Sandwich Complexes

DOI: 10.1002/anie.200604585

Arene-Sandwiched Silver(I) Pyrazolates**

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Trinuclear coinage-metal (Cu, Ag, Au) complexes have garnered considerable interest in recent years owing in large part to their fascinating luminescence properties.[1–10] Some of these compounds also show very interesting π-acid/base properties that lead to the formation of extended binary stacks with arenes.[11,12] In general, these adducts form structures in which the trinuclear metal complex $[M_3L_3]$ or its dimer $[(M_3L_3)_2]$ unit interleaves with the arene Ar to form extended binary stacks of the general formula $[\{(M_3L_3)Ar\}_\infty]$ (Figure 1, type **A**) or $[\{(M_3L_3)_2Ar\}_\infty]$ (type **B**). For example, Balch and co-workers reported that $[\{(MeN{=}COMe)Au\}_3]$ forms adducts of type **A** or **B** with nitro-9-fluorenones and form supramolecular extended stacks in which $[\{(MeN{=}COMe)Au\}_3]$ or its dimer serves as the π base and nitro-9-fluorenones serve as the π acid.[4] Burini et al. described the isolation of supramolecular type **B** adducts involving the π base $[\{[(p\text{-tolyl})N{=}COEt]Au\}_3]$ and perfluoroarene acceptors such as hexafluorobenzene and octafluoronaphthalene.[13]

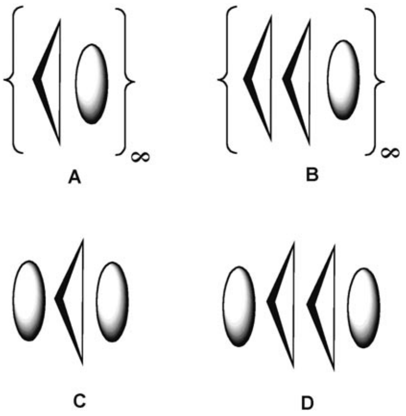

Figure 1. Different types of sandwich structures which result from the π-acid/base chemistry of trinuclear d^{10} metal complexes (triangles) with arenes (ovals).

Similar to the gold(I) adducts described above, the trinuclear pyrazolate complexes of Cu^I, Ag^I, and Au^I are generally also π bases with the basicity order Au > Cu > Ag for a given pyrazolate.[12] However, we demonstrated that it is possible to achieve a polarity reversal in the $[M_3L_3]$ complex by using highly fluorinated pyrazolate (pz) ligands.[12] These π-acidic $[M_3L_3]$ complexes permit the use of more common π bases such as aromatic hydrocarbons for the adduct formation. For example, gold(I) pyrazolate $[\{[3,5\text{-}(CF_3)_2pz]Au\}_3]$ forms a type **B** stack with toluene.[12] Herein, we report an interesting discovery involving the most acidic member of the coinage-metal family, the silver(I) analogue $[\{[3,5\text{-}(CF_3)_2pz]Ag\}_3]$ (**1**).[14] In particular, we show that it is possible to obtain several new classes of π-acid/base sandwich complexes (Figure 1, type **C** and **D**, as well as an extended form of type **C**) by using complex **1** along with some arenes. The most widely explored trinuclear d^{10} π acid in arene chemistry concerns a Hg^{II} complex $[\{(o\text{-}C_6F_4)Hg\}_3]$.[15–19] The research group of Gabbaï has demonstrated its use in the isolation of a series of one-dimensional organometallic polymers (type **A**) which contain arene donors such as benzene, naphthalene, and pyrene.[20–22]

During the synthesis of **1**,[14] we observed that it was difficult to remove the aromatic solvent from the final product. A careful study of this behavior shows that **1** is indeed a good π acid and interacts with aromatic hydrocarbons through secondary Ag⋯π interactions to form interesting sandwich structures. For example, crystals of **1** obtained from benzene feature $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ sandwiches which represents a type **C** structure (Figure 2a).[23–25] The distances between the two benzene centroids to the centroid of **1** in $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ are 3.18 and 3.23 Å. The shortest separation between a silver and a carbon atom of the benzene ring is 3.109 Å. These separations are significantly smaller than the sum of the van der Waals radii of Ag and C (3.42 Å).[26] There is an additional benzene molecule for each $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ unit in the crystal lattice, but the molecule lies between the $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ units at an angle (see the Supporting Information). There are no face-to-face contacts between the adjacent $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ units.

