

Multimetallic Arrays: Bi-, Tri-, Tetra-, and Hexametallic Complexes Based on Gold(I) and Gold(III) and the Surface Functionalization of Gold Nanoparticles with Transition Metals

Edward R. Knight,[†] Nina H. Leung,[†] Amber L. Thompson,[†] G. Hogarth,[‡] and James D. E. T. Wilton-Ely^{*,†,§,⊥}

Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K., Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., and Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

Received December 24, 2008

Reaction of $[\text{AuCl}(\text{PPh}_3)]$ with the zwitterion $\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2$ yields $[(\text{Ph}_3\text{P})\text{Au}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]\text{BF}_4$. Treatment of this species with NEt_3 and CS_2 followed by $[\text{AuCl}(\text{PPh}_3)]$ leads to $\{[(\text{Ph}_3\text{P})\text{Au}]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\}$, which can also be obtained directly from $[\text{AuCl}(\text{PPh}_3)]$ and $\text{KS}_2\text{CNC}_4\text{H}_8\text{NCS}_2\text{K}$. A heterobimetallic variant, $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}(\text{PPh}_3)]^+$, can be prepared by the sequential reaction of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]^{2+}$ with NEt_3 and CS_2 followed by $[\text{AuCl}(\text{PPh}_3)]$. Reaction of the same ruthenium precursor with $[(\text{dppm})(\text{AuCl})_2]$ under similar conditions yields the trimetallic complex $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}_2(\text{dppm})]^{2+}$. Attempts to prepare the compound $[(\text{dppm})\text{Au}_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]^{2+}$ from $[(\text{dppm})(\text{AuCl})_2]$ led to isolation of the known complex $\{[(\text{dppm})\text{Au}_2](\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\}^{2+}$ via a symmetrization pathway. $\{[(\text{dppf})\text{Au}_2](\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\}^{2+}$ was successfully prepared from $[(\text{dppf})(\text{AuCl})_2]$ and crystallographically characterized. In addition, a gold(III) trimetallic compound, $\{[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)_2\text{Au}]^{3+}$, and a tetrametallic gold(I) species, $\{[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}]_2\}^{2+}$, were also synthesized. This methodology was further exploited to attach the zwitterionic $(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)$ unit to the surface of gold nanoparticles, which were generated in situ and found to be $3.4 (\pm 0.3)$ and $14.4 (\pm 2.5)$ nm in diameter depending on the method employed. Nanoparticles with a mixed surface topography were also explored.

Introduction

The vast number of dithiocarbamate complexes reported for the d-block elements¹ confirms the versatility of this ligand, allowing it to accommodate the varied requirements of the metals involved. In particular, the extensive metal-centered electrochemistry of dithiocarbamate complexes² and the ability to stabilize a range of oxidation states are important features in their applications, which encompass materials science, medicine, and agriculture.¹

In the solid state, dithiocarbamate complexes of gold often display short gold–gold inter- or intramolecular contacts. The presence of such interactions between formally closed-shell gold(I) centers has led to a great deal of interest in polymetallic assemblies of monovalent gold. This phenomenon of “aurophilicity”³ is attributed to correlation effects and electrostatic contributions.⁴ Of all the donor types employed in the construction of these compounds, sulfur and phosphorus species are the most common, and their compounds have found use in fields as diverse as medicine, electronics, and the decoration of ceramics.⁵

* To whom correspondence should be addressed. E-mail: j.wilton-ely@imperial.ac.uk.

[†] University of Oxford.

[‡] University College London.

[§] Imperial College London.

[⊥] Current address: Imperial College London.

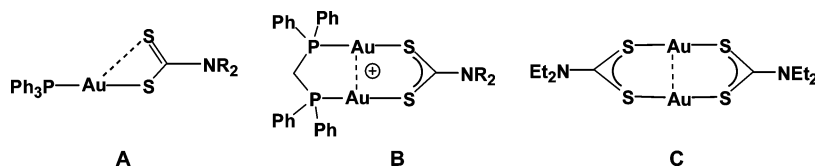
(1) Hogarth, G. *Prog. Inorg. Chem.* **2005**, *53*, 71–561.

(2) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23–98.

(3) (a) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10. (b) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931–1951. (c) Katz, M. J.; Sakaib, K.; Leznoff, D. B. *Chem. Soc. Rev.* **2008**, *37*, 1884–1895.

(4) (a) Pykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456. (b) Runeberg, N.; Schütz, M.; Werner, H. J. *J. Chem. Phys.* **1999**, *110*, 7210–7215.

Scheme 1. Binding Modes of Gold in Selected Dithiocarbamate Compounds



Dithiocarbamate and other sulfur-donor ligands have been reviewed in a number of contexts.^{1,6,7} The bonding modes adopted by gold(I) with dithiocarbamates can often vary despite the limitations created by the inherent preference for a linear coordination geometry.^{1,6,7} As a result monodentate coordination is common, and an asymmetric anisobidentate mode (A, Scheme 1) is not unusual.⁸ This is found to be the case in monomeric gold(I) phosphine complexes with dithiocarbamates where the two gold–sulfur distances differ significantly. Another commonly observed mode is that in which each sulfur atom bonds to a single gold atom. The short Au–Au distance in such compounds constitutes a stabilizing metal–metal interaction.^{3c} Both dppm and dppf often coordinate in this fashion, and the (dppm)Au₂ unit is known to coordinate to dithiocarbamates in this mode (B, Scheme 1).

A crystallographic study of the compound [Au₂(S₂CNEt₂)₂] (C, Scheme 1) has shown the intramolecular Au–Au distance to be 2.78 Å,⁹ which is considerably shorter than the metal–metal distance of 2.88 Å in gold metal.¹⁰ As with much chemistry of monovalent gold, phosphine co-ligands have been used extensively in dithiocarbamate complexes.^{1,6,7} In particular, bidentate and monodentate modes have been investigated in complexes based on polyphosphine backbones.¹¹

Very recently dithiocarbamates have been reported to act as good ligands for gold surfaces, either in the coating of nanoparticles¹² or to form monolayers on Au(111) surfaces.¹³

While polyfunctional variants of many ligands have been used to create multimetallic systems, this approach has rarely been exploited with dithiocarbamates. With gold in particular, almost all previous reports have ignored the potential of

modifying the substituents on the nitrogen atom, and have instead largely concentrated on the commercially available dimethyl- and diethyldithiocarbamate salts.^{1,6,7}

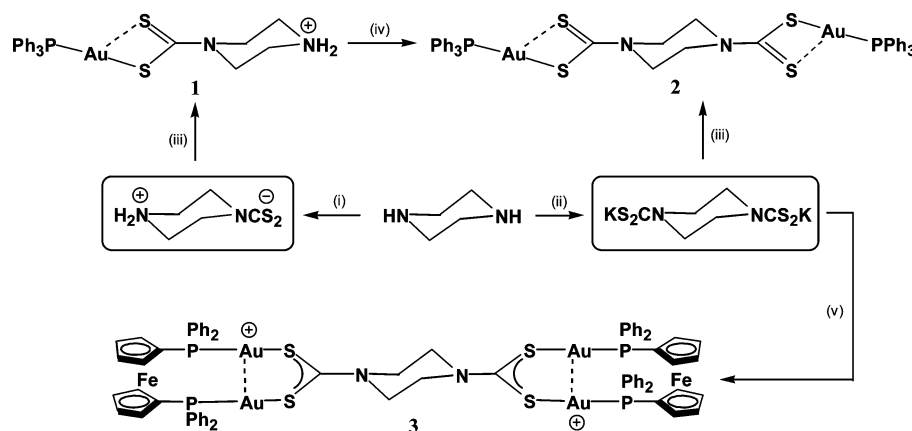
Recent work employing gold(III) bis(dithiocarbamate) nodes¹⁴ in the construction of supramolecular networks¹⁵ by Beer has provided an excellent illustration of the potential of this ligand class. Our recent contributions in this area have focused on the use of a zwitterionic piperazine dithiocarbamate, S₂CNC₄H₈NH₂.¹⁶ This species can be used to coordinate to a first metal center, while retaining the potential to bond to a second on deprotonation and functionalization with CS₂. A general strategy for the synthesis of multimetallic complexes is being developed using this method.¹⁶ Here we wish to report the application of this approach to the construction of homo- and heteronuclear compounds based on gold in its most common oxidation states.

