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Short Metal–Metal Separations in a Highly Luminescent Trimetallic Ag(I) Complex Stabilized by Bridging NHC Ligands

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Reaction of 1,3-bis(2-pyridinylmethyl)-1*H*-imidazolium salt, $[H(pyCH_2)_2\text{-}im]X$ ($X = BF_4^-$ or Cl^-), with silver oxide in acetonitrile readily yields yellow-brown $[((pyCH_2)_2im)_2Ag]X$, **1**·BF_4 or **1**·Cl. The chloride salt crystallizes with 3.650 Å intermolecular Ag···Ag interactions while **1**·BF_4 shows no short intermolecular interaction. Addition of excess $Ag(BF_4)$ produces the homoleptic carbene bridged trimetallic species, $[(\mu\text{-NHC})_3Ag_3](BF_4)_3$, **2**. This species contains very short Ag–Ag separations between 2.7249(10) and 2.7718(9) Å. In solution, these complexes are photoluminescent.

Investigations into the attractive interactions between closed-shell metal atoms and ions continue to generate much interest.[1] It is now well-established that Au(I) complexes aggregate with metal−metal separations shorter than the sum of their van der Waals radii.[2−4] Recent examples also demonstrate that the strength of these interactions is sufficient to overcome the anticipated Coulombic repulsion between like-charged metal complexes, and extensive networks of cationic complexes can be formed in the solid state. This notion is strikingly exemplified by the observation of short intermolecular Au(I)···Au(I) contacts (2.9643(6)−2.9803(6) Å) between the cationic centers in the homoleptic $[(C_6H_{11}NC)_2Au](PF_6)$ complex[5] compared to the much longer separations found in the closely related neutral Au(I) compounds, $(C_6H_{11}NC)AuCN$ (3.426(3) and 3.442(3) Å).[6] This attraction, termed "aurophilicity",[7] is attributed to correlation and relativistic effects and can be as strong as a hydrogen bond.[8−10] To a lesser degree, similar, yet weaker, associations are observed in Ag(I) chemistry,[11,12] although the nature of these associations is somewhat controversial.

We too are interested in metal−metal interactions and have extensively used multidentate phosphine ligands to incarcerate metal ions and atoms in the center of metallocryptand cages.[13] In these complexes, the guest metal is held very tightly allowing for the metal−metal interactions to be probed in solution. Recently, we developed a research program to employ the now-ubiquitous N-heterocyclic carbene (NHC) ligands[14,15] as supports for maintaining metal−metal interactions between closed-shell ions. NHC ligands are considered better σ donors than most phosphines,[16] significantly simpler to synthesize, air-stable, and although not realized with d^{10} ions, they have the potential for metal−ligand back−bonding.[17] Here we report the preparation, structure, and luminescence properties of a homoleptic triangulo-$[(\mu\text{-NHC})_3Ag_3]^{3+}$ complex containing bridging carbene ligands spanning unusually short Ag(I)−Ag(I) separations.

Treatment of 1,3-bis(2-pyridinylmethyl)-1H-imidazolium salt,[18] $[H(pyCH_2)_2im]X$ ($X = BF_4^-$ or Cl^-), with silver oxide in acetonitrile readily yields yellow-brown $[((pyCH_2)_2im)_2Ag](X)$, **1**·BF_4 or **1**·Cl. Complex **1**·BF_4 (supporting info.) crystallizes[19] in the monoclinic space group *C*2/*c* with the asymmetric unit containing one-half of the complex and the Ag(1) atom residing on a crystallographic inversion center. The structure of **1**·BF_4 is typical of $[Ag(NHC)_2]^+$ complexes and consists of a linearly coordinated Ag(I) center with short