Interestingly, the crystals of **1** obtained from a benzene/dichloromethane mixture are different and contain adducts of type **D** that consist of discrete $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$ units (Figure 2b), with the dimers of **1** having two Ag⋯Ag contacts. The complex crystallizes in *C*2/*c* space group and $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$ sits on an inversion center. The closest Ag⋯Ag separation between the trimers (3.2894(4) Å) is significantly smaller than the sum of the van der Waals radii of Ag (3.44 Å).[26] The shortest Ag⋯Ag separation between the trimers observed in the free complex **1** is slightly shorter at

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[**] H.V.R.D. thanks the Robert A. Welch Foundation (grant Y-1289) and the AFOSR through the SPRING program in Texas for financial support of this research.

Supporting information for this article, including details of the synthesis, characterization, and additional figures, is available on the WWW under http://www.angewandte.org or from the author. CCDC-626776 to CCDC-626779 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

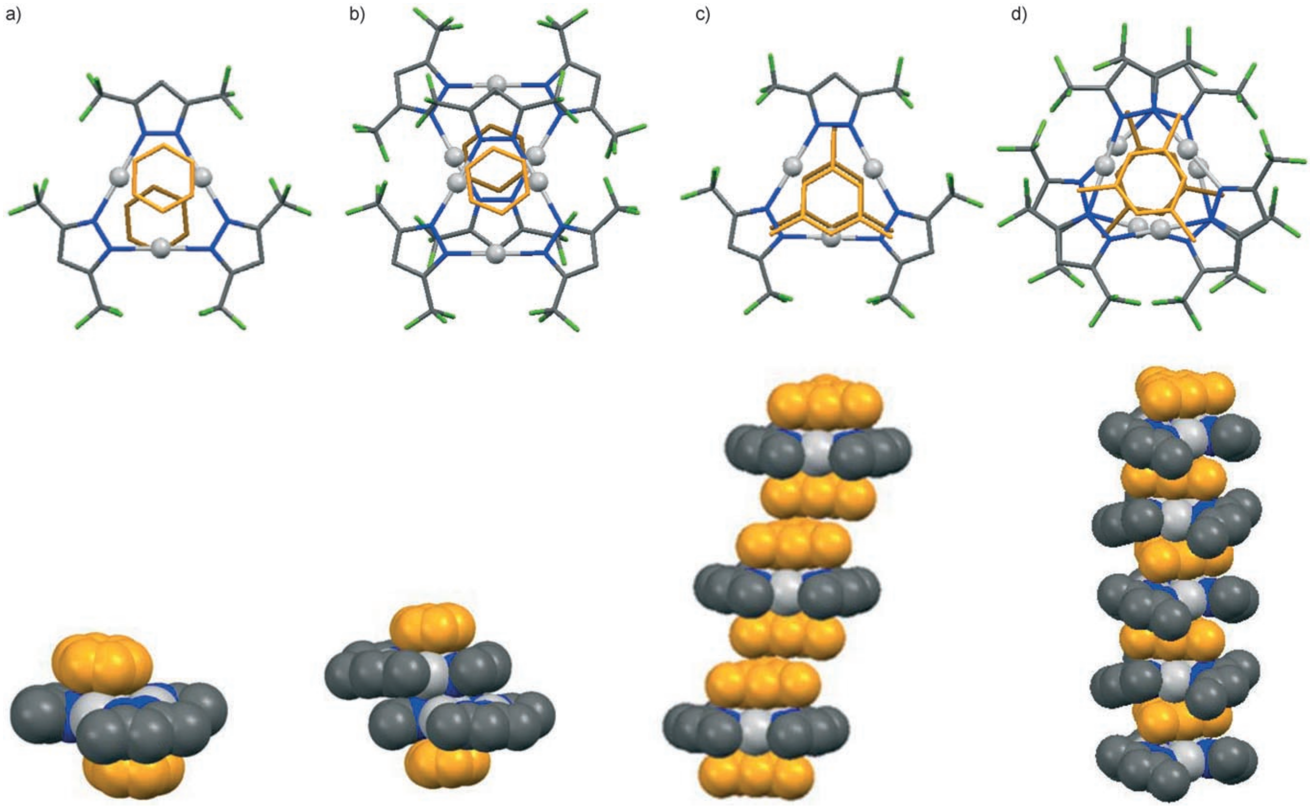

Figure 2. X-ray structures. Top (upper) and side (lower) views of a) $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ and b) $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$. c) Top (upper) view of $[(\text{Mes})(\mathbf{1})(\text{Mes})]$ and (below) a portion of the supramolecular chain $\{(\text{Mes})(\mathbf{1})(\text{Mes})\}_\infty$ resulting from π stacking. d) Top (upper) and side (lower) view of a portion of the $\{(\mathbf{1})(\text{Mes})\}_\infty$ chain. Hydrogen atoms (and fluorine atoms in side view) have been omitted for clarity. Atom coloring: yellow: arene, green: fluorine, dark gray: carbon, light gray: silver, blue: nitrogen.