Results and Discussion

Gold Complexes. A number of symmetrical bimetallic transition metal complexes has been prepared using the bridging ligand, KS₂CNC₄H₈NCS₂K.¹⁷ We have also shown that this double salt readily reacts with 2 equiv of *cis*-[RuCl₂(dppm)₂] to yield the homobimetallic compound [(dppm)₂Ru]₂(S₂CNC₄H₈NCS₂)₂]²⁺ by displacement of both chloride ligands.^{16a,b} In the sphere of gold chemistry, this approach has been used independently in the preparation by Yam, Li, Yu, and co-workers of the gold(I) tetrametallic

- (5) *Gold - Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley & Sons Inc.: New York, 1999.
- (6) Mohamed, A. A.; Abdou, H. E.; Chen, J.; Bruce, A. E.; Bruce, M. R. M. *Comments Inorg. Chem.* **2002**, *23*, 321–334.
- (7) Fackler, J. P., Jr.; van Zyl, W. E.; Prihoda, B. A. in reference 5.
- (8) For a recent example, see Arias, J.; Bardají, M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 1597–1606.
- (9) Heinrich, D. D.; Wang, J. C.; Fackler, J. P., Jr. *Acta Crystallogr. Sect. C* **1990**, *C46*, 1444–1447.
- (10) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441–451.
- (11) (a) Bardají, M.; Laguna, A. *Inorg. Chim. Acta* **2001**, *318*, 38–44. (b) Bardají, M.; Laguna, A. *Inorg. Chem.* **2000**, *39*, 3560–3566. (c) Contel, M.; Edwards, A. J.; Garrido, J.; Hursthouse, M. B.; Laguna, M.; Terroba, R. J. *Organomet. Chem.* **2000**, *607*, 129–136. (d) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Villacampa, M. D.; Jones, P. G. *J. Cluster Sci.* **2000**, *11*, 153–167. (e) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Gimeno, M. C.; Laguna, A. *Inorg. Chem.* **1998**, *37*, 5532–5536. (f) Bardají, M.; Laguna, M.; Merchán, F. *Inorg. Chim. Acta* **1994**, *215*, 215–218. (g) Bardají, M.; Blasco, A.; Jiménez, J.; Jones, P. G.; Laguna, A.; Laguna, M.; Merchán, F. *Inorg. Chim. Acta* **1994**, *223*, 55–61. (h) Bardají, M.; Connelly, N. G.; Gimeno, M. C.; Jiménez, J.; Jones, P. G.; Laguna, A.; Laguna, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1163–1167. (i) Uson, R.; Laguna, A.; Laguna, M.; Castilla, M. L.; Jones, P. G.; Meyer-Bäse, K. *J. Organomet. Chem.* **1987**, *336*, 453–460.

- (12) (a) Wessels, J. M.; Nothofer, H.-G.; Ford, W. E.; von Wrochem, F.; Scholz, F.; Vossmeier, T.; Schroeder, A.; Weller, H.; Yasuda, A. *J. Am. Chem. Soc.* **2004**, *126*, 3349–3356. (b) Zhao, Y.; Pérez-Segarra, W.; Shi, Q.; Wei, A. *J. Am. Chem. Soc.* **2005**, *127*, 7328–7329. (c) Vickers, M. S.; Cookson, J.; Beer, P. D.; Bishop, P. T.; Thiebaut, B. *J. Mater. Chem.* **2006**, *16*, 209–215. (d) Cormode, D. P.; Davis, J. J.; Beer, P. D. *J. Inorg. Organomet. Polym.* **2008**, *18*, 32–40. (e) Sharma, J.; Chhabra, R.; Yan, H.; Liu, Y. *Chem. Commun.* **2008**, 2140–2142.
- (13) (a) Morf, P.; Raimondi, F.; Nothofer, H.-G.; Schnyder, B.; Yasuda, A.; Wessels, J. M.; Jung, T. A. *Langmuir* **2006**, *22*, 658–663. (b) Cao, R., Jr.; Díaz, A.; Cao, R.; Otero, A.; Cea, R.; Rodríguez-Argüelles, M. C.; Serra, C. *J. Am. Chem. Soc.* **2007**, *129*, 6927–6930. (c) Zhu, H.; Coleman, D. M.; Dehen, C. J.; Geisler, I. M.; Zemlyanov, D.; Chmielewski, J.; Simpson, G. J.; Wei, A. *Langmuir* **2008**, *24*, 8660–8666.
- (14) (a) Fox, O. D.; Cookson, J.; Wilkinson, E. J. S.; Drew, M. G. B.; MacLean, E. J.; Teat, S. J.; Beer, P. D. *J. Am. Chem. Soc.* **2006**, *128*, 6990–7002. (b) Wong, W. W. H.; Cookson, J.; Evans, E. A. L.; McInnes, E. J. L.; Wolowska, J.; Maher, J. P.; Bishop, P.; Beer, P. D. *Chem. Commun.* **2005**, 2214–2216.
- (15) Cookson, J.; Beer, P. D. *Dalton Trans.* **2007**, 1459–1472.
- (16) (a) Wilton-Ely, J. D. E. T.; Solanki, D.; Hogarth, G. *Eur. J. Inorg. Chem.* **2005**, 402, 7–4030. (b) Knight, E. R.; Solanki, D.; Hogarth, G.; Holt, K. B.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2008**, *47*, 9642–9653. (c) Knight, E. R.; Cowley, A. R.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2009**, 607–609. (d) Macgregor, M. J.; Thompson, A. L.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Organometallics* **2009**, *28*, 197–208.

Scheme 2. Preparation of Mono-, Bi-, and Hexametallic Complexes^a

^a (i) CS₂, short stir; (ii) CS₂ long stir; (iii) ClAu(PPh₃); (iv) NEt₃, CS₂, [ClAu(PPh₃)]; (v) 2 dppf(AuCl)₂.

complex $[(\text{dppm})\text{Au}_2]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{PF}_6)_2$.¹⁸ A particularly intriguing feature of this species is the chiral, cyclic, supramolecular structure in which 16 gold units are held together by aurophilic interactions in the solid state. The same researchers have recently reported fascinating arrangements using a different bis(dithiocarbamate) ligand to prepare an Au₁₂ cluster with *D*₂ symmetry¹⁹ and an unprecedented Au₃₆ arrangement directed by aurophilic interactions.²⁰

In the context of our ongoing research focusing on the zwitterion S₂CNC₄H₈NH₂ and, to a lesser extent, KS₂CNC₄H₈NCS₂K,^{16a,b} we chose to explore the reactivity of these ligands toward gold. Surprisingly, it appears from our literature searches that, apart from the aforementioned $[(\text{dppm})\text{Au}_2]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{PF}_6)_2$, no other gold complexes have been reported bearing these dithiocarbamate ligands. Stirring a solution of [AuCl(PPh₃)] with S₂CNC₄H₈NH₂ in the presence of NaBF₄ yielded the bright yellow mononuclear complex $[(\text{Ph}_3\text{P})\text{Au}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]\text{BF}_4$ (**1**). Two distinct piperazine environments were observed as multiplets at 3.31 and 4.36 ppm, while a larger multiplet integrating to 15 protons was observed in the aromatic region for the triphenylphosphine protons. The presence of this ligand was also confirmed by a singlet in the ³¹P NMR spectrum at 38.0 ppm. Good elemental analysis and mass spectrometry data confirmed the overall composition (Scheme

