**Diphosphine-bridged digold(I) compounds: Structural and computational studies on the
aurophilic interaction in $\text{Au}_2\text{Cl}_2(\mu\text{-bpcd})$ and $\text{Au}_2\text{Cl}_2(\mu\text{-bmi})$**

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Graphical Abstract

Highlights:

- syntheses and X-ray diffraction structures of new $\text{Au}_2\text{Cl}_2(\mu\text{-diphosphine})$ compounds
- dinuclear gold(I) compounds
- DFT calculations

Keywords: gold(I) dimers, aurophilic interaction, diphosphine, X-ray crystallography, DFT

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Abstract

The reaction of AuCl(tht) with the diphosphine donors 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) and 2,3-bis(diphenylphosphino)-N-phenylmaleimide (bmi) in a 2:1 stoichiometry affords the diphosphine-bridged digold(I) complexes Au₂Cl₂(bpcd) (**1**) and Au₂Cl₂(bmi) (**2**), respectively. **1** and **2** have been isolated and characterized in solution by IR and NMR spectroscopy (¹H and ³¹P), and the solid-state structures established by X-ray crystallography. The X-Au-Au-X (X = Cl, P) atoms in both Au₂ dimers exhibit a gauche-type (staggered) interaction based on a torsion angle of -54° for **1** (X = Cl) and -70° for **2** (X = Cl, mean angle for the two independent molecules). Each Au₂ product displays a weak aurophilic interaction based on a Au-Au internuclear distance on the order of 2.9 Å. The bonding in **1** and **2** has been investigated by electronic structure calculations and the composition of the HOMO and LUMO levels determined in the case of **2**. The potential energy surface for the interconversion of **2** to an alternative staggered conformation has been computed, and this transformation takes place through an eclipsed transition structure. The preference for a structure that contains a staggered orientation of Cl-Au-Au-Cl and P-Au-Au-Cl atoms is discussed.

1. Introduction

The current interest in the synthesis of gold(I) compounds and their use as catalyst precursors are well-documented, and the number of reports on gold-based chemistry now rivals that of many of the other transition metals.¹ Within the diverse genre of gold(I) compounds known, the subgroup containing a diphosphine scaffold that serves to tether two gold(I) centers in proximity has received much recent attention because of the structural control the ancillary diphosphine can exert on the aurophilic interaction between the gold(I) atoms.² Numerous examples of compounds of the general formula Au₂X₂(μ-PP) exist where the diphosphine functions as a bridging ligand to enhance the intramolecular metal-metal contact between the two gold(I) centers. Increased aurophilic interactions in Au₂ compounds are known to promote interesting photoluminescence chemistry, as recorded for several diphosphine-bridged Au₂ compounds that possess a rigid scaffold such as 1,2-(Z)-1,2-bis(diphenylphosphino)ethylene (dppen) or 1,2-bis(diphenylphosphino)benzene (dppbz).³ The use of chemically more interesting and architecturally sophisticated diphosphine ligands in the construction of the new Au₂ systems has been the subject of an increasing number of reports.⁴ And the recent study of Fenske and

coworkers using the redox-active diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma) and related derivatives has provided several novel $\text{Au}_2\text{X}_2(\mu\text{-PP})$ derivatives.⁵ The investigation of bma as an ancillary ligand in mononuclear organometallic compounds and its ability to function as an electron reservoir (non-innocent ligand) was pioneered by Fenske,⁶ with important subsequent studies reported by Tyler,⁷ and our group.⁸ The diphosphines 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) and 2,3-bis(diphenylphosphino)-N-phenylmaleimide (bmi) are structurally related to bma and straightforward synthetic protocols for their syntheses exist using the starting materials hexachlorocyclopentadiene and 2,3-dichloromaleic anhydride, respectively. Scheme 1 shows the structures of these particular diphosphines. While the stability and redox properties of transition-metal compounds containing an ancillary bpcd or bmi ligand parallel that of the bma analog, the former two ligands are considerably less prone to deleterious hydrolysis, a feature that plagues the stability and potentially complicates the isolation of bma-substituted derivatives.⁹

Scheme 1

In order to study the effect on the product distribution, if any, that other structurally similar diphosphines to bma have on the reaction with $\text{AuCl}(\text{tht})$, we have investigated the ligand substitution reaction using 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd)^{6a} and 2,3-bis(diphenylphosphino)-N-phenylmaleimide (bmi).¹⁰ Herein we present our spectroscopic, structural, and computational data on the dinuclear gold(I) compounds **1** and **2**.