3.2037(4) Å.[12] The centroids of the benzene ring and of **1** in $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$ are separated by 3.28 Å and the closest contact between the silver and carbon atoms of the benzene ring is at 3.187 Å.[27] Again, there are no π–π stacking between the neighboring $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$ units.

We have also explored the π-acid/base chemistry between **1** and mesitylene (Mes) in different solvents. In mesitylene alone, **1** forms sandwich molecules of the type $[(\text{Mes})(\mathbf{1})(\text{Mes})]$ (Figure 2c). There is a crystallographic mirror plane bisecting the molecule, in which **1** is essentially planar and the nonmethylated carbon atoms of the two mesitylene molecules sit above and below the three silver atoms. The closest Ag···C(Mes) separation is 3.196 Å, and the centroids of the mesitylene unit are separated from **1** by 3.21 and 3.23 Å. These distances are well within the van der Waals contact distance of Ag and C (3.42 Å) which indicates significant binding. In addition, $[(\text{Mes})(\mathbf{1})(\text{Mes})]$ units form extended somewhat-slanted, stacks with the general formula $[\{(\text{Mes})(\mathbf{1})(\text{Mes})\}_\infty]$. The adjacent mesitylene units lie off center, and the closest intermolecular C···C distance is about 3.7 Å (separation of the centroid of the Mes unit to the neighboring carbon atom is 3.61 Å). These C···C distances are slightly longer than the sum of the van der Waals radii of two carbon atoms (3.40 Å). The overall supramolecular structure may be described as an extended form of type **C**. Note however that it is different from the discrete type **C** form that involves benzene.

The crystals of **1** obtained from a mesitylene/dichloromethane solution adopt a $[\{(\mathbf{1})(\text{Mes})\}_\infty]$ columnar structure of type **A** (Figure 2d), which is the most common stacking pattern for arene sandwiches of trinuclear Hg^{II} as well as of some Au^{I} systems.[15,16,28,29] The $\{(\mathbf{1})(\text{Mes})\}$ unit sits on a threefold rotation axis. The **1**–Mes–**1**–Mes planes are separated by 3.32, 3.19, and 3.32 Å which indicates relatively tight contacts. The shortest Ag···C(Mes) distance is 3.25 Å. The rings of **1** show a notable distortion from planarity, perhaps as a result of the steric repulsion between the methyl groups and pyrazole rings.

Comparison of the Ag···C(arene) distances of four arene sandwiches of **1** indicates that, although the methyl groups in mesitylene make it more sterically bulky than benzene, the separation between **1** and the arene ring in the mesitylene and benzene systems are of similar magnitude. This is perhaps a result of the more basic mesitylene π system compensating for the adverse steric effects. In addition, all these face-to-face contacts between **1** and the arene are shorter than the van der Waals contact distance. Similar strong binding has been seen between $[\{(o\text{-}C_6F_4)Hg\}_3]$ and arenes.[15,20] These contacts between the arene carbon atoms and the complex **1** are longer than the Ag^{I}–C bonds of the arene adducts of ionic silver salts that usually show η^1- or η^2-bonded arenes with Ag–C distances ranging from 2.16(3) to 2.921(9) Å.[30]

Crystals of $[(C_6H_6)(\mathbf{1})(C_6H_6)]$ lose some of the benzene molecules under reduced pressure at room temperature, thus resulting in material with the approximate composition $[(\mathbf{1})(C_6H_6)_{0.5}]$ within 30 minutes, as evident from the data from elemental analysis and ^{1}H NMR spectroscopy. The removal of arene from the crystalline materials of $[(C_6H_6)(\mathbf{1})_2(C_6H_6)]$ or the mesitylene adducts $[\{(Mes)(\mathbf{1})(Mes)\}_\infty]$ and $[\{(\mathbf{1})(Mes)\}_\infty]$ proved more difficult, and heating or longer exposure to reduced pressure was required. The NMR spectra and elemental analysis of these crystals dried under reduced pressure for about 30 mins show data consistent with the compositions in the structurally characterized samples. Room-temperature ^{1}H NMR spectra taken in $CDCl_3$ show no chemical shift difference between the aromatic proton signals of adducts and the corresponding signals of the free components, **1** and the arene. This suggests that these π-acid/base adducts are too weak to survive (that is, they dissociate) in solution, or to influence the chemical shifts in solution.