2). In the light of the fascinating structural complexity found in the tetragold compound mentioned above,¹⁸ two symmetrical piperazine-bridged gold complexes were synthesized using the double salt as a linker. Treatment of KS₂CNC₄H₈NCS₂K with 2 equiv of [AuCl(PPh₃)] led to smooth formation of $[(\text{Ph}_3\text{P})\text{Au}]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)$ (**2**) through loss of the chloride ligands (Scheme 2). A singlet piperazine resonance at 4.33 ppm was seen in the ¹H NMR spectrum, and integration of the relevant resonances indicated the presence of two triphenylphosphine ligands. The equivalence of the two ends of the molecule was confirmed by a singlet in the ³¹P NMR spectrum at 35.9 ppm. The composition of **2** was supported by elemental analysis and a molecular ion in the Fast Atom Bombardment (FAB) mass spectrum at *m/z* = 1153. Anisobidentate coordination was assumed based on literature precedent for $[(\text{R}_3\text{P})\text{Au}(\text{S}_2\text{CNR}'_2)]$ complexes.¹

Employing the same method, a tetragold species $[(\text{dppf})\text{Au}_2]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{PF}_6)_2$ (**3**) was prepared, which gave rise to a new phosphine resonance at 32.0 ppm in the ³¹P NMR spectrum. In addition to broadened resonances for the cyclopentadienyl protons of the dppf ligand, a singlet resonance was found for the piperazine protons at 4.59 ppm in the ¹H NMR spectrum. Elemental analysis, IR spectroscopy, and mass spectrometry further confirmed the formulation. Diffraction quality single crystals were grown by diffusion of diethyl ether vapor onto an acetonitrile/methanol (1:1) solution of **3** and the structure determined (Figure 1).

The hexametallic compound has S–C–S bond angles of 123.9(5)° and 124.6(5)°, the smallest of which is significantly smaller than those of 125.0(7)° and 129.0(7)° in $[\text{Au}_2(\text{S}_2\text{CNEt}_2)_2]$.⁹ The most directly comparable structure is $[(\text{dppm})\text{Au}_2]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]^{2+}$; however, the S–C–S angles of the eight different molecules that make up the Au₁₆ ring in the solid state structure of this complex range from 112.3(6)° to 145.0(10)°,¹⁸ making the comparison less helpful. The C–S bond distances found in compound **3**, which range between 1.727(9) and 1.743(9) Å are, on average, marginally longer than those of 1.701(8) and 1.730(8) Å in the previously reported complex $[(\text{dppm})_2\text{Ru}]_2$.

- (17) Some metal complexes of piperazine bis(dithiocarbamates) have been reported: (a) Esmadi, F. T.; Irshaidat, T. Z. A. *Synth. React. Inorg. Met.-Org. Chem.* **2000**, *30*, 1347–1362. (b) Glidewell, C.; Johnson, I. L. *Polyhedron* **1988**, *7*, 1371–1375. (c) Siddiqi, K. S.; Zaidi, F. R.; Zaidi, S. A. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 569–578. (d) Marcotrigiano, G.; Pellacani, G. C.; Preti, C.; Tosi, G. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1018–1020. (e) Hulanicki, A.; Shishkova, L. *Chem. Anal. (Warsaw)* **1965**, *10*, 837–845. (f) Yin, H. D.; Ma, C. L.; Wang, Y.; Fang, H. X.; Shao, J. X. *Acta Chim. Sinica* **2002**, *60*, 897–903. (g) Yin, H.; Wang, C. *Appl. Organomet. Chem.* **2004**, *18*, 145–146. (h) Tian, L.; Shang, Z.; Yu, Q.; Li, D.; Yang, G. *Appl. Organomet. Chem.* **2004**, *18*, 253–254. (i) Yin, H. D.; Wang, C. H.; Xing, Q. J. *Chin. J. Struct. Chem.* **2004**, *23*, 490–493. (j) Tombeux, J.; van Poucke, L. C.; Eeckhaut, Z. *Spectrochim. Acta* **1972**, *28A*, 1943–1947.
- (18) Yu, S.-Y.; Zhang, Z.-X.; Cheng, E. C.-C.; Li, Y.-Z.; Yam, V. W.-W.; Huang, H.-P.; Zhang, R. J. *Am. Chem. Soc.* **2005**, *127*, 17994–17995.
- (19) Sun, Q.-F.; Lee, T. K.-M.; Li, P.-Z.; Yao, L.-Y.; Huang, J.-J.; Huang, J.; Yu, S.-Y.; Li, Y.-Z.; Cheng, E. C.-C.; Yam, V. W.-W. *Chem. Commun.* **2008**, 5514–5516.
- (20) Yu, S.-Y.; Sun, Q.-F.; Lee, T. K.-M.; Cheng, E. C.-C.; Li, Y.-Z.; Yam, V. W.-W. *Angew. Chem., Int. Ed.* **2008**, *47*, 4551–4554.

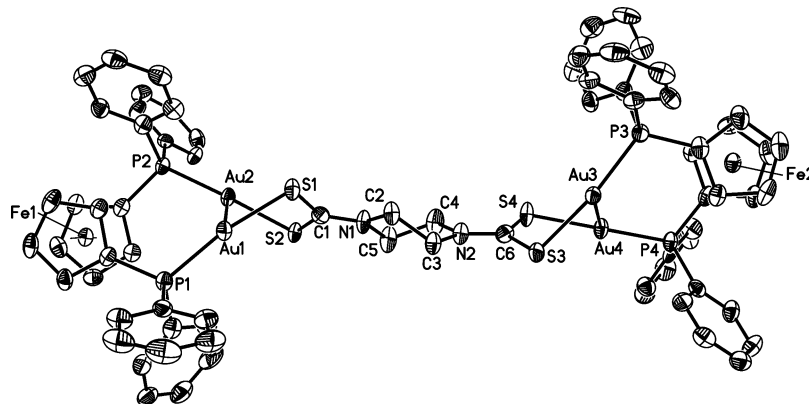


Figure 1. Molecular structure of the dication in $[(\text{dppf})\text{Au}_2](\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{PF}_6)_2$ (**3**). Selected bond lengths (Å) and angles (deg): Au1–P1 = 2.268(2), Au1–S1 = 2.324(2), Au1–Au2 = 3.0072(4), Au2–P2 = 2.273(2), Au2–S2 = 2.323(2), Au3–P3 = 2.268(2), Au3–S3 = 2.336(2), Au3–Au4 = 3.0368(4), Au4–P4 = 2.267(2), Au4–S4 = 2.3220(19), S1–C1 = 1.733(8), S2–C1 = 1.743(9), S3–C6 = 1.727(9), S4–C6 = 1.739(9), N1–C1 = 1.307(10), N2–C6 = 1.325(11), P1–Au1–S1 = 168.16(8), P2–Au2–S2 = 171.72(8), P3–Au3–S3 = 170.40(8), P4–Au4–S4 = 167.05(8), S1–C1–S2 = 123.9(5), S3–C6–S4 = 124.6(5).

$(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)](\text{BF}_4)_2$.^{16a} In compound **3**, the C–N bond distances in the dithiocarbamate unit are 1.307(10) and 1.325(11) Å, indicating the multiple bond character present (average distance for C–N is 1.47 Å and 1.29 Å for C=N).²¹ The ruthenium example mentioned above displays a regular chair conformation for the piperazine ring; however, in compound **3** the ring is twisted between boat and chair conformations. The intramolecular gold–gold distances within each digold unit are Au(1)–Au(2): 3.0072(4) Å and Au(3)–Au(4): 3.0368(4) Å. Although much greater than those found in $[\text{Au}_2(\text{S}_2\text{CNEt}_2)_2]$ (2.78 Å) and $[(\text{dppm})\text{Au}_2]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]^{2+}$ (2.90 Å), these distances are still significantly shorter than the sum of the van der Waals radii (3.32 Å)¹⁰ and indicate a significant metal–metal interaction.³ The view along the gold–gold interactions reveals a “crossed swords” arrangement of the P–Au–S linkages, which is a common feature in previously reported gold(I) complexes.²² It has been noted that the flexibility afforded by the Cp rings in the dppf ligand permits subtly different structures to be formed compared to other diphosphine digold units.²³

Complexes Combining Ruthenium and Gold. A preliminary study^{16a} demonstrated how the functionalization of $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2](\text{BF}_4)_2$ with NEt_3 and CS_2 generates the metala-dithiocarbamate species $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2]$ in situ. Furthermore, addition of metal fragments to this species permits bimetallic species to be prepared. If an identical fragment is introduced, symmetrical species, such as $[(\text{dppm})_2\text{Ru}]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]^{2+}$, are obtained; however, the great advantage of this approach lies in the access it provides to heterobimetallic species.