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(1) Fernandez, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022.
(2) Schmidbaur, H. *Nature* **2001**, *413*, 31.
(3) Hamel, A.; Mitzel, N. W.; Schmidbaur, H. *J. Am. Chem. Soc.* **2001**, *123*, 5106.
(4) Bachman, R. E.; Fioritto, M. S.; Fetics, S. K.; Cocker, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5376.
(5) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033.
(6) White-Morris, R. L.; Stender, M.; Tinti, D. S.; Balch, A. L.; Rios, D.; Attar, S. *Inorg. Chem.* **2003**, *42*, 000.
(7) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3.
(8) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3*, 1451.
(9) Pyykkö, P.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3*, 1458.
(10) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(11) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 10371.
(12) Codina, A.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Rodríguez, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 6781.
(13) Catalano, V. J.; Malwitz, M. A.; Noll, B. C. *Inorg. Chem.* **2002**, *41*, 6553.
(14) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2001**, *48*, 1.
(15) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.
(16) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416.
(17) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *Chem. Commun.* **1997**, 1963.
(18) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617−618*, 546.

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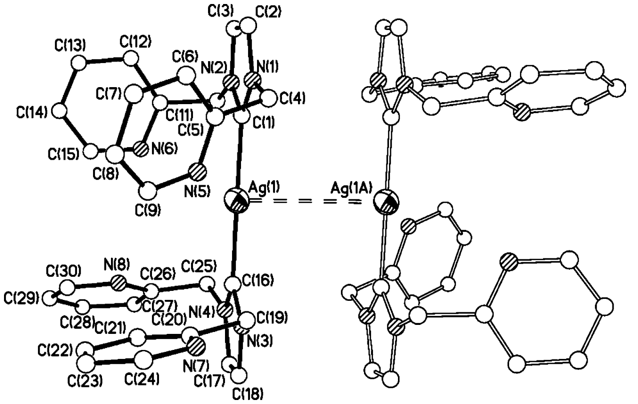
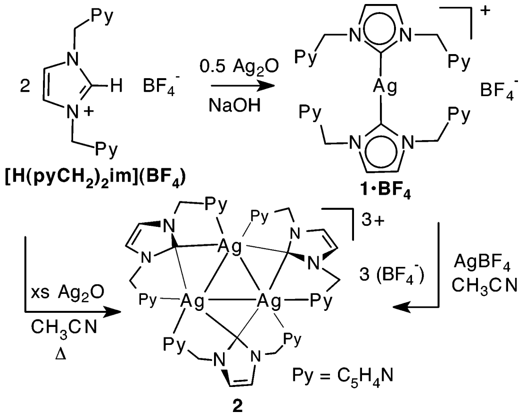


Figure 1. Thermal ellipsoid plot of cationic portion of **1**·Cl emphasizing intermolecular interactions with a symmetry equivalent complex. Selected bond lengths (Å) and angles (deg): Ag(1)···Ag(1A) 3.650, Ag(1)−C(1) 2.083(6), Ag(1)−C(16) 2.082(6), N(1)−C(1)−Ag(1) 127.2(4), N(2)−C(1)−Ag(1) 128.8(4), N(1)−C(1)−N(2) 103.8(5), N(3)−C(16)−Ag(1) 128.7(5), N(4)−C(16)−Ag(1) 127.8(4), N(3)−C(16)−N(4) 103.3(5), C(1)−Ag(1)−C(16) 175.0(2).

Scheme 1



Ag(1)−C separations of 2.093(4) Å. The two imidazole rings are rigorously coplanar, and the shortest Ag(I)···Ag(I) interaction is very long at 8.545 Å. Compound **1**·Cl (Figure 1) crystallizes[20] in the triclinic space group $P\bar{1}$ with similar metrical parameters to **1**·BF_4. The main differences are that in **1**·Cl the two imidazole rings are very slightly canted with a dihedral angle of 5.2° and the 2-picolyl arms are splayed back to allow a 3.65 Å intermolecular Ag···Ag interaction.