2. Experimental

2.1. Materials and equipment

The $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ used in the preparation of $\text{AuCl}(\text{tht})$ ¹¹ was purchased from Pressure Chemical Co. or prepared from a gold ingot and aqua regia.¹² The diphosphines *bpcd* and *bmi* were prepared from the corresponding dichlorides and $\text{Ph}_2\text{PSiMe}_3$ according to published/modified procedures.^{6a,10} The tetrahydrothiophene (*tht*) and $\text{Ph}_2\text{PSiMe}_3$ reagents and all solvents were purchased from Aldrich Chemical Co.; the former two reagents were used as received. All reaction and NMR solvents were distilled from an appropriate drying agent prior to use and stored under argon in Schlenk storage vessels equipped with a high-vacuum Teflon stopcock.¹³

The FT-IR spectra were recorded in amalgamated 0.1 mm NaCl cells, while the ^1H and ^{31}P NMR spectra were recorded at 400 and 162 MHz, respectively, on a Varian VXR-400 spectrometer. The ^1H chemical shifts have been referenced to the residual protons in the NMR solvent and the ^{31}P chemical shifts referenced to external H_3PO_4 (^{31}P), taken to have $\delta = 0.0$.

2.2. Synthesis of $\text{Au}_2\text{Cl}_2(\text{bpcd})$ (**1**) and $\text{Au}_2\text{Cl}_2(\text{bmi})$ (**2**)

Since the synthetic procedure for the preparation of compounds **1** and **2** is identical, we will present the details for the synthesis of **1**. Here 0.10 g (0.31 mmol) of $\text{AuCl}(\text{tht})$ was charged to a small Schlenk flask under argon, followed by the addition of 20 mL of CH_2Cl_2 via syringe. The solution was then treated with 72 mg (0.16 mmol) of *bpcd* and the contents were stirred at room temperature for 2 hr. TLC analysis confirmed the complete consumption of the *bpcd* ligand using CH_2Cl_2 as the mobile phase. While the desired product showed mobility on the TLC plate, decomposition of the product was evident on the TLC plate, and we employed an extraction protocol for the purification of **1**. The volatiles were removed under vacuum, and the crude residue was extracted with Et_2O , after which the crude product was taken up in CH_2Cl_2 and then layered with Et_2O to promote crystallization. The vessel containing **1** and $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ was placed in the refrigerator for 2 days, after which time the crystals of **1** were isolated by filtration, washed with Et_2O , and dried under vacuum to yield 0.12 g (86%) of **1** as a yellow solid. IR (CH_2Cl_2): $\nu(\text{CO})$ 1756 (m), 1724 (vs) cm^{-1} . ^1H NMR (CDCl_3): δ 3.18 (s, CH_2), 7.40 (t, 8H, meta aryl, $J = 7.4$ Hz), 7.52 (t, 4H, para aryl, $J = 7.4$ Hz), 7.64 (m, 8H, ortho aryl). ^{31}P NMR (CDCl_3): δ 14.72 (s). Yield of **2**: 82% (0.13 g). IR (CH_2Cl_2): $\nu(\text{CO})$ 1777 (w), 1717 (vs) cm^{-1} . ^1H NMR (CDCl_3): δ 7.20-7.72 (m, 25H, aryl). ^{31}P NMR (CDCl_3): δ 14.20 (s).