Sequential treatment of a solution of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)](\text{BF}_4)_2$ with NEt_3 , CS_2 , and $[\text{ClAu}(\text{PPh}_3)]$ resulted in a colorless product, which displayed a new, somewhat broadened singlet in the ^{31}P NMR spectrum at 37.5 ppm. Little change was observed in the ^1H NMR

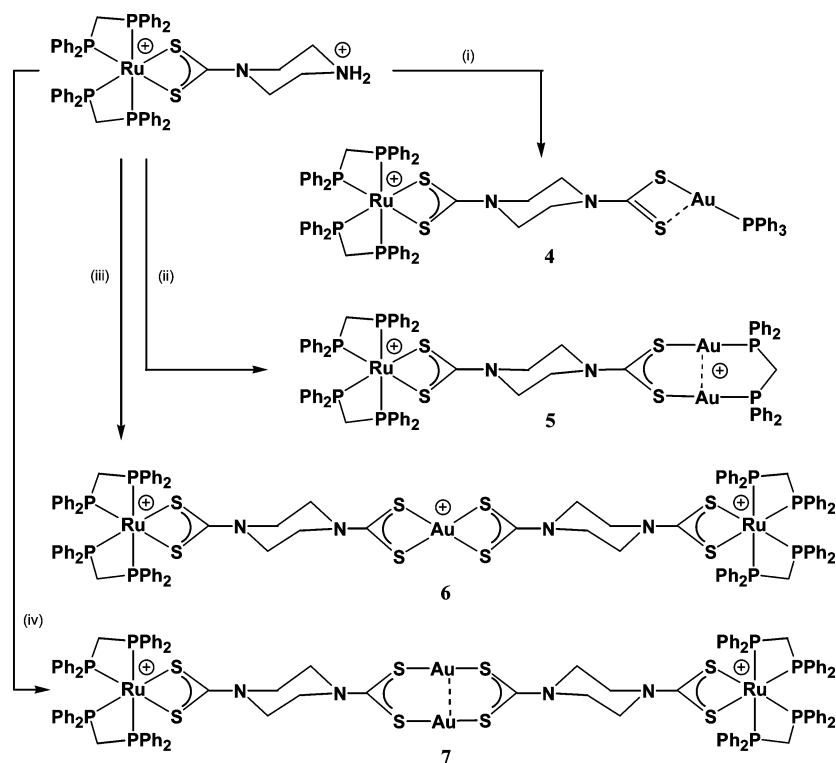
spectrum apart from greater activity in the aromatic region. However, a molecular ion at $m/z = 1566$ and elemental analysis data confirmed the formulation as $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}(\text{PPh}_3)]\text{BF}_4$ (**4**).

In situ generation of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]$ and subsequent treatment with $[(\text{dppm})(\text{AuCl})_2]$ led to the heterotrimetallic complex $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}_2(\text{dppm})](\text{BF}_4)_2$ (**5**). The ^{31}P NMR spectrum displayed a new broadened singlet at 37.8 ppm, corresponding to the dppm ligand spanning two gold centers, while those bonded in a bidentate fashion at ruthenium gave rise to triplets at –5.0 and –18.3 ppm ($J_{\text{PP}} = 35.5$ Hz). In addition to consistent ^1H NMR and IR spectroscopic data, a molecular ion at $m/z = 1883$ and elemental analysis confirmed the formulation.

A further Ru_2Au compound, $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]_2\text{Au}](\text{BF}_4)_3$ (**6**) was prepared, but of very different composition to **5**. With this complex the investigations were extended to gold(III), using the well-known propensity of the d^8 metal center to accommodate two dithiocarbamate moieties in a square planar motif.¹⁴ Synthesis was achieved by in situ functionalization of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)](\text{BF}_4)_2$ with NEt_3 , CS_2 followed by addition of half an equivalent of HAuCl_4 (Scheme 3). A distinctive color change was observed from pale yellow to dark brown, and the formulation of the complex was indicated by a molecular ion at $m/z = 2410$ in the FAB mass spectrum. This was further supported by elemental analysis.

A tetrametallic Ru_2Au_2 species was also obtained on treatment of a solution of the zwitterion $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]$ (generated in situ, as above) with an equimolar equivalent of $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene). The chloride and thiacycle ligands were readily displaced to give a dication as shown in Scheme 3. Spectroscopic data were found to be similar to the other complexes bearing the $(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)$ unit, so confirmation of the composition rested on mass spectrometry (MALDI) and elemental analysis, both of which were in agreement with the formulation $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]_2\text{Au}_2(\text{BF}_4)_2$ (**7**).

- (21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *Chem. Soc., Perkin Trans.* **1987**, S1–S19.
- (22) (a) Zank, J.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1998**, 323–324. (b) Wilton-Ely, J. D. E. T.; Schier, A.; Mitzel, N. W.; Nogai, S.; Schmidbaur, H. *J. Organomet. Chem.* **2002**, 643, 313–323.
- (23) Gimeno, M. C.; Laguna, A. *Gold Bull.* **1999**, 32, 90–95.

Scheme 3. Preparation of Heterometallic Complexes^a

^a (i) NEt₃, CS₂, [AuCl(PPh₃)]; (ii) NEt₃, CS₂, [dppm(AuCl)₂]; (iii) NEt₃, CS₂, 0.5 HAuCl₄; (iv) NEt₃, CS₂, [AuCl(tht)].

The dithiocarbamate complex [(dppm)Au₂(S₂CNC₄H₈NH₂)]²⁺ was considered to be a potentially useful starting point for further reactions; however, reaction of [(dppm)-(AuCl)₂] with the zwitterion S₂CNC₄H₈NH₂ led to isolation of the previously reported bimetallic complex [(dppm)-Au₂]₂(S₂CNC₄H₈NCS₂)²⁺ (Supporting Information).¹⁸ Such symmetrization behavior has also been observed by us in some palladium and platinum compounds.²⁴

Symmetrization and ligand exchange have some precedent in dithiocarbamate chemistry. Indeed, Laguna and co-workers^{11h} have successfully used this approach to prepare the mixed dithiocarbamate ylide species [Au₂{μ-(CH₂)₂PPh₂}(μ-S₂CNR₂)] from the reaction of [Au₂{μ-(CH₂)₂PPh₂}]₂ and [Au₂(μ-S₂CNR₂)₂]. However, the process here is not a straightforward substitution pathway as a new CS₂ unit needs to be generated to convert [(dppm)Au₂(S₂CNC₄H₈NH₂)]²⁺ to [(dppm)Au₂]₂(S₂CNC₄H₈NCS₂)²⁺. This may be achieved by deprotonation of the ammonium unit in [(dppm)Au₂(S₂CNC₄H₈NH₂)]²⁺ to form [(dppm)Au₂(S₂CNC₄H₈NH)]⁺, which could then use the amine nitrogen to attack the CS₂ carbon of another [(dppm)Au₂(S₂CNC₄H₈NH₂)]²⁺ molecule, displacing a piperazine unit and generating the symmetrical product [(dppm)Au₂]₂(S₂CNC₄H₈NCS₂)²⁺.

It has been demonstrated by Fackler and Coucouvanis²⁵ that nucleophilic substitution can occur at the carbon atom of coordinated dithiocarbamates. They reported that a *trans*-

amination reaction occurs between piperidine and [Ni(S₂CNH₂)₂], with the -NH₂ acting as a leaving group. Xanthates, with a more electrophilic carbon due to the increased electronegativity of oxygen, show similar substitution reactions. For example, the same paper reports that the xanthate [Ni(S₂COEt)₂] also reacts with piperidine to form the bis(dithiocarbamate). Nucleophilic substitution reactions of dithiocarbamates have also been demonstrated with palladium and platinum but in all reported cases a primary amine is replaced by a secondary amine.