Addition of excess $AgBF_4$ to **1**·BF_4 in acetonitrile at room temperature yields an off-white material identified by X-ray crystallography[21] to be $[((pyCH_2)_2im)_3Ag_3](BF_4)_3$, **2** (Scheme 1). As shown in Figure 2, the cation contains three cationic Ag(I) centers in a nearly equilateral arrangement with exceptionally short Ag−Ag separations of 2.7718(9), 2.7688(9), and 2.7249(10) Å for Ag(1)−Ag(2), Ag(1)−Ag(3), and Ag(2)−Ag(3), respectively. Each dimetallic unit is bridged by a carbene with Ag−C separations ranging from 2.223(8) to 2.266(7) Å. Bridging NHC ligands are rare, and only one other example could be found. Youngs and co-workers[22] recently reported an unsymmetrically bound NHC ligand in a tetranuclear Ag_4 cluster with Ag−C separations between 2.15 and 2.41 Å. Because of the perpendicular orientation of the carbene ligands of **2** to the trigonal Ag_3 face, the pyridine rings must alternate their coordination above and below the Ag_3 plane giving the complex D_{3d} symmetry. This sufficiently blocks the Ag_3 face toward further ligand coordination, and attempts to add a capping ligand such as sulfide ion were unsuccessful.

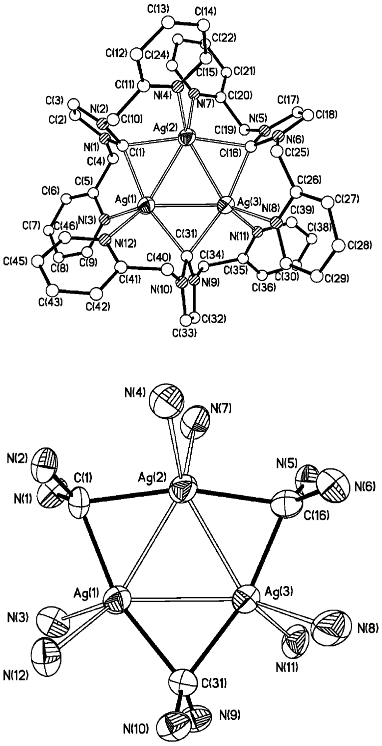


Figure 2. Top: thermal ellipsoid plot of **2**. Bottom: the core of **2** showing the Ag3 core. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(2) 2.7718(9), Ag(2)−Ag(3) 2.7249(10), Ag(1)−Ag(3) 2.7688(9), Ag(1)−C(1) 2.255(8), Ag(1)−C(31) 2.261(8), Ag(2)−C(1) 2.266(7), Ag(2)−C(16) 2.257(8), Ag(3)−C(16) 2.223(8), Ag(3)−C(31) 2.237(7), Ag(1)−N(3) 2.406(7), Ag(1)−N(12) 2.379(6), Ag(2)−N(4) 2.409(7), Ag(2)−N(7) 2.379(6), Ag(3)−N(8) 2.416(7), Ag(3)−N(11) 2.361(7), C(1)−Ag(1)−C(31) 162.8(3), C(1)−Ag(2)−C(16) 163.7(3), C(16)−Ag(3)−C(31) 166.0(3), Ag(1)−C(1)−Ag(2) 75.6(2), Ag(2)−C(16)−Ag(3) 74.9(3), Ag(1)−C(31)−Ag(3) 76.0(2), Ag(1)−Ag(2)−Ag(3) 60.49(2), Ag(2)−Ag(3)−Ag(1) 60.60(2), Ag(3)−Ag(1)−Ag(2) 58.92(2), N(3)−Ag(1)−N(12) 91.8(3), N(4)−Ag(2)−N(7) 94.4(3), N(8)−Ag(3)−N(11) 95.2(3).

