3	1.385(3)	C34	C35	1.395(3)
C64	C66	1.394(4)	C41	C38	1.531(4)
C64	C100	1.536(3)	C72	C73	1.387(3)
C64	C63	1.391(3)	C72	C71	1.390(4)
C45	C46	1.392(4)	C117	C116	1.378(3)
C45	C44	1.387(3)	C59	C7	1.507(3)
C45	C48	1.534(3)	C67	C61	1.388(3)
C118	C119	1.363(5)	C116	C121	1.381(7)
C118	C117	1.374(4)	C116	C122	1.49(4)
C01T	C84	1.387(3)	C116	B1	1.624(4)
C01T	C83	1.389(4)	C44	C43	1.386(3)
C115	C110	1.377(4)	C50	C48	1.513(4)
C115	C114	1.380(4)	C4	C9	1.393(3)
C19	C17	1.527(4)	C75	C74	1.521(4)
C10	C11	1.528(3)	C75	C76	1.536(5)
C10	C5	1.529(3)	C75	C77	1.525(4)
C10	C21	1.519(3)	C75	C71	1.532(3)
C97	C96	1.534(4)	C9	C8	1.392(3)
C107	C106	1.373(4)	C51	C48	1.566(4)
C107	C108	1.380(3)	C63	C62	1.391(3)
C89	C86	1.538(4)	C86	C83	1.532(3)
C47	C46	1.381(4)	C86	C88	1.534(4)
C47	C42	1.392(3)	C38	C40	1.541(5)
C87	C86	1.530(4)	C38	C35	1.525(3)
C113	C112	1.367(5)	C36	C35	1.387(3)
C113	C114	1.383(5)	C36	C37	1.388(3)
C93	C92	1.381(3)	C61	C62	1.384(3)
C93	C96	1.531(3)	C61	C60	1.531(3)
C93	C94	1.392(3)	C95	C94	1.382(3)
C31	C9	1.526(3)	C33	C32	1.387(3)

C31	C42	1.527(3)	C48	C49	1.505(4)
C31	C32	1.523(3)	C8	C7	1.389(3)
C11	C16	1.387(3)	C60	C57	1.525(3)
C11	C12	1.376(3)	C60	C68	1.517(3)
C119	C120	1.369(6)	C6	C7	1.389(3)
C119	C123	1.43(4)	C42	C43	1.387(3)
C5	C4	1.401(3)	C54	C55	1.390(3)
C5	C6	1.391(3)	C54	C53	1.387(3)
C39	C38	1.532(4)	C32	C37	1.387(3)
C16	C15	1.382(4)	C27	C28	1.481(4)
C85	C84	1.393(3)	C78	C53	1.517(3)
C85	C80	1.382(3)	C56	C57	1.394(3)
C85	C78	1.531(3)	C56	C55	1.385(3)
C23	C24	1.379(4)	C29	C28	1.483(5)
C23	C22	1.379(4)	C28	C30	1.580(7)
C82	C80	1.383(4)	C73	C68	1.385(3)
C82	C83	1.394(4)	C13	C14	1.384(4)
C104	C109	1.389(3)	C120	C121	1.374(8)
C104	C105	1.379(4)	C123	C122	1.41(5)
C26	C25	1.390(4)	C128	C127	1.393(6)
C26	C21	1.380(4)	C128	C129	1.386(6)
C112	C111	1.369(5)	C126	C125	1.351(5)
C52	C57	1.392(3)	C126	C127	1.379(6)
C52	C53	1.393(3)	C125	C124	1.380(5)
C25	C24	1.378(4)	C124	C129	1.361(6)
C99	C96	1.533(4)	C131	C132	1.371(5)
C24	C28	1.532(4)	C131	C130	1.375(6)
C66	C67	1.379(3)	C132	C130[1]	1.385(5)
C109	C108	1.388(3)	C130	C132[1]	1.385(5)
C109	B1	1.634(4)			

[1]2-X,2-Y,1-Z

Table 5 Bond Angles for 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N2	C4	122.81(18)	C9	C4	N2	118.90(19)
C1	N2	C2	110.82(18)	C9	C4	C5	122.6(2)
C2	N2	C4	126.36(18)	C74	C75	C76	109.1(3)
C1	N1	C52	119.00(18)	C74	C75	C77	108.2(3)
C1	N1	C3	111.34(18)	C74	C75	C71	109.7(2)
C3	N1	C52	129.53(18)	C77	C75	C76	108.7(3)
C66	C64	C100	120.2(2)	C77	C75	C71	112.2(2)