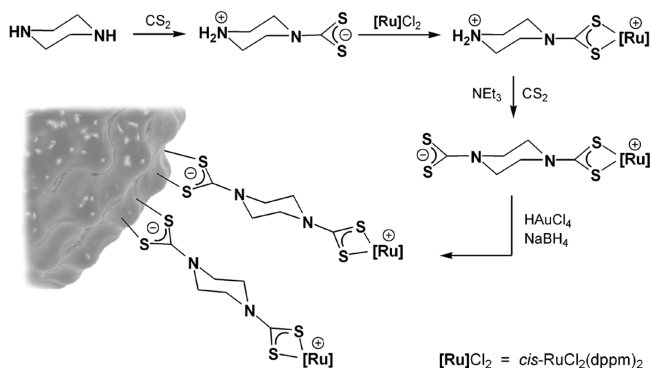
Attempts to form symmetrical bimetallic complexes with [LAuCl] (where L = CN^tBu and As(C₆H₄Me-2)Ph₂) were ultimately unsuccessful. In both cases a yellow precipitate formed immediately upon reaction of the relevant gold(I) chloride with the double salt. The yellow product turned brown on drying in air, and this brown solid proved insoluble in all common laboratory solvents. It is likely that both of the ligands (L) were displaced, and reaction with the double salt led to formation of a gold polymer. When L = As(C₆H₄Me-2)Ph₂, the insoluble product was analyzed to give a composition that fitted that of a gold (II) polymer [Au(S₂CNC₄H₈NCS₂)]_n.

Functionalization of Gold Nanoparticles. The generation of the metala-dithiocarbamate [L_nM(S₂CNC₄H₈NCS₂)] underpinned the synthetic routes described above. The application of such species to the emerging field of functionalized gold nanoparticles was then explored.^{16c} These materials have received much attention²⁶ since their pioneering development²⁷ but very few reports exist in which the surface

(24) Knight, E. R.; Leung, N. H.; Lin, Y. H.; Cowley, A. R.; Watkin, D. J.; Thompson, A. L.; Hogarth, G.; Wilton-Ely, J. D. E. *T. Dalton Trans.* **2009**, in press, DOI: 10.1039/b821947h.

(25) Fackler, J. P., Jr.; Coucouvanis, D.; Seidel, W. C.; Masek, R. C.; Holloway, W. *Chem. Commun.* **1967**, 924–925.

(26) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346.

Scheme 4. Functionalization of Gold Nanoparticles with Ruthenium Units

is modified to incorporate transition metal functionality.²⁸ Despite the widespread use of thiols to stabilize gold colloids, dithiocarbamates were only first used very recently in this manner.¹² The first report of complexed metals being tethered to the surface through dithiocarbamates appeared shortly afterward.^{12c}

In a modification of the procedure reported by Brust and Schiffrin,^{27b} the zwitterionic complex $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2]$ was generated in situ and added to a solution of HAuCl_4 reduced by sodium borohydride in the presence of the phase transfer agent, *n*-tetraoctylammonium bromide (Scheme 4).

The black material obtained (**NP1**) was characterized by multinuclear NMR spectroscopy (³¹P, ¹H) in CDCl_3 (in which it is sparingly soluble), revealing broadened resonances at chemical shifts slightly displaced from those observed in the molecular precursor. Transmission Electron Microscopy (TEM) was used to analyze the average diameter of the nanoparticles, which was revealed to be $3.4 (\pm 0.3)$ nm (Figure 2). While the method employed above is widespread, an alternative method has been reported in which nanoparticles are prepared by reduction of HAuCl_4 with NaBH_4 in the presence of trisodium citrate.²⁹ The citrate surface species can then be displaced by thiols or, in our modification, the zwitterion $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2]$. This yielded blue nanoparticles (**NP2**), which were shown by TEM to be of larger diameter (14.4 ± 2.5 nm) than **NP1** (Figure 2). Both **NP1** and **NP2** were analyzed by UV-vis spectroscopy and found to display absorptions with $\lambda_{\text{max}} = 265, 333$ nm. These bands are also observed in $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2](\text{BF}_4)_2$ ^{16b} and were assigned to LMCT behavior. Surface plasmon resonance bands (SPR) at around 520 nm are often observed for nanoparticles with sizes in the range 2–20 nm; however, the bands attributed to SPR were observed at 574 and 683 nm for **NP1** and **NP2**, respectively. Reports have

found that the value of the SPR band can depend on interparticle interactions, surface charge, and the solvent system used. For example, in chloroform solution, the SPR band is often observed to be shifted away from the typical value.³⁰ From the diameter of the gold nanoparticles determined by TEM measurements, the approximate number of gold atoms in **NP1** was calculated to be around 1600 with 550 at the surface. This contrasts with the substantially greater surface area of **NP2** (11000 surface atoms with 145000 core gold atoms). The surface area will be an important variable in the application of nanoparticle materials in applications such as sensing and catalysis. In preliminary work aimed at the latter application, it was discovered that the nanoparticles display well-behaved, reversible electrochemistry with a Ru(II)/Ru(III) couple at 0.73 V (vs Fc/Fc^+). This potential is slightly shifted from that found in the complex $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2](\text{BF}_4)_2$.^{16b} Astruc and co-workers^{31,32} have recently demonstrated the potential for sensing anions using dendronized nanoparticle surfaces of ferrocenyl-amide units. The preorganization of the transition metals units because of their immobilization on the gold surface gives rise to a positive dendritic effect leading to much greater shifts in the CV trace from interactions with anions than found using unbound species in solution. The anions can be washed from the electrode modified with the nanoparticles and the system reused.

To further explore the potential for surface modification of these materials, a mixed surface topology was introduced. This was achieved by treatment of the TOAB-stabilized nanoparticles with equimolar quantities of 1-dodecanethiol and the metala-dithiocarbamate $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2]$ using a method pioneered by Astruc and co-workers for mixtures of thiols.³² Unlike materials **NP1** and **NP2**, the nanoparticles (**NP3**) obtained from the thiol/metala-dithiocarbamate mixture proved to be insoluble in all common laboratory solvents. As a result, analysis was limited to EDX, solid state IR spectroscopy, and TEM. After repeated washing with dichloromethane, water, and methanol to remove species not attached to the surface, **NP3** showed the presence of Au, Ru, S, and P (EDX), while a $\nu(\text{CS})$ stretch characteristic of a coordinated dithiocarbamate ligand (999 cm^{-1}) was evident in the solid state infrared spectrum (KBr disk) along with similar bands to those observed in a spectrum of the free thiol (measured as a thin film). However, the TEM images showed agglomerated nanoparticles rather than discrete units (Figure 2), and the insolubility of the material is probably connected to the interparticle interactions. The origin of this aggregation is difficult to determine unambiguously but could be due to an absence of electrostatic

(27) (a) Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408–3413. (b) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802. (c) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1655–1656. (d) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17–30.

(28) Wilton-Ely, J. D. E. *T. Dalton Trans.* **2008**, 25–29.

(29) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735–743.

(30) (a) Huang, S.; Minami, K.; Sakaue, H.; Shingubara, S.; Takahagi, T. *J. Appl. Phys.* **2002**, *92*, 7486–7490. (b) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17–30.

(31) (a) Astruc, D.; Daniel, M.-C.; Ruiz, J. *J. Chem. Commun.* **2004**, 2637–2649. (b) Labande, A.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2002**, *124*, 1782–1789. (c) Labande, A.; Astruc, D. *Chem. Commun.* **2000**, 1007–1008.

(32) Daniel, M.-C.; Ruiz, J.; Nlate, S.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **2003**, *125*, 2617–2628.