In CD_3CN solution, the $^{13}C\{^1H\}$ resonance for the carbene carbon of **2** appears as a non-first-order multiplet at 175.3 ppm with extensive coupling to all three Ag atoms (supporting info.). The presence of both ^{107}Ag and ^{109}Ag ($I = {}^1/_2$) greatly complicates the analysis. However, an effective simulation of this resonance for the major isotopomer was

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(19) Crystal data for **1**·BF_4: $C_{30}H_{28}AgBF_4N_8$, $M_f = 695.28$, monoclinic, $a = 14.2974(12)$ Å, $b = 9.0256(7)$ Å, $c = 24.091(3)$ Å, $\beta = 102.519(19)°$, $V = 3034.(5)$ Å^3, $T = 298(2)$ K, $C2/c$, $Z = 4$, 2000 independent reflections used for solution and refinement by full-matrix least-squares on F^2, absorption correction by using a semiempirical method derived from azimuthal scans. R_w ($I > 2\sigma$) = 0.0327, R_w (all data) = 0.0426.

(20) Crystal data for **1**·Cl: $C_{30}H_{28}AgClN_8O$, $M_f = 659.92$, triclinic, $a = 10.9525(13)$ Å, $b = 11.3411(17)$ Å, $c = 13.2381(15)$ Å, $\alpha = 108.800(12)°$, $\beta = 101.3641(12)°$, $\gamma = 99.519(10)°$, $V = 1479.0(3)$ Å^3, $T = 298(2)$ K, $P\bar{1}$, $Z = 2$, 4958 independent refs. $R_w(I > 2\sigma) = 0.0575$, R_w (all data) = 0.1107.

(21) Crystal data for **2**·0.25 CH_3CN: $C_{45.50}H_{38}Ag_3B_3F_{12}N_{12.25}$, $M_f = 1340.42$, monoclinic, $a = 12.236(2)$ Å, $b = 35.861(4)$ Å, $c = 12.669(2)$ Å, $\beta = 91.421(17)°$, $V = 5557.7(15)$ Å^3, $T = 298(2)$ K, $P2_1/c$, $Z = 4$, 7726 independent reflns. R_w ($I > 2\sigma$) = 0.0557, R_w (all data) = 0.1225.

(22) Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Chem. Commun.* **2001**, 1780.

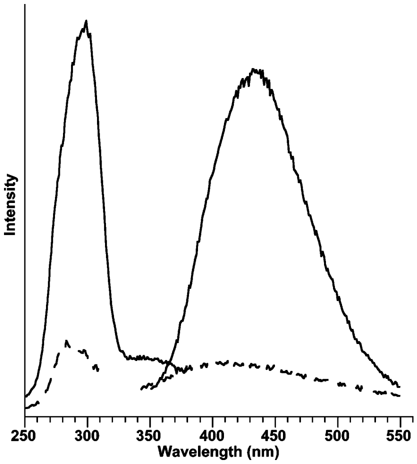

Figure 3. Emission ($\lambda_{ex} = 305$ nm) (right) and excitation (left) spectra of **1**·BF_4 (- - -, $c = 9.49 \times 10^{-5}$ M) and **2** (—, $c = 9.46 \times 10^{-5}$ M) in acetonitrile.

achieved using $^1J_{AgC} = 104.5$ Hz, $^2J_{AgC} = 8.0$ Hz, and $^3J_{AgC} = 3.0$ Hz, suggesting that metal−carbene π-bonding is absent. For the monometallic complex, **1**·BF_4, a broad resonance at 182.3 ppm without any resolved $^1J_{AgC}$ was observed.

As shown in Figure 3, equimolar acetonitrile solutions of **1** or **2** are emissive; however, the emission from **2** is considerably stronger. When excited at 305 nm (CH_3CN), the trimetallic compound, **2**, shows a broad emission centered at 435 nm while the monometallic species, **1**·BF_4, emits at slightly higher energy (413 nm). The carbene precursor, $[H(pyCH_2)_2im](BF_4)$, is also emissive. When excited at 358 nm, a single broad band at 450 nm is observed. All three compounds have absorptions in the UV region between 240 and 260 nm that tail toward 300 nm; however, **2** has an additional band that appears as a shoulder at 300 nm.

