

A Silver(I)–Gold(II) Hexanuclear Guanidinate–Benzoate Cluster with Short Au–Au Bonds

Ahmed A. Mohamed · Hanan E. Abdou ·
Andrew Mayer · John P. Fackler Jr.

Received: 12 March 2008 / Published online: 10 September 2008
© Springer Science+Business Media, LLC 2008

Abstract Attempts to remove the halide atoms from $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, **1**, Hhpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, with Ag(I) benzoate lead to the formation of the Au(I)–Ag(I) product, $[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$, **2**. This material is stable to air and light at room temperature and shows a UV–vis spectrum in THF with absorbances at 575, 440, 345, and 273 nm. The mixed metal product crystallizes as green crystals in the monoclinic space group $P2_1/n$. The Au–Au distances of 2.4473(19) Å are the shortest gold–gold distances reported to date. The gold...silver distance is 3.344(3) Å and the silver...silver distance is 2.771(6) Å. This latter distance is short compared with the Ag...Ag distance of 2.902(3) Å in the eight-membered silver benzoate dimer starting material. The Au(II) hpp and Ag(I) benzoate components are linked by carboxylate groups and two gold–silver interactions. This result stands in structural contrast to terminal carboxylate products observed with Au(II) ylides and amidinates wherein the carboxylate is not bridging to another metal atom.

Keywords Silver–gold cluster · Gold–gold bond · Guanidinate · Benzoate · Carboxylate

Introduction

The chemistry of Au(I) with nitrogen ligands has produced rich results with amidinates, carbeniates, imidazolates, guanidates, and pyrazolates [1]. Species containing the Y-shaped CN_3 unit in ligands have attracted attention recently [2].

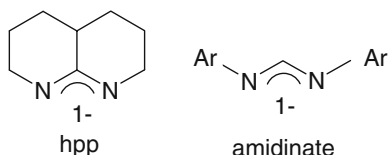
Dedicated to the memory of F. Albert Cotton (1930–2007).

A. A. Mohamed · H. E. Abdou · A. Mayer · J. P. Fackler Jr. (✉)
Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M
University, College Station, TX 77843-3255, USA
e-mail: fackler@mail.chem.tamu.edu

Neutral guanidines $[(R_2N)_2CNR]$, and the deprotonated anions, (-1) $[(RN)_2CNR_2]^-$ and $(2-)$ $[(RN)_2CNR]^{2-}$ are capable of forming a variety of coordination modes with a wide range of metal ions from all parts of the periodic Table [3]. It has long been speculated that the high basicity of guanidine (pK_a 13.6) is associated with the delocalization of the six pi electrons across the CN_3 unit [4]. The bicyclic guanidine-like ligand Hhpp, Hhpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, is an especially interesting example with its constrained N...N “bite” distance. Work with the deprotonated Hhpp ligand was pioneered by Cotton and co-workers who showed that the di-metal complexes with Cr(II), Mo(II), or W(II), ionize easily and even more readily than cesium [5].

Recent studies have shown that some gold–nitrogen complexes react with Ag(I) to form mixed metal gold–silver complexes [6]. In products formed by reacting a trinuclear Au(I) carbenate or benzylimidazolate complex with a Ag(I) salt, the Au(I) complex acts as an electron-rich base. As found in the complex, $[Ag\{[Au(\mu-N^3, C^2-bzim)]_3\}_2]BF_4 \cdot CH_2Cl_2$, a Ag(I) ion interacts with six Au(I) atoms. Organic solvent soluble mixed metal complexes with a specific Au/Ag stoichiometry form when Au(I) carbenates or benzylimidazolates react with Ag(I) 3,5-diphenylpyrazolates [7]. When the trinuclear Ag(I) 3,5-diphenylpyrazolate is reacted with a dinuclear amidinate, $[Au_2(2,6-Me_2Ph-form)_2]$, mixed metal tetranuclear clusters form [8]. Mixed-metal complexes incorporating the $[hpp]^-$ anion also have been synthesized. A titanium complex is an example of a trimetallic species, $[Me_2Al(hpp)_2TiCl_2 \cdot AlMe_3]$, containing [hpp] ligands. The [hpp] anion chelates to the titanium and bridges to an $AlMe_2$ unit via nitrogen atoms [9].