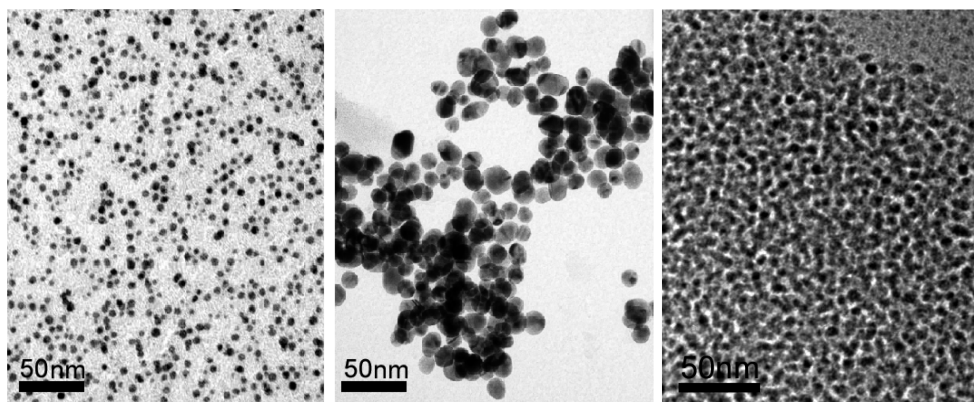


Figure 2. TEM images of nanoparticles NP1 (left), NP2 (center) and NP3 (right).

repulsion in the areas covered by thiols rather than cationic metal units. The average diameter of these nanoparticles NP3 was found to be approximately 3 nm. Such agglomeration is similar to that observed in TEM images of nanoparticles linked by 1,4-cyclohexane-bis(dithiocarbamate) and 1,4-phenylene-bis(dithiocarbamate).^{12a}

Direct synthesis of nanoparticles from molecular precursors in a “one pot” procedure was also explored using the precedent of Nakamoto and co-workers,³³ who found that thermolysis of a gold(I) thiolate complex, $[\text{C}_{14}\text{H}_{29}\text{Me}_3\text{N}][\text{Au}(\text{SC}_{12}\text{H}_{25})_2]$, at 180 °C for 5 h under nitrogen produces gold nanoparticles passivated by a thiolate shell. However, under modified conditions (ethanol reflux, addition of NaBH_4), complexes **6** (Au^{III}) and **7** (Au^{I}) failed to yield gold nanoparticles with $\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2$ surface groups (TEM). Despite this “one pot” method not being successful, the fact that the ligand $\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2$ can be prepared in multigram quantities in 30 min^{16b} and that it readily forms dithiocarbamate complexes with many transition metal complexes (all under aerobic conditions) means that this methodology can be used to introduce a wide variety of metal units onto the surface of gold nanoparticles in just a few hours. This is in contrast to the much more demanding synthesis of (mainly polydentate) chelates with long thiol tethers, which has been the previous method of choice for attaching transition metal units to gold nanoparticles.²⁸

Conclusion

This report demonstrates a versatile approach to the linking of mono- and digold units through a piperazine-based dithiocarbamate spacer. The application to heterometallic assemblies is particularly significant, as demonstrated by the gold–ruthenium species prepared. Such mixed-metal species are not usually accessible using conventional bifunctional spacers. Unexpectedly, the attempted preparation of $[(\text{dppm})\text{Au}_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]^{2+}$ as an entry point to this chemistry was subverted by a symmetrization process. However, this drawback was successfully avoided by preparing heterometallics commencing from the opposite end of the molecule, by generation of the metala-dithiocarbamate $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)]$ unit. The versatility and utility

of the approach described here is illustrated by its application to the introduction of transition metals onto the surface of gold nanoparticles, paving the way for facile functionalization of these materials for applications in catalysis and sensing.

Experimental Section

General Comments. All experiments were carried out under aerobic conditions, and the majority of the complexes appear indefinitely stable toward the atmosphere in solution or in the solid state. Solvents were used as received from commercial sources. Syntheses of the following compounds have been described elsewhere: $\text{KS}_2\text{CNC}_4\text{H}_8\text{NCS}_2\text{K}$,^{17j} $[\text{AuCl}(\text{PPh}_3)]$,³⁴ $[\text{dppm}(\text{AuCl})_2]$,³⁴ $[\text{dppf}(\text{AuCl})_2]$,³⁵ and $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)](\text{BF}_4)_2$.^{16b} Fast Atom Bombardment (FAB) mass spectral data were obtained using an Autospec Q instrument. The mass spectra for compounds **2** and **5** were obtained from the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. Infrared data were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, KBr plates were used for solid state IR spectroscopy, and characteristic phosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using a Varian Mercury 300 spectrometer in CDCl_3 unless otherwise indicated. All couplings are in hertz. Elemental analysis data were obtained from London Metropolitan University. Samples were recrystallized from a mixture of dichloromethane and ethanol for elemental analysis. Solvates were confirmed by integration of the ^1H NMR spectrum. Transmission Electron Microscopy (TEM) was performed at University College London using a JEOL 100 instrument operating at 100 kV. A JEOL JEM-2000F instrument fitted with a Link Pentafet EDX detector operating at 200 kV was used for Energy Dispersive X-ray (EDX) analysis at the University of Oxford (Begbroke Science Park). The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes.

Synthesis of $[(\text{Ph}_3\text{P})\text{Au}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)]\text{BF}_4$ (1**).** $\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2$ (98 mg, 0.604 mmol) and NaBF_4 (88 mg, 0.802 mmol) were dissolved in methanol (20 mL) and added to a dichloromethane solution (20 mL) of $[\text{AuCl}(\text{PPh}_3)]$ (200 mg, 0.404 mmol). The reaction was stirred for 2 h in the dark, and then all solvent removed. Acetone (50 mL) was added to dissolve the crude product, and the solution filtered through diatomaceous earth to remove NaCl and

(33) Nakamoto, M.; Yamamoto, M.; Fukusumi, M. *Chem. Commun.* **2002**, 1622–1623.

(34) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748–1754.

(35) Hill, D. T.; Giraldo, G. R.; McCabe, F. L.; Johnson, R. K.; Stupik, P. D.; Zhang, J. H.; Reiff, W. M.; Eggleston, D. S. *Inorg. Chem.* **1989**, *28*, 3529–3533.

excess NaBF_4 . All solvent was again removed, and the residue triturated in diethyl ether (30 mL) to give a bright yellow product, which was washed with diethyl ether (10 mL) and dried. Yield: 168 mg (59%). IR (KBr/nujol): 1708, 1607, 1587, 1311, 1260, 1240, 1082 ($\nu_{\text{B-F}}$), 998 (ν_{CS}) cm^{-1} . NMR ^1H : 3.31, 4.36 (s x 2, $\text{NC}_4\text{H}_8\text{N}$, 8H), 7.34–7.48 (m, C_6H_5 , 15H) ppm. ^{31}P : 38.0 (s, PPh_3) ppm. MS (ES) m/z (abundance %): 621 (68) $[\text{M}]^+$. Analysis: Calculated for $\text{C}_{23}\text{H}_{25}\text{AuBF}_4\text{N}_2\text{P}_2\text{S}_2$: C, 39.0; H, 3.6; N, 4.0%. Found: C, 39.1; H, 3.7; N, 4.0%.

Synthesis of $[(\text{Ph}_3\text{P})\text{Au}]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)$ (2). (a) $\text{KS}_2\text{CNC}_4\text{H}_8\text{NCS}_2\text{K}$ (25 mg, 0.079 mmol) was dissolved in methanol (10 mL) to which a dichloromethane solution (10 mL) of $[\text{AuCl}(\text{PPh}_3)]$ (80 mg, 0.162 mmol) was added. The reaction was stirred for 3.5 h in the dark and then all solvent removed. Diethyl ether (15 mL) was added, and the solid triturated in a sonic bath. The cream product was filtered and washed with water (10 mL), ethanol (10 mL), and hexane (10 mL). Yield: 83 mg (89%). (b) Compound **1** (20 mg, 0.028 mmol) was dissolved in acetone (5 mL), and one drop (excess) each of NEt_3 and CS_2 were added and the reaction stirred for 10 min. To this was added a dichloromethane solution (10 mL) of $[\text{AuCl}(\text{PPh}_3)]$ (14 mg, 0.028 mmol). The reaction was stirred for 1 h, and all solvent removed. The same workup was employed as in (a) to give 29 mg (90%) of product. IR (KBr/nujol): 1272, 1247, 1201, 996 (ν_{CS}), 907 cm^{-1} . NMR ^1H : 4.33 (s, $\text{NC}_4\text{H}_8\text{N}$, 8H), 7.41–7.64 (m, C_6H_5 , 30H) ppm. ^{31}P : 35.9 (s, PPh_3) ppm. MS (FAB) m/z (abundance %): 1155 (2) $[\text{M}]^+$. Analysis: Calculated for $\text{C}_{42}\text{H}_{38}\text{Au}_2\text{N}_2\text{P}_2\text{S}_4$: C, 43.7; H, 3.3; N, 2.4%. Found: C, 43.7; H, 3.2; N, 2.3%.