The presence of the exceptionally short Ag−Ag separations in the cationic complex, **2**, is particularly noteworthy. Although there are numerous Ag_3 clusters reported in the literature, surprisingly few Ag_3 clusters containing exclusively neutral ligands exist. For example, the well-studied phosphine bridged $[Ag_3(Ph_2CH_2PPh_2)_3]^{3+}$ complexes usually contain anionic auxiliary ligands coordinated to the triangular face,[23−25] or in the absence of phosphines, the Ag clusters contain anionic backbone or auxiliary ligands[26] that reduce the electrostatic intermetallic repulsion as demonstrated in aryl-bridged Ag_4 clusters that have Ag···Ag separations between 2.73 and 2.74 Å.[27,28] In the absence of anionic ligands, the metal−metal separations are often much longer,[29] suggesting that the argentophilic attraction is either extremely weak or nonexistent. The ability of NHC ligands to act as electronic mimics of anionic aryl ligands to stabilize multimetallic clusters was first put forth by Youngs and co-workers[22] whose tetranuclear NHC-bridged silver complex also contains very short Ag−Ag separations ranging from 2.7680(9) to 2.9712 (11) Å.

Also surprising is the scarcity of reports of photoluminescence from metal−NHC complexes. Lin and co-workers[30] reported the emission properties of a series of Au−benzimidazol-2-ylidene complexes that show dual emission bands in the solid-state assigned to either an intraligand transition or a metal−metal state originating from weak intermolecular aurophilic interactions. In solution, these metal−metal interactions are interrupted, and the intraligand band dominates the spectrum. Similarly, they reported the emission from $[Ag(Me_2im)_2](AgCl_2)$ where the emission was assigned to metal centered transitions resulting from the extended chains of Ag(I) cations and Ag(I) anions.[31] Similarly, Zhang and co-workers[32] reported the emission of an (anthracenylmethyl-NHC)AgI polymeric complex and assigned its low energy (600 nm) emission to a metal centered state. The fact that the carbene precursor, $[H(pyCH_2)_2im]X$, is luminescent suggests that the emission in **1** and **2** may be ligand based; however, the possibility of a metal-centered or a metal-to-ligand-charge transfer state in **2** cannot be ruled out without further investigation.[33,34]

The application of NHC ligands to support short metal−metal interactions is proving to be a promising area of study. With their excellent donor properties and ease of synthesis, NHC ligands could one day rival tertiary phosphines as the "ligand of choice" in many transition metal applications. Along these lines, we are continuing to explore NHC ligands as simple substitutes for the synthetically cumbersome multidentate phosphines to stabilize attractive interactions between closed-shell, late metal ions.

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Supporting Information Available: Complete experimental procedures and crystallographic data in CIF format for **1**·BF_4, **1**·Cl, and **2** along with X-ray structural diagram for **1**·BF_4 and ^{13}C NMR spectrum for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *Organometallics* **1997**, *16*, 2032.
(24) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K. K. *Chem. Commun.* **1997**, 963.
(25) Zhou, W.-B.; Dong, Z.-C.; Song, J.-L.; Zeng, H.-Y.; Cao, R.; Guo, G.-C.; Huang, J.-S.; Li, J. *J. Cluster Sci.* **2002**, *13*, 119.
(26) Su, C.-Y.; Kang, B.-S.; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **2000**, 1831.
(27) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3509.
(28) Nesmeyanov, A. N.; Sedova, N. N.; Struchkov, Y. U. T.; Andrianov, V. G.; Stakheeva, E. N.; Sazonova, V. A. *J. Organomet. Chem.* **1978**, *153*, 115.
(29) Albano, V. G.; Castellari, C.; Iapalucci, M. C.; Longoni, G.; Monari, M.; Paselli, A.; Zacchini, S. *J. Organomet. Chem.* **1999**, *573*, 261.
(30) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216.
(31) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852.
(32) Liu, Q. X.; Xu, F. B.; Li, Q. S.; Zeng, X. S.; Leng, X. B.; Chou, Y. L.; Zhang, Z. Z. *Organometallics* **2003**, *22*, 309.
(33) Sabin, F.; Ryu, C. K.; Ford, P. C.; Vogler, A. *Inorg. Chem.* **1992**, *31*, 1941.
(34) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323.