2.3. X-ray Crystallographic Data

Single crystals of **1**·CH₂Cl₂ and **2**·CHCl₃ suitable for X-ray diffraction analysis were obtained by slow evaporation of the halogenated solvent containing each compound. The crystal structure determinations of both compounds were carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer, which was equipped with an Oxford low-temperature cryostat and Mo-target X-ray tube (wavelength = 0.71073 Å). The X-ray datasets were collected at 100(2) K. Data collection, indexing, and initial cell refinements were carried out using APEX2,¹⁴ with the frame integrations and final cell refinements carried out using SAINT.¹⁵ An absorption correction was applied using the program SADABS,¹⁶ and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions and were refined using a riding model. The structures were examined using the Addsym subroutine of PLATON to ensure that no additional symmetry could be applied to the finalized models.¹⁷ Both structures were solved and refined using the SHELXTL program package software.¹⁸ Refinement details and structural parameters for **1**·CH₂Cl₂ and **2**·CHCl₃ are summarized in Table 1, with selected bond distances and angles presented in Tables 2 and 3.

Place Tables 1-3 Here

2.4. Computational methodology and modeling details

The reported calculations were performed with the hybrid DFT functional B3LYP, as implemented by the Gaussian 09 program package.¹⁹ This functional utilizes the Becke three-parameter exchange functional (B3),²⁰ combined with the correlation functional of Lee, Yang, and Parr (LYP).²¹ The gold atoms were described by the Stuttgart-Dresden effective core potential (ecp) and SDD basis set,²² while the 6-31G(d') basis set was employed for the remaining atoms.²³

All reported geometries were fully optimized, and analytical second derivatives were evaluated at each stationary point to determine whether the geometry was an energy minimum (positive eigenvalues) or a transition structure (one negative eigenvalue). Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies. The resulting potential energies and enthalpies are reported in kcal/mol relative to the specified standard. Internal reaction coordinate (IRC) calculations were performed on **TSBC** in order to

establish the reactant and product species associated with the transition-state structure. The natural charges and Wiberg bond indices were computed using Weinhold's natural bond orbital (NBO) program, as executed by Gaussian 09.^{24,25} The geometry-optimized structures presented here have been drawn with the *JIMP2* molecular visualization and manipulation program.²⁶

3. Results and discussion

3.1. Synthesis, spectroscopic data, and solid-state structures

Treatment of AuCl(tht) with either bpcd or bmi in a 1:2 ratio in CH₂Cl₂ solvent at room temperature affords the dinuclear compounds Au₂Cl₂(μ-bpcd) (**1**) and Au₂Cl₂(μ-bmi) (**2**), respectively. Scheme 2 outlines these reactions. Both products were isolated by recrystallization in good yields (> 80%) as yellow solids. The color of **1** and **2** is interesting in comparison to the red color reported for Au₂Cl₂(μ-bma).⁵ The IR and NMR spectroscopic data recorded for **1** and **2** are consistent with their formulated structures. The vibrationally coupled ν(CO) bands at 1756 and 1724 cm⁻¹ in **1** are readily assigned to the antisymmetric and symmetric carbonyl stretches.²⁷ The ν(CO) bands in **2** appear at 1777 and 1717 (vs) cm⁻¹ and nature of these coupled oscillators is the same as that in **1**. Normal mode analysis of the DFT optimized structures of **1** and **2** confirmed the vibrational assignments. The ¹H NMR spectrum of **1** revealed four resonances at δ 3.18, 7.40, 7.52, and 7.64 in a 1:4:2:4 integral ratio, with the highest field resonance unequivocally assigned the CH₂ moiety associated with the 4-cyclopentadien-1,3-one ring. The aryl hydrogens appear as a closely spaced set of three resonances whose assignments were confirmed by ¹H COSY and ¹H-³¹P NOESY experiments. The ¹H NMR spectrum of **2** is only slightly more complicated due to the presence of the additional maleimide aryl group, and the aryl hydrogens appear as an overlapping series of multiplets from δ 7.20-7.72. Finally, a sharp ³¹P singlet was recorded in the ³¹P NMR spectrum of **1** (δ 14.72) and **2** (δ 14.20).