Synthesis of $[(\text{dppf})\text{Au}]_2(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{PF}_6)_2$ (3). $\text{KS}_2\text{CNC}_4\text{H}_8\text{NCS}_2\text{K}$ (11 mg, 0.035 mmol) was dissolved in methanol (10 mL). A dichloromethane solution (10 mL) of $[(\text{dppf})(\text{AuCl})_2]$ (75 mg, 0.074 mmol) was added dropwise followed by a solution of NH_4PF_6 (15 mg, 0.092 mmol) in methanol (10 mL). The reaction was stirred for 3 h at 5 °C and then all solvent removed. The residue was taken up in a minimum volume of dichloromethane and filtered through diatomaceous earth (Celite). Diethylether (15 mL) was added to precipitate the yellow product. This was washed with diethylether (5 mL) and dried. Yield: 66 mg (74%). IR (KBr/nujol): 1311, 1279, 1173, 1101, 1032, 997 ($\nu_{\text{C-S}}$), 837 ($\nu_{\text{P-F}}$) cm^{-1} . NMR ^1H (CD_2Cl_2): 4.34, 4.52 (s(br) x 2, C_5H_4 , 2 x 8H), 4.59 (s, $\text{NC}_4\text{H}_8\text{N}$, 8H), 7.53–7.70 (m, C_6H_5 , 40H) ppm. ^{31}P (CD_2Cl_2): 32.0 (s, dppf) ppm. MS (FAB) m/z (abundance %): 2277 (10) $[\text{M} + \text{PF}_6]^+$. Analysis: Calculated for $\text{C}_{74}\text{H}_{64}\text{Au}_4\text{F}_{12}\text{Fe}_2\text{N}_2\text{P}_6\text{S}_4$: C, 36.7; H, 2.7; N, 1.2%. Found: C, 36.6; H, 2.8; N, 1.3%.

Synthesis of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}(\text{PPh}_3)]\text{BF}_4$ (4). $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2][\text{BF}_4]_2$ (100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL), treated with NEt_3 (5 drops, excess), and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for 5 min. $[\text{AuCl}(\text{PPh}_3)]$ (41 mg, 0.083 mmol) was added as a solid, and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth (Celite). The crude product was redissolved in dichloromethane (5 mL) and diethylether (30 mL) added to precipitate the colorless product. This was washed with diethylether (10 mL) and dried. Yield: 87 mg (63%). IR (KBr/nujol): 1310, 1277, 1207, 1055 (ν_{BF}), 997 (ν_{CS}) cm^{-1} . NMR ^1H (d^6 -acetone): 3.73, 3.92, 4.14, 4.23 (m x 4, $\text{NC}_4\text{H}_8\text{N}$, 8H), 4.75, 5.36 (m x 2, PCH_2P , 2 x 2H), 6.69, 7.00, 7.24, 7.40, 7.60, 7.63 (m x 6, C_6H_5 , 55H) ppm. ^{31}P (d^6 -acetone): -18.0, -3.0 (t x 2, dppm, $J_{\text{PP}} = 34.5$ Hz), 37.5 (s(br), PPh_3) ppm. MS (FAB) m/z (abundance %) = 1566

(3) $[\text{M}]^+$. Analysis: Calc. for $\text{C}_{74}\text{H}_{67}\text{AuBF}_4\text{N}_2\text{P}_3\text{RuS}_4$: C, 53.8; H, 4.1; N, 1.7%. Found: C, 54.0; H, 4.0; N, 1.6%.

Synthesis of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Au}_2(\text{dppm})](\text{BF}_4)_2$ (5). $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2][\text{BF}_4]_2$ (75 mg, 0.062 mmol) was dissolved in dichloromethane (10 mL), treated with NEt_3 (3 drops, excess), and stirred for 5 min. Carbon disulfide (2 drops, excess) was added, and the reaction stirred for 5 min. $[(\text{dppm})-(\text{AuCl})_2]$ (53 mg, 0.062 mmol) was added as a solid and the reaction stirred for 1 h. Ethanol (10 mL) was added and the pale yellow product precipitated under reduced pressure. This was washed with ethanol (10 mL), hexane (10 mL) and dried. Yield: 120 mg (94%). IR (KBr/nujol): 1308, 1277, 1216, 1157, 1098, 1056 (ν_{BF}), 998 (ν_{CS}), 912 cm^{-1} . NMR ^1H : 3.74, 3.92, 4.13, 4.28 (m x 4, $\text{NC}_4\text{H}_8\text{N}$, 8H), 4.56, 4.94 (m x 2, PCH_2P , 6H), 6.50, 6.63, 7.04, 7.31, 7.61, 7.73 (m x 6, C_6H_5 , 60H) ppm. ^{31}P NMR: -18.3, -5.0 (t x 2, dppmRu, $J_{\text{PP}} = 35.5$ Hz), 37.8 (s(br), dppmAu) ppm. MS (FAB) m/z (abundance %): 1883 (15) $[\text{M}]^+$. Analysis: Calculated for $\text{C}_{81}\text{H}_{74}\text{Au}_2\text{B}_2\text{F}_8\text{N}_2\text{P}_6\text{RuS}_4$: C, 47.2; H, 3.6; N, 1.4%. Found: C, 47.2; H, 3.5; N, 1.3%.

Synthesis of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)_2\text{Au}](\text{BF}_4)_3$ (6). $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2](\text{BF}_4)_2$ (100 mg, 0.083 mmol) was dissolved in a mixture of chloroform (10 mL) and methanol (10 mL), treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (4 drops, excess) was added, and the reaction stirred for 5 min. Tetrachloroauric acid (14 mg, 0.041 mmol) was added as a solution in methanol (7 mL) causing a color change from yellow to brown. The reaction was stirred for 3 h. All solvent was removed, and the residue was taken up in a minimum amount of chloroform and filtered through diatomaceous earth (Celite). Ethanol (30 mL) was added, and the brown product precipitated under reduced pressure. This was washed with ethanol (10 mL), hexane (10 mL), and dried. Yield: 69 mg (63%). The complex can be recrystallized from dichloromethane and ethanol. IR (KBr/nujol): 1277, 1216, 1095, 1057 ($\nu_{\text{B-F}}$), 998 ($\nu_{\text{C-S}}$) cm^{-1} . NMR ^1H (CD_2Cl_2): 3.66, 3.76, 4.16, 4.25 (m x 4, $\text{NC}_4\text{H}_8\text{N}$, 16H), 4.52, 4.95 (m x 2, PCH_2P , 2 x 4H), 6.49, 6.95, 7.08, 7.34, 7.65 (m x 5, C_6H_5 , 80H) ppm. ^{31}P NMR (CD_2Cl_2): -18.3, -4.9 [t x 2, dppm, $J_{\text{PP}} = 34.6$ Hz] ppm. MS (FAB) m/z (abundance %): 2694 (2) $[\text{M} + 3\text{BF}_4 + \text{Na}]^+$, 2606 (1) $[\text{M} + 2\text{BF}_4 + \text{Na}]^+$, 2410 (1) $[\text{M}]^+$. Analysis: Calculated for $\text{C}_{112}\text{H}_{104}\text{Au}_3\text{B}_3\text{F}_{12}\text{N}_4\text{P}_8\text{Ru}_2\text{S}_8 \cdot 4\text{CH}_2\text{Cl}_2$: C, 46.3; H, 3.8; N, 1.9%. Found: C, 46.2; H, 3.5; N, 2.1%.