Oxidative-addition reactions of halogens to dinuclear Au(I) ylide and thiolate complexes are known to produce stable, metal-metal bonded dinuclear Au(II) complexes with terminal halide ligands [10]. Recently similar results were obtained using a sterically bulky amidinate ligand [11].



In further work exploring the reaction chemistry of group 11 amidinates materials, we studied the oxidative-addition of benzoyl peroxide to the dinuclear $Au_2(2,6-Me_2Ph-form)_2$ [11]. This reaction produced the product characterized crystallographically as $Au_2(2,6-Me_2Ph-form)_2(PhCOO)_2 \cdot 0.5C_7H_8$ [11]. The product shows the formation of stable Au(II)–O bonds similar to results found previously with the dinuclear Au(II) ylides [12]. Thus we expected that the dinuclear Au(II) guanidine derivative, $Au_2(hpp)_2Cl_2$, **1**, Hhpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, would react with $Ag(O_2CPh)$ to form the product, $Au_2(hpp)_2(PhCOO)_2$. Although halide substitution did occur, the Au(II)/Ag(I) cluster $[(PhCOO)_2Au_4(hpp)_4Ag_2(PhCOO)_4]$, **2**, was obtained instead.

While we have been unsuccessful in many attempts by direct synthesis or reduction to isolate a Au(I) product, $[\text{Au}_2(\text{hpp})_2]$, we have discovered that solvent conditions can determine whether the dinuclear Au(II) species, $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, occurs or to a tetranuclear Au(I) species, $[\text{Au}_4(\text{hpp})_4]$, results when Nahpp is reacted with a Au(I) starting material. It appears that the nuclearity of the hpp products depends upon several factors including the solvent used [1e, f].

Density Functional Theory (DFT) and MP2 calculations for $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$ find that the Highest Occupied Molecular Orbital (HOMO) is predominately hpp and chlorine-based with some Au–Au δ^* character and that the Lowest Unoccupied Molecular Orbital (LUMO) has metal-to-ligand (M–L) and metal-to-metal (M–M) σ^* character (approximately 50% hpp/chlorine, and 50% gold) [1f]. Hence the terminal ligand atoms bonded to the Au(II) influence the Au–Au and Au–hpp bonding.

Here we describe the structure of the product of the reaction of the dinuclear Au(II) guanidinate, $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, with silver benzoate. This product, $[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$, **2**, is another example of the small number of compounds containing a Au(II)–oxygen bond. This product is stable as a solid and in solution.

Synthesis

General Methods

All syntheses were performed under a nitrogen atmosphere, and all glassware was oven-dried prior to use. THF, CH_2Cl_2 , ethanol, and Hhpp were purchased from Aldrich. The solvent, THF, was dried over Na/K alloy and CH_2Cl_2 over P_2O_5 . All solvents, except ethanol, were freshly distilled under nitrogen prior to use. UV–vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer. ^1H spectra were recorded on a Unity Plus 300 NMR spectrometer using the CHCl_3 in the solvent peak to reference the chemical shifts (δ).