Scheme 2

The identity of compounds **1** and **2** was next established by X-ray crystallography. The molecular structure of **1**·CH₂Cl₂, which is depicted in Figure 1, confirms the dinuclear composition of the product where each AuCl unit is bound to an individual phosphine moiety. The Au(1)-Au(2) bond distance of 2.9156(4) Å is smaller than the sum of the van der Waals radii,²⁸ and whose magnitude supports the existence of a weak, intramolecular aurophilic interaction between the two gold centers as a result of relativistic-induced gold-gold contacts.^{29,30} The formal oxidation state of each gold atom is +1, and the coordination geometry about each Au(I) center is nearly linearly with angles of 173.72(6) ° and 172.69(6)° found for the P(1)-Au(1)-Cl(1) and P(2)-Au(2)-Cl(2) linkages, respectively. The mean Au-P bond distance of 2.232 Å is similar to those Au-P distances in the diphosphine-bridged compounds Au₂Cl₂(μ-bma),⁵ Au₂I₂(μ-dppen),³¹ and Au₂Cl₂(μ-dppbz).³² The torsion angles for the P(1)-Au(1)-Au(2)-P(2) and Cl(1)-Au(1)-Au(2)-Cl(2) linkages deviate from planarity and are ca. 49° and -54°, respectively. The orientation of these groups about the Au(1)-Au(2) vector is not unlike the staggered (gauche) arrangement of adjacent substituents in the chair conformation of cyclohexane rings, as depicted below in the side-on Newman-type projection looking down the Au-Au bond in **1**.

(phenyl groups and dione ring omitted for clarity)

Place Figure 1 Here

DFT calculations were performed on **1** to verify the ground-state structure (gas phase) relative to the crystallographic structure. The geometry-optimized structure of **A** is shown

alongside **1** in Figure 1. Good agreement between the structures is observed, especially with respect to the torsional disposition of the phosphine and chloride groups about the Au-Au vector. Examination of the selected natural charges (red) and Wiberg bond indices (WBIs, blue) computed for species **A** (Scheme 3) supports the description of **A** having a weak Au-Au bond. A WBI of 0.15 is computed for the Au-Au bond while a mean WBI of 0.59 (Au-P) and 0.68 (Au-Cl) was found for the pairwise equivalent Au-P and Au-Cl bonds. The charges on the Au, Cl, and P centers (averaged) are 0.19, -0.50, and 1.04 and are consistent with the nature of these groups.

Scheme 3

The basic framework of **2** is similar to that of compound **1**. The X-ray diffraction structure of **2**·CHCl₃ consists of two independent molecules in the asymmetric unit that are not significantly different in nature, and Figure 2 shows one of these molecules. One of these molecules occupies a special position in the unit cell and has a slightly different geometry around Au-Au bond (the torsion angles P-Au-Au-P in both molecules are 70.3° and 65.3°, respectively). The bmi ligand coordinates a single AuCl fragment at each of its phosphine groups, and this tethering of the gold centers by the rigid diphosphine promotes the attractive gold-gold interaction extant in **2**. The Au(1)-Au(1A) bond distance of 2.9810(5) Å is comparable to the Au-Au bond distance in **1**. The Au-P and Au-Cl bond distances and P-Au-Cl bond angles in **2** are unremarkable relative to **1** and require no comment. The disposition of the phosphine and chloride ligands about the Au(1)-Au(1A) bond in **2** exhibits a staggered-type array with torsion angles of ca. -70° (Cl-Au-Au-Cl) and -63° (P-Au-Au-P).

Place Figure 2 Here

The DFT-optimized structure of species **B** (Figure 2) reproduces the important structural features found in the solid-state structure. The charges computed for the Au, P, and Cl atoms and

the WBIs for the Au-Au, Au-P, and Au-Cl bonds parallel those data reported for species **A** (Scheme 3). We also examined the nature of the HOMO and LUMO in **B** to gain insight into the important frontier orbitals; Scheme 4 shows these orbitals. The HOMO may be described as an antibonding Au-Au bond that contains significant contributions from the ancillary chlorides. The overlap in each Au-Cl bond is also strongly antibonding in character. The staggered orientation of the chloride ligands in **2** helps to minimize unfavorable intramolecular antibonding interactions between the halides (*vide infra*). The LUMO in **B** is localized exclusively on the heterocyclic ring and displays the commonly found π^* nodal pattern associated with Ψ_4 of a six-pi electron system.³³