C63	C64	C66	116.7(2)	C71	C75	C76	108.9(2)
C63	C64	C100	123.1(2)	C4	C9	C31	121.3(2)
C46	C45	C48	120.2(2)	C8	C9	C31	121.1(2)
C44	C45	C46	116.6(2)	C8	C9	C4	117.6(2)
C44	C45	C48	123.2(2)	C62	C63	C64	121.7(2)
F12	C118	C119	119.7(3)	C87	C86	C89	108.1(2)
F12	C118	C117	121.1(3)	C87	C86	C83	111.8(2)
C119	C118	C117	119.2(3)	C87	C86	C88	109.5(2)
C84	C01T	C83	121.7(2)	C83	C86	C89	109.7(2)
F9	C115	C110	121.0(2)	C83	C86	C88	108.0(2)
F9	C115	C114	115.4(3)	C88	C86	C89	109.7(2)
C110	C115	C114	123.5(3)	C90	C91	C92	121.1(2)
C11	C10	C5	112.80(19)	C39	C38	C40	110.1(3)
C21	C10	C11	115.25(19)	C41	C38	C39	107.9(3)
C21	C10	C5	110.01(18)	C41	C38	C40	108.8(3)
F4	C107	C106	120.0(2)	C35	C38	C39	112.0(2)
F4	C107	C108	119.7(2)	C35	C38	C41	109.6(2)
C106	C107	C108	120.3(2)	C35	C38	C40	108.4(2)
C46	C47	C42	121.4(2)	C35	C36	C37	121.3(2)
F7	C113	C112	121.0(3)	C67	C61	C60	118.9(2)
F7	C113	C114	119.2(4)	C62	C61	C67	117.7(2)
C112	C113	C114	119.8(3)	C62	C61	C60	123.4(2)
C92	C93	C96	122.4(2)	C61	C62	C63	120.9(2)
C92	C93	C94	116.5(2)	C93	C96	C97	108.2(2)
C94	C93	C96	121.0(2)	C93	C96	C99	110.1(2)
C9	C31	C42	113.59(18)	C99	C96	C97	109.5(2)
C32	C31	C9	109.88(18)	C98	C96	C97	109.1(2)
C32	C31	C42	114.97(18)	C98	C96	C93	111.8(2)
C16	C11	C10	119.3(2)	C98	C96	C99	108.1(2)
C12	C11	C10	123.4(2)	C94	C95	C90	120.8(2)
C12	C11	C16	117.1(2)	C34	C33	C32	120.7(2)
F13	C119	C118	120.4(3)	C45	C48	C51	108.6(2)
F13	C119	C120	120.7(3)	C50	C48	C45	110.2(2)
F13	C119	C123	117.3(12)	C50	C48	C51	107.3(2)
C118	C119	C120	118.8(3)	C49	C48	C45	112.4(2)
C118	C119	C123	116.3(12)	C49	C48	C50	111.5(3)
C4	C5	C10	120.9(2)	C49	C48	C51	106.8(3)
C6	C5	C10	121.8(2)	C7	C8	C9	122.0(2)
C6	C5	C4	117.2(2)	C57	C60	C61	110.87(18)
C15	C16	C11	121.7(2)	C68	C60	C61	110.26(18)
C84	C85	C78	122.8(2)	C68	C60	C57	116.70(18)
C80	C85	C84	117.4(2)	C7	C6	C5	122.1(2)

C80	C85	C78	119.8(2)	C85	C80	C82	121.8(2)
C22	C23	C24	121.9(3)	C47	C42	C31	121.6(2)
C80	C82	C83	121.2(2)	C43	C42	C47	116.8(2)
C47	C46	C45	121.8(2)	C43	C42	C31	121.2(2)
F1	C104	C109	118.9(2)	C8	C7	C59	120.8(2)
F1	C104	C105	115.7(2)	C8	C7	C6	118.5(2)
C105	C104	C109	125.4(2)	C6	C7	C59	120.7(2)
C21	C26	C25	121.3(3)	C53	C54	C55	121.4(2)
C01T	C84	C85	120.9(2)	C01T	C83	C82	117.0(2)
F6	C112	C113	120.1(3)	C01T	C83	C86	119.8(2)
F6	C112	C111	120.4(4)	C82	C83	C86	123.2(2)
C113	C112	C111	119.5(3)	F5	C108	C107	114.8(2)
C57	C52	N1	118.49(19)	F5	C108	C109	121.1(2)
C57	C52	C53	123.4(2)	C107	C108	C109	124.1(2)
C53	C52	N1	117.77(19)	C33	C32	C31	122.6(2)
C24	C25	C26	121.8(3)	C33	C32	C37	117.8(2)
C23	C24	C28	119.1(3)	C37	C32	C31	119.5(2)
C25	C24	C23	116.6(3)	C3	C2	N2	106.73(19)
C25	C24	C28	124.2(3)	C90	C78	C85	111.03(18)
N2	C1	Ag1	131.57(16)	C53	C78	C85	110.00(18)
N1	C1	Ag1	123.36(15)	C53	C78	C90	114.45(18)
N1	C1	N2	104.76(18)	C55	C56	C57	121.7(2)
C67	C66	C64	121.6(2)	C34	C35	C38	120.1(2)
C104	C109	B1	120.6(2)	C36	C35	C34	116.9(2)
C108	C109	C104	112.7(2)	C36	C35	C38	123.0(2)
C108	C109	B1	126.7(2)	C95	C94	C93	122.0(2)
C26	C21	C10	121.1(2)	C24	C28	C30	107.3(3)
C26	C21	C22	116.7(2)	C27	C28	C24	111.4(3)
C22	C21	C10	122.1(2)	C27	C28	C29	112.6(3)
C69	C70	C71	121.6(2)	C27	C28	C30	105.8(4)
F3	C106	C107	120.7(2)	C29	C28	C24	113.0(3)
F3	C106	C105	120.8(2)	C29	C28	C30	106.2(4)
C107	C106	C105	118.5(2)	C52	C57	C60	118.74(19)
C11	C12	C13	121.0(2)	C52	C57	C56	116.8(2)
C2	C3	N1	106.34(19)	C56	C57	C60	124.4(2)
F2	C105	C104	121.2(2)	C44	C43	C42	121.6(2)
F2	C105	C106	119.8(2)	C68	C73	C72	120.8(2)
C106	C105	C104	119.0(2)	C54	C55	C58	119.3(2)
C91	C90	C95	117.7(2)	C56	C55	C58	121.4(2)
C91	C90	C78	122.0(2)	C56	C55	C54	119.3(2)
C95	C90	C78	120.3(2)	C52	C53	C78	119.67(19)
C70	C69	C68	121.0(2)	C54	C53	C52	117.3(2)