Synthesis of $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, **1**

The dinuclear Au(II) species, $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, was synthesized by a modification of the procedure previously published [1e, f]. 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (Hhpp) (139.0 mg, 1.0 mmol) and sodium hydroxide (40.0 mg, 1.0 mmol) were stirred in a flask with 50.0 mL THF for three days to form the sodium salt, Na[hpp]. To the flask, solid (THT)AuCl (THT = tetrahydrothiophene) (321.0 mg, 1.0 mmol) was added. The solution was stirred in air for 24 h to form a dark green solution, after filtering off the NaCl and black residues. The product, $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, formed by hexanes precipitation was filtered and dried under vacuum (200.0 mg, yield 54%). Orange crystals suitable for structural analysis were grown from a THF solution layered with hexanes. ^1H NMR (CDCl_3 , ppm): $\delta = 1.95$ (quin, CH_2), 3.40 (t, CH_2), 3.51 (t, CH_2). UV–vis (1.1×10^{-4} in THF at RT), λ_{max} (nm): ($\lambda_{\text{L/M-cm}}$) 425 (29.9×10^3), 405 (26.7×10^3), 350 (27.3×10^3).

Synthesis of $[(PhCOO)_2Au_4(hpp)_4Ag_2(PhCOO)_4]$, **2**

The dinuclear complex, $Au_2(hpp)_2Cl_2$, **1**, reacted with excess ($3\times$) silver benzoate in 1:1 THF/ CH_3CN . The mixture was stirred overnight to form a green solution, and was filtered to remove the $AgCl(s)$. Green crystals form upon slow evaporation of the solvent mixture, although the yield of product was not determined. UV–Vis (THF): λ_{max} (nm), ϵ ($L/M^{-1} cm^{-1}$): 575, 27,200; 440, 29,900; 303, 26,000; 273, 29,800.

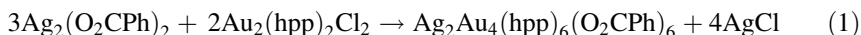
Structure Determination

Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using cryogenic grease. Omega scans of 0.3° per frame for 60 s were used such that a hemisphere was collected. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections [13]. Data reductions were performed using SAINT software [14]. The structure was solved by direct methods using SHELXS-97 and refined by least squares on F_2 , with SHELXL-97 incorporated in SHELXTL-PC V 5.03 [15, 16]. The structure was determined in the space group $P2_1/n$ by analysis of systematic absences. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model.

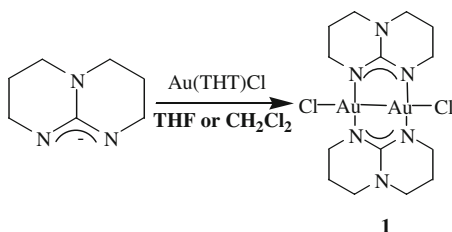
Results and Discussion

Synthesis

The reaction of the dinuclear complex $Au_2(hpp)_2Cl_2$, **1**, with silver benzoate was done in situ in a 1:1 mixture of THF/ CH_3CN . A preliminary report of the formation of **2** has been described [11]. The stoichiometry of the reaction was not determined although no other crystalline products were observed. Presumably the product is formed according to Eq. 1 of Scheme 1.



Scheme 1 Synthesis of **2**



The UV–vis spectrum of $[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$ in THF shows strong absorbances at around 575 and 440, 345, and 273 nm. The charge-transfer character of the absorbances for these deeply colored solutions also has been noted in all the oxidative-addition products of the dinuclear Au(II) amidinates (Cl, Br, I, PhCOO) [11]. This contrasts with the colors of the Au(II) ylide complexes which give pale yellow oxidative-addition products [1a]. The colors of the Au(II) amidinate complexes are dark orange to brown. Calculations have shown that the HOMO and LUMO in the ylide complexes contain considerably less ligand character [1] than with the amidinates and guanidinate products. Hence the strong charge-transfer character of the absorbances observed with the Au(II) nitrogen ligand complexes compared with the ylides is reasonable.