Scheme 4

3.2. DFT modeling of alternative conformations for **B**

The stability of **B** relative to other possible conformations was next explored. Here a series of step-scan calculations were performed as a function of the torsional angle of the direct substituents attached to the gold atoms. Allowing the ancillary chlorides to approach each other affords an eclipsed conformation that was subsequently confirmed as a transition state (**TSBC**) that connects the staggered structures **B** and **C**. Figure 3 illustrates the course of this reaction and shows **TSBC** to lie 15.0 kcal/mol above **B**. The imaginary eigenvalue associated with the transition-state structure consists of a low-energy torsional vibration involving the Cl-Au-Au-Cl atoms. This motion is conceptualized in the lower portion of Figure 3, where the “scissoring” of phosphine and chloride groups give rise to **TSBC**. Species **C**, which is 1.2 kcal/mol less stable than **B**, was established as the product by an IRC calculation. The main difference between **B** and **C** concerns the twist angles of the aryl groups on the two PPh_2 moieties.

Place Figure 3 Here

Finally, the attractive interaction between the gold atoms in **B** is underscored by an examination of the “anti” conformation that was obtained from a step-scan calculation. The Cl-Au-Au-Cl torsional angle was increased incrementally to 180°, ultimately affording species **D** (below) as a stable minimum that is 1.4 kcal/mol less stable than **B**. Noteworthy features of **D** include an intranuclear Au···Au distance that is more than 6.7 Å in length and a Cl-Au···Au-Cl torsional angle of 141°. The expanded distance between the gold centers in **D** is accompanied by an 85% decrease in the WBI for the Au-Au compared to **B**.

4. Conclusions

The synthesis of the new digold(I) compounds $\text{Au}_2\text{Cl}_2(\mu\text{-bpdc})$ and $\text{Au}_2\text{Cl}_2(\mu\text{-bmi})$ have been prepared and characterized by spectroscopic methods and X-ray crystallography. The presence of a weak Au-Au bond in each product has been established by DFT calculations and the orbital composition of the HOMO and LUMO in $\text{Au}_2\text{Cl}_2(\mu\text{-bmi})$ determined. The staggered disposition observed for the ancillary phosphine and chloride ligands at the adjacent gold centers is thermodynamically favored over the corresponding eclipsed conformation that functions as the transition-state structure between the different staggered conformations. Currently, we are examining the redox and photophysical properties of other diphosphine-bridged digold compounds, the results of which will be reported in due course.

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Appendix A. Supplementary Data

CCDC 1487256 and 1487254 contain the supplementary crystallographic data for compounds **1**·CH₂Cl₂ and **2**·CHCl₃, respectively; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A complete listing of the atomic coordinates of the optimized structures reported here is available from MGR upon request.

Table 1. X-ray crystallographic data and processing parameters for **1**·CH₂Cl₂ and **2**·CHCl₃

Compd	1 ·CH ₂ Cl ₂	2 ·CHCl ₃
CCDC entry no.	1487256	1487254
cryst system	monoclinic	monoclinic
Space group	P21/n	C2/c
a, Å	13.634(1)	34.907(2)
b, Å	16.817(1)	14.203(1)
c, Å	13.708(1)	26.598(1)
β, deg	102.330(1)	128.565(1)
V, Å ³	3070.5(4)	10310.7(9)
mol formula	C ₃₀ H ₂₄ Au ₂ Cl ₄ O ₂ P ₂	C ₁₀₄ H ₇₇ Au ₆ Cl ₁₂ N ₃ O ₆ P ₆
fw	1014.17	3257.71
formula units per cell (Z)	4	4
D _{calcd} (Mg/m ³)	2.194	2.099
λ (Mo Kα), Å	0.71073	0.71073
μ (mm ⁻¹)	10.025	8.965
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
abs corr factor	0.5281/0.2853	0.7101/0.3504
Total reflections	36161	58265
Independent reflections	6733	10151
Data/res/parameters	6733/0/362	10151/0/620
R1 ^a [I ≥ 2σ(I)]	0.0308	0.0343
wR2 ^b (all data)	0.1299	0.1210
GOF on F ²	1.039	1.068
Δρ(max), Δρ(min) (e/Å ³)	1.913,-2.913	2.104,-3.322
^a R1 = Σ F _o - F _c /Σ F _o ; ^b R2 = {Σ[w(F _o ² - F _c ²) ²]/Σ[w(F _o ²) ²]} ^{1/2}		

Table 2. Selected X-ray diffraction and DFT