C102	C100	C64	112.4(2)	C54	C53	C78	122.8(2)
C102	C100	C103	108.3(2)	C14	C13	C12	122.5(2)
C103	C100	C64	108.3(2)	C69	C68	C60	122.3(2)
C101	C100	C64	109.6(2)	C73	C68	C69	118.0(2)
C101	C100	C102	107.6(3)	C73	C68	C60	119.6(2)
C101	C100	C103	110.7(3)	C70	C71	C75	119.8(2)
C115	C110	C111	114.7(3)	C72	C71	C70	116.9(2)
C115	C110	B1	126.2(2)	C72	C71	C75	123.3(2)
C111	C110	B1	118.9(2)	C36	C37	C32	121.3(2)
F10	C111	C112	117.5(3)	C15	C14	C17	121.2(2)
F10	C111	C110	119.1(3)	C13	C14	C15	116.0(2)
C112	C111	C110	123.4(3)	C13	C14	C17	122.8(2)
C16	C15	C14	121.8(2)	F14	C120	C119	119.6(4)
C93	C92	C91	121.9(2)	F14	C120	C121	120.5(5)
C19	C17	C20	107.0(2)	C119	C120	C121	119.8(4)
C19	C17	C14	111.7(2)	F15	C121	C116	119.6(5)
C18	C17	C19	109.4(2)	F15	C121	C120	116.5(5)
C18	C17	C20	108.8(2)	C120	C121	C116	123.8(5)
C18	C17	C14	108.9(2)	F17	C123	C119	121(2)
C14	C17	C20	110.9(2)	F17	C123	C122	118(3)
F8	C114	C115	120.4(3)	C122	C123	C119	119(3)
F8	C114	C113	120.5(3)	F16	C122	C116	122(3)
C115	C114	C113	119.1(3)	F16	C122	C123	119(3)
C23	C22	C21	121.6(2)	C123	C122	C116	119(3)
C33	C34	C35	122.0(2)	C109	B1	C110	114.6(2)
C73	C72	C71	121.6(2)	C116	B1	C109	114.9(2)
F11	C117	C118	116.5(2)	C116	B1	C110	109.8(2)
F11	C117	C116	118.8(2)	C129	C128	C127	118.8(4)
C118	C117	C116	124.7(3)	C125	C126	C127	120.7(4)
C66	C67	C61	121.3(2)	C126	C125	C124	119.7(4)
C117	C116	C121	113.2(3)	C126	C127	C128	119.9(4)
C117	C116	C122	112.9(16)	C129	C124	C125	121.0(4)
C117	C116	B1	121.9(2)	C124	C129	C128	119.9(4)
C121	C116	B1	124.8(3)	C132	C131	C130	119.6(4)
C122	C116	B1	119.8(14)	C131	C132	C130[1]	120.1(4)
C43	C44	C45	121.7(2)	C131	C130	C132[1]	120.2(4)
C5	C4	N2	118.48(19)				

[1]2-X,2-Y,1-Z

H. References

[1] Weber, S.G.; Loos, C.; Rominger, F.; Straub, B.F. *ARKIVOC* **2012**, *iii*, 226 – 242.