Crystal Structure

The mixed Au(II)–Ag(I) complex, **2**, crystallizes in the monoclinic space group $P2_1/n$ as green crystals (Table 1). The long needles show a gold–gold distance of 2.4473(19) Å, the shortest gold–gold distance reported (Table 2). The orange crystals of $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$ show a gold–gold distance of 2.4752(9) Å, slightly longer than **2** but much shorter than the distance observed in the Au(I) amidinate $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2]$ (2.712 Å) [11]. The distance is also shorter than the distance observed in the Au(II) amidinate, $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{Cl}_2]$ (2.518 Å) [11]. This dramatic decrease in the Au(II)–Au(II) distance in **2** compared with the Au(I) material is a result of the formation of two Au–Cl bonds and a single Au–Au bond along a common axis, forming a stable $d^9\text{--}d^9$ system. The presence of terminal Au–O bonding also slightly shortens the Au–Au distance, as had been observed with terminal Au–O bonding in the dinuclear Au(II) ylides [12].

Table 1 Data collection and structure refinement details for complex **2**

Formula	$\text{C}_{70}\text{H}_{72}\text{Ag}_2\text{Au}_4\text{N}_{12}\text{O}_{12}$
F_w	2277.02
T (K)	110 K
Radiation source	Mo–K α
λ (Å)	0.71073
Cryst syst	Monoclinic
Space group	$P2_1/n$
A (Å)	18.6460(4)
B (Å), β (°)	8.7000(7), 91.39(3)
C (Å)	21.530(4)
V (Å ³)	3490.4(12)
Z	2
m	11.210
Q (max) and Q (min)	1.873 and -3.024
Completeness	98.4
Collections	38617/8038
GOF	1.377
$R1$, $wR2$	0.1174, 0.1374

Table 2 Selected bond lengths [Å] and angles [°] for complex **2**

Bond distances (Å)			
Au(1)–Au(2)	2.4473(19)	Ag(1)–O(6)	2.15(3)
Au(2)–Ag(1)	3.344(3)	Ag(1)–O(5)	2.19(3)
Ag(1)–Ag(1A)	2.771(6)	Ag(1)–O(4)	2.38(2)
Au(1)–O(1)	2.09(2)	O(1)–C(15)	1.29(4)
Au(2)–O(3)	2.12(2)	C(15)–O(2)	1.21(4)
Au(1)–N(1)	2.01(3)	Au(2)–N(2)	1.99(3)
N(2)–C(1)	1.36(4)	N(1)–C(1)	1.36(4)
N(3)–C(1)	1.35(4)		
Bond angles (°)			
Au(1)–Au(2)–Ag(1)	104.25(8)	O(2)–C(15)–O(1)	125(3)
O(4)–C(22)–O(3)	125(3)	O(6A)–Ag(1)–O(5)	163.3(9)
O(5)–C(29)–O(6A)	124(4)	N(1)–C(1)–N(2)	119(3)

The molecular structures of $\text{Mo}_2(\text{hpp})_4$ and $\text{W}_2(\text{hpp})_4$ show M–M distances of 2.067(1) and 2.162(1) Å, respectively [5] and are among complexes with the shortest Mo_2^{4+} or W_2^{4+} quadruple bonds known. These materials are oxidized more easily than cesium atoms. The guanidinate ligand clearly supports electron loss from electron-rich dinuclear metal complexes. Various attempts to obtain the Au(I) product, $[\text{Au}_2(\text{hpp})_2]$, by direct synthesis or by reduction of the $[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$ by a variety of reagents including potassium/graphite to date have failed.

The $\text{Ag}\cdots\text{Ag}$ distance in **2** is 2.771(6) Å, somewhat shorter than the $\text{Ag}–\text{Ag}$ distance in the eight-membered dimer silver benzoate starting material (2.902(3) Å) [17]. A typical $\text{Ag}–\text{Ag}$ distance for silver carboxylate compounds is in the 2.80–2.90 Å range [18]. The X-ray structure of **2** shows that the silver dimer, pairs of gold dimers, and the terminal carboxylate groups form a helical stranded polymer, connected by the Au–Au bonds and the bridging carboxylate groups.