Synthesis of $[(\text{dppm})_2\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)_2\text{Au}](\text{BF}_4)_2$ (7). A solution of $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2][\text{BF}_4]_2$ (100 mg, 0.083 mmol) in dichloromethane (30 mL) and methanol (15 mL) was treated with NEt_3 (4 drops, excess) followed by a 5 min stir and carbon disulfide (3 drops, excess) followed by a 10 min stir. A colorless dichloromethane solution (20 mL) of $[\text{AuCl}(\text{tht})]$ (27 mg, 0.083 mmol) was added, and the yellow solution became progressively darker during a 20 min stir. All volatiles were removed under vacuum leaving a yellow-brown crude solid which was taken up in a minimal amount of dichloromethane and filtered through diatomaceous earth (Celite). Ethanol (10 mL) was added, and the product was precipitated under reduced pressure. The brown solid was isolated by filtration and washed with cold ethanol (5 mL) and dried. Yield: 98 mg (85%). IR (KBr/nujol): 1604, 1386, 1235, 1152, 1060 ($\nu_{\text{B-F}}$), 999 ($\nu_{\text{C-S}}$) cm^{-1} . NMR ^1H (CD_2Cl_2): 3.37–4.28 (m, $\text{NC}_4\text{H}_8\text{N}$, 16H), 4.52, 4.93 (m x 2, PCH_2P , 2 x 4H), 6.48, 6.78–7.77 (m x 2, C_6H_5 , 80H) ppm. ^{31}P NMR (CD_2Cl_2): -17.9, -5.0 (m x 2, dppm) ppm. MALDI-MS m/z (abundance %): 2691 (3) $[\text{M} + \text{BF}_4]^+$, 2609 (1) $[\text{M}]^+$. Analysis: Calculated for $\text{C}_{112}\text{H}_{104}\text{Au}_2\text{B}_2\text{F}_8\text{N}_4\text{P}_8\text{Ru}_2\text{S}_8$: C, 48.4; H, 3.8; N, 2.0%. Found: C, 48.4; H, 3.8; N, 2.0%.

Table 1

	3·1.75(Et ₂ O)
chemical formula	C ₈₁ H _{81.5} Au ₄ F ₁₂ Fe ₂ N ₂ O _{1.75} P ₆ S ₄
Fw	2552.66
crystal system	orthorhombic
crystal color	orange block
crystal size (mm)	0.30 × 0.12 × 0.09
space group	<i>Pca</i> 2 ₁
<i>a</i> (Å)	35.0136(3)
<i>b</i> (Å)	11.0802(1)
<i>c</i> (Å)	22.1520(2)
<i>V</i> (Å ³)	8594.04(13)
<i>Z</i>	4
<i>D</i> _{calcd} (g/cm ³)	1.970
<i>T</i> (K)	150(2)
μ (Mo K α) (mm ⁻¹)	7.413
Flack <i>x</i> (8531 Friedel pairs)	−0.002(4)
<i>F</i> (000)	4902
reflections collected	60097
unique reflections (<i>R</i> _{int})	18911 (8.20%)
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	4.15%
<i>wR</i> ₂ (all data)	8.86%

Synthesis of NP1. An aqueous solution (7 mL) of HAuCl₄ (18.6 mg, 0.055 mmol) was rapidly stirred with a chloroform solution (7 mL) of the phase transfer reagent TOAB (89.9 mg, 0.164 mmol) until complete transfer of the AuCl₄[−] anion had occurred. The organic layer was collected, to which was added a chloroform solution (7 mL) of [Ru(S₂CNC₄H₈NCS₂)(dppm)₂] (152 mg, 0.137 mmol), freshly prepared in situ from [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂ (165 mg, 0.137 mmol), NEt₃ (5 drops, excess), and carbon disulfide (4 drops, excess). The orange solution was stirred at 4 °C for 10 min. An aqueous solution (15 mL) of NaBH₄ (116 mg, 3.07 mmol) was added dropwise over 10 min to the stirred solution at 4 °C, causing a color change from orange to dark brown. The solution was stirred for a further 2 h with the temperature below 10 °C. The organic layer was isolated and washed with water (3 × 5 mL) and then concentrated (~ 5 mL) under reduced pressure. Water was added to precipitate the dark brown product, and the mixture stored at −18 °C for 18 h. The supernatant liquid was decanted, and the product washed with water (5 × 10 mL), warm ethanol (3 × 10 mL), and dried.

Synthesis of NP2. HAuCl₄ (11.2 mg, 0.033 mmol) in water (35 mL) was brought to the boil with vigorous stirring. To this solution was added trisodium citrate (37.8 mg, 0.129 mmol) in water (4 mL), and boiling continued for 10 min. The heating source was removed, and the reaction stirred for a further 15 min. In a separate reaction flask, [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂ (100 mg, 0.083 mmol) was dissolved in methanol (10 mL), treated with NEt₃ (5 drops, excess), and the reaction stirred for 5 min. Carbon disulfide (4 drops, excess) was added, and the reaction stirred for 5 min. This solution was added dropwise to the previously prepared citrate stabilized nanoparticles resulting in precipitation of a fine blue solid. The reaction was stirred for a further 3 h, stored at −18 °C for 18 h, and the blue precipitate collected by filtration and washed with water (5 × 10 mL), warm ethanol (3 × 10 mL), and air-dried.

Synthesis of NP3. A colorless solution of the phase transfer agent, TOAB (419 mg, 0.766 mmol) in toluene (10 mL), was rapidly stirred with a yellow aqueous solution (10 mL) of HAuCl₄ (86 mg, 0.219 mmol) until complete transfer of [AuCl₄][−] had occurred. The organic layer was isolated. [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂ (132 mg, 0.109 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt₃ (3 drops, excess), followed by a 5 min stir, and carbon disulfide (2 drops, excess), added followed by another 5 min stir. This yellow solution was added to the organic layer together with dodecanethiol

(22 mg, 0.109 mmol). An aqueous solution (10 mL) of NaBH₄ (91 mg, 2.408 mmol) was slowly added dropwise to the stirred reaction mixture over 10 min. The burgundy solution became a dark black mixture which was left to stir for 3 h. Chloroform (100 mL) was added, and the organic (lower) layer was collected and the mixture stored at −18 °C for 12 h. The supernatant was decanted off and chloroform (20 mL) was added to remove excess thiol, and the mixture was stored for a further 12 h at −18 °C. The supernatant was decanted off, and the black solid collected by filtration, washed with dichloromethane (50 mL), water (50 mL), and methanol (50 mL) and dried.

Crystallography. Crystals of **3** were grown by slow diffusion of diethyl ether vapor onto an acetonitrile/methanol (1:1) solution of the complex. Single crystal X-ray data were collected using graphite monochromated Mo K α radiation (λ = 0.71073 Å) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N₂ open-flow cooling device,³⁶ and the data were collected at 150(2) K. Series of ω -scans and ϕ -scans were performed in such a way as to cover a sphere of data to a maximum resolution between 0.70 and 0.77 Å. Cell parameters and intensity data for **3** were processed using the DENZO-SMN package,³⁷ and the structure was solved by direct methods and refined by full-matrix least-squares on *F*² using SHELXTL software.³⁸ Intensities were corrected for absorption effects by the multiscan method based on multiple scans of identical and Laue equivalent reflections (using the SORTAV software).³⁹

Where possible non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were positioned geometrically and refined using a riding model. In the case of the disordered hexafluorophosphate anion, and the partially occupied ether solvent molecule, anisotropic refinement was not possible, so they were modeled with isotropic displacement parameters. Refinement of the Flack *x* parameter⁴⁰ gave a value of −0.002(4) (given 8531 Friedel equivalent reflections). Crystal data and structure refinement parameters are included in Table 1. Crystallographic data (excluding structure factors) for the structure of **3** has been deposited with the Cambridge Crystallographic Data Centre (CCDC 699269). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. Merton College is gratefully acknowledged for the provision of a Fellowship by J.D.E.T.W.-E. We thank the OUP John Fell Fund for consumables and Johnson Matthey Ltd for a generous loan of ruthenium trichloride and tetrachloroauric acid. We thank Dr. S. Firth (UCL) and Dr. Yi Du (Oxford) for measurement of TEM images and Dr. K. B. Holt (UCL) for electrochemical measurements.

Supporting Information Available: Crystallographic data for the structure of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC802442D

(36) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105–107.

(37) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; p 276.

(38) *SHELXTL*, version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1999.

(39) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38.

(40) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.