In summary, herein we have described the isolation of sandwich molecules and supramolecular stacks which contain the acidic $[\{[3,5\text{-}(CF_3)_2pz]Ag\}_3]$ moiety and electron-rich aromatic π systems and in which the aggregation patterns depend on the solvent and the arene. These adducts also represent the first sandwich complexes of silver pyrazolates and arenes. The high affinity of $[\{[3,5\text{-}(CF_3)_2pz]Ag\}_3]$ for electron-rich arenes is consistent with the computational data.[12] We are currently investigating the π-acid/base chemistry involving **1** with fused arenes. Preliminary data also indicate that some of the resulting adducts are brightly luminescent.

Received: November 9, 2006

Keywords: host–guest systems · Lewis acids · N ligands · sandwich complexes · silver

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[1] P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625.
[2] V. W. W. Yam, K. K. W. Lo, *Mol. Supramol. Photochem.* **1999**, *4*, 31.
[3] M. Enomoto, A. Kishimura, T. Aida, *J. Am. Chem. Soc.* **2001**, *123*, 5608.
[4] M. M. Olmstead, F. Jiang, S. Attar, A. L. Balch, *J. Am. Chem. Soc.* **2001**, *123*, 3260.
[5] G. Yang, R. G. Raptis, *Inorg. Chem.* **2003**, *42*, 261.
[6] K. Fujisawa, Y. Ishikawa, Y. Miyashita, K.-i. Okamoto, *Chem. Lett.* **2004**, *33*, 66.
[7] H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary, M. A. Omary, *J. Am. Chem. Soc.* **2005**, *127*, 7489.
[8] H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072.
[9] T. Grimes, M. A. Omary, H. V. R. Dias, T. R. Cundari, *J. Phys. Chem. A* **2006**, *110*, 5823.
[10] Q.-S. Li, C.-Q. Wan, R.-Y. Zou, F.-B. Xu, H.-B. Song, X.-J. Wan, Z.-Z. Zhang, *Inorg. Chem.* **2006**, *45*, 1888.
[11] M. A. Omary, A. A. Mohamed, M. A. Rawashdeh-Omary, J. P. Fackler, *Coord. Chem. Rev.* **2005**, *249*, 1372.
[12] M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage, H. V. R. Dias, *Inorg. Chem.* **2005**, *44*, 8200.
[13] A. Burini, A. A. Mohamed, J. P. Fackler, *Comments Inorg. Chem.* **2003**, *24*, 253, and references therein.
[14] H. V. R. Dias, S. A. Polach, Z. Wang, *J. Fluorine Chem.* **2000**, *103*, 163.
[15] M. Tsunoda, F. P. Gabbaï, *J. Am. Chem. Soc.* **2000**, *122*, 8335.
[16] A. Burini, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni, R. J. Staples, *J. Am. Chem. Soc.* **2000**, *122*, 11264.
[17] M. R. Haneline, F. P. Gabbaï, *C. R. Chim.* **2004**, *7*, 871.
[18] M. R. Haneline, F. P. Gabbaï, *Angew. Chem.* **2004**, *116*, 5587; *Angew. Chem. Int. Ed.* **2004**, *43*, 5471.
[19] C. Burress, O. Elbjeirami, M. A. Omary, F. P. Gabbaï, *J. Am. Chem. Soc.* **2005**, *127*, 12166.
[20] M. R. Haneline, M. Tsunoda, F. P. Gabbaï, *J. Am. Chem. Soc.* **2002**, *124*, 3737.
[21] M. A. Omary, R. M. Kassab, M. R. Haneline, O. Elbjeirami, F. P. Gabbaï, *Inorg. Chem.* **2003**, *42*, 2176.
[22] T. J. Taylor, V. I. Bakhmutov, F. P. Gabbaï, *Angew. Chem.* **2006**, *118*, 7188; *Angew. Chem. Int. Ed.* **2006**, *45*, 7030.
[23] T. Murahashi, M. Fujimoto, M.-a. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* **2006**, *313*, 1104.
[24] T. Murahashi, T. Uemura, H. Kurosawa, *J. Am. Chem. Soc.* **2003**, *125*, 8436.
[25] J. K. Burdett, E. Canadell, *Organometallics* **1985**, *4*, 805.
[26] M. Winter, WebElements periodic table (Professional Edition). http://www.webelements.com (accessed May 2006).
[27] J. B. King, M. R. Haneline, M. Tsunoda, F. P. Gabbaï, *J. Am. Chem. Soc.* **2002**, *124*, 9350.
[28] T. J. Taylor, C. N. Burress, L. Pandey, F. P. Gabbaï, *Dalton Trans.* **2006**, 4654.
[29] M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni, A. Burini, *J. Am. Chem. Soc.* **2001**, *123*, 9689.
[30] M. Munakata, L. P. Wu, G. L. Ning, *Coord. Chem. Rev.* **2000**, *198*, 171.