The $\text{Au}\cdots\text{Ag}$ distance in the $[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$ is ~ 3.344 Å. The Au(II) hpp and Ag(I) benzoate units are linked by carboxylate groups and gold–silver interactions. In **2** the $\text{Ag}\cdots\text{Au}$ distance is not strongly metallophilic (The sum of the covalent radii of metallic gold and silver is 2.89 Å.) and in accord with the reported values of many other $\text{Ag}–\text{Au}$ complexes. The Au(II) atoms are in a square planar arrangement with angles in the range 87.31–92.74°, typical of other Au(II) complexes. The N–Au–N angles deviate slightly from linearity, 174.86 and 175.68°.

The benzoates bonded to Au(II) in **2** adopt a similar spatial geometry (although one is bridging to Ag(I)) to that observed in the Au(II) ylide complexes [12]. The benzoate units are *anti* to each other, Fig. 1. The carbon-to-oxygen atom distances in the carbonyls are of similar bond length to the free carbonyl O atoms (av. 1.257 vs. 1.264 Å). The Au(II) atoms have nearly square planar coordination geometries with formation of bonds to a second Au center, two N atoms and one O atom. The terminal carboxylate Au(II) ylide complexes, showed the shortest Au–Au distances observed, 2.56–2.58 Å, with these ligands [12, 19, 20], Table 3. The short Au(II)–Au(II)

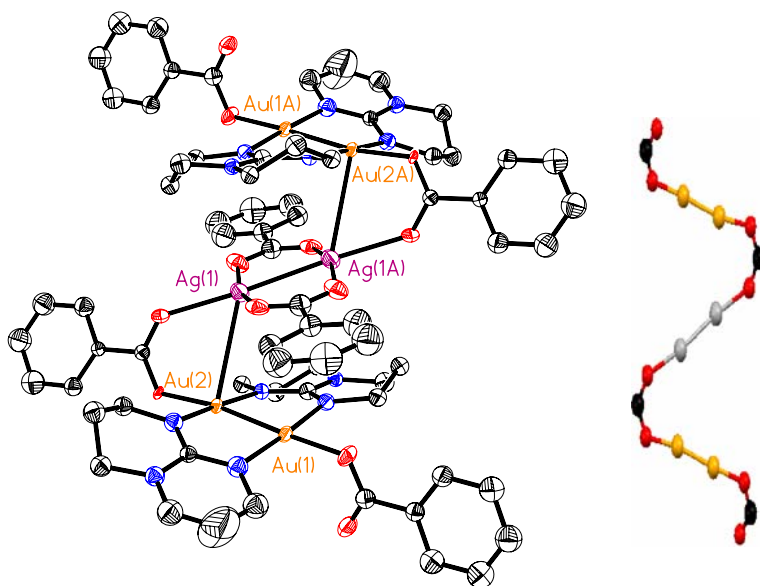


Fig. 1 Ellipsoid drawing of the structure of $[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$, **2**. The helical chain of atoms along the metal–metal axes also is shown

Table 3 Dinuclear Au(II) ylide, guanidinate, and amidinate complexes characterized by X-ray studies

Complex	$d(\text{Au}^{\text{II}}-\text{Au}^{\text{II}})$	$d(\text{Au}-\text{X})$	Ref.
$[\text{ClAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuCl}]$	2.600(1)	2.388(8)	[19]
$[\text{PhCO}_2\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuO}_2\text{CPh}]$	2.561(2)	2.117(13)	[20]
$[\text{MeCO}_2\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuO}_2\text{CMe}]$	2.592(1)	2.144(12)	[12]
$[\text{ClAu}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuCl}]$	2.517(7)	2.356(2)	[11]
$[\text{PhCO}_2\text{Au}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuO}_2\text{CPh}]$	2.489(10)	2.045(8)	[11]
$[\text{Au}_2(\text{hpp})_2\text{Cl}_2]$, 1	2.4752(9)	2.408(3)	[1e, f]
$[(\text{PhCOO})_2\text{Au}_4(\text{hpp})_4\text{Ag}_2(\text{PhCOO})_4]$, 2	2.4473(19)	2.09(2)	a

a. This work

distance in these carboxylate complexes results from the weak electron donating ability of the carboxylate ligand and hence its structural *trans* influencing ability compared with halides [10a].

Analysis of the carbon–nitrogen bond distances within the framework of compound **2** is useful, and distinguishes the C=N imine from the C–N amine bonds, which have typical bond distances of 1.28 and 1.38 Å, respectively [21]. The d_{CN} parameter, ~ 0.01 Å in compound **2**, defined as the difference in C–N bond lengths between the imino and amino bonds [$d(\text{C}-\text{N})-d(\text{C}=\text{N})$] provides a useful method for assessing the extent of delocalization in the NCN in the solid state. The NCN is fully delocalized in compound **2**, based on the very small differences observed in the guanidinate system.

Supporting Information

CCDC-670138 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment The Robert A. Welch Foundation, Houston, Texas is acknowledged for financial support.

References

- (a) J. P. Fackler, Jr. (2002). *Inorg. Chem.* **41**, 6959–6972. (b) A. Burini, A. A. Mohamed, and J. P. Fackler (2003). *Comment. Inorg. Chem.* **24**, 253–280. (c) A. A. Mohamed, H. E. Abdou, M. D. Irwin, J. M. Lopez-de-Luzuriaga, and J. P. Fackler, Jr. (2004). *J. Clus. Sci.* **14**, 253–265. (d) H. E. Abdou, A. A. Mohamed, and J. P. Fackler, Jr. (2005). *Inorg. Chem.* **44**, 166–168. (e) A. A. Mohamed, A. P. Mayer, H. E. Abdou, M. D. Irwin, L. M. Pérez, and J. P. Fackler, Jr. (2007). *Inorg. Chem.* **46**, 11165–11172. (f) M. D. Irwin, H. E. Abdou, A. A. Mohamed, and J. P. Fackler, Jr. (2003). *Chem. Commun.* **23**, 2882–2883. (g) R. G. Raptis, H. H. Murray, III, and J. P. Fackler Jr. (1987). *J. Chem. Soc., Chem. Commun.* 737–739. (h) R. G. Raptis, H. H. Murray, and J. P. Fackler, Jr. (1988). *Acta Crystallogr.* **C44**, 970–973. (i) R. G. Raptis and J. P. Fackler, Jr. (1988). *Inorg. Chem.* **27**, 4179–4182. (j) G. Yang and R. G. Raptis (2003). *Inorg. Chem.* **42**, 261–263. (k) G. Yang and R. G. Raptis (2003). *Inorg. Chimica Acta* **352**, 98–104. (l) H. E. Abdou, A. A. Mohamed, and J. P. Fackler, Jr. (2007). *Inorg. Chem.* **46**, 9692–9699.
- (a) J. Barker and M. Kilner, (1994). *Coordin. Chem. Rev.* **133**, 219–300 and references cited therein. (b) S. Patai, *The Chemistry of Amidines and Imidates*, vol. 1 (Wiley, New York, 1975).
- (a) P. J. Bailey and S. Pace (2001). *Coordin. Chem. Rev.* **214**, 91. (b) D. A. Kissounko, M. V. Zabalov, G. P. Brusova, and D. A. Lemenovskii (2006). *Russ. Chem. Rev.* **75**, 351.
- A. Gobbi and G. J. Frenking (1993). *Am. Chem. Soc.* **115**, 2362.
- (a) F. A. Cotton, N. E. Gruhn, J. Gu, P. Huang, D. L. Lichtenberger, C. A. Murillo, L. O. Van Dorn, and C. C. Wilkinson (2002). *Science* **298**, 1971–1974. (b) C. C. Wilkinson (2005). Ph.D. Thesis, Texas A&M University. (c) D. B. Soria, J. Grundy, M. P. Coles, and P. B. Hitchcock (2005). *J. Organomet. Chem.* **690**, 2278–2284. (d) F. A. Cotton, J. C. Durivage, N. E. Gruhn, D. L. Lichtenberger, C. A. Murillo, L. O. Van Dorn, and C. C. Wilkinson (2006). *J. Phys. Chem. B* **110**, 19793–19798.
- M. A. Rawashdeh-Omary, M. A. Omary, and J. P. Fackler, Jr. (2002). *Inorg. Chimica Acta* **334**, 376.
- (a) A. A. Mohamed, R. Galassi, P. Fabrizio, A. Burini, and J. P. Fackler, Jr. (2006). *Inorg. Chem.* **45**, 7770–7776. (b) A. A. Mohamed, J. P. Fackler, Jr., and A. Burini (2005). *J. Am. Chem. Soc.* **127**, 1604–1605.
- H. E. Abdou (2006). Ph.D. Thesis. Texas A&M University.
- (a) M. P. Coles and P. B. Hitchcock (2001). *J. Chem. Soc., Dalton Trans.* 1169. (b) M. P. Coles and P. B. Hitchcock (2003). *Organometallics*, **22**, 201.
- (a) J. P. Fackler, Jr. (1997). *Polyhedron* **16**, 1–17. (b) T. G. Carlson, J. P. Fackler, Jr, R. J. Staples, and R. E. Wimpenny (1995). *Inorg. Chem.* **34**, 426. (c) M. Laguna and A. Laguna, (1999). *Coordin. Chem. Rev.* **193**, 837.
- H. E. Abdou and A. A. Mohamed, and J. P. Fackler, Jr. (2007). *Inorg. Chem.* **46**, 9692–9699.
- (a) L. C. Porter and J. P. Fackler, Jr. (1986). *Acta Crystallogr.* **C42**, 1646. (b) B. Trzcinska-Bancroft, M. N. I. Khan, and J. P. Fackler, Jr. (1988). *Organometallics* **7**, 993.
- SMART V 4.043 Software for the CCD Detector System, Bruker Analytical X-ray Systems, Madison, WI, 1995.
- SAINT V 4.035 Software for the CCD Detector System, Bruker Analytical X-ray Systems, Madison, WI, 1995.

15. G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structure* (University of Göttingen, Germany, 1997).
16. SHELXTL 5.03 (PC-Version), *Program Library for Structure Solution and Molecular Graphics*, Bruker Analytical X-ray Systems, Madison, WI, 1995.
17. B. T. Usabaliev, E. M. Movsumov, I. R. Amiraslanov, A. I. Akhmedov, A. A. Musaev, and Kh. S. Mamedov (1981). *Zhur. Struk. Khim.* **22**, 98.
18. P. Pyykko, *Chem. Rev.* **97**, 597 and references cited therein.
19. (a) J. Basil, H. H. Murray, J. P. Fackler, Jr., J. Tocher, A. M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T. J. Delord, and D. O. Marler (1985). *J. Am. Chem. Soc.* **107**, 6908. (b) R. J. H. Clark, J. H. Tocher, J. P. Fackler, Jr., R. Neira, H. H. Murray, and H. Knachel, (1986). *J. Organomet. Chem.* **303**, 437. (c) H. H. Murray, J. P. Fackler, Jr., L. C. Porter, and A. M. Manzany (1986). *J. Chem. Soc. Chem. Commun.* 321.
20. (a) H. Knachel, D. S. Dudis, and J. P. Fackler, Jr. (1984). *Organometallics* **3**, 1312. (b) L. C. Porter and J. P. Fackler, Jr. (1986). *Acta Crystallogr.* **C42**, 1128.
21. M. P. Coles (2006). *Dalton Trans.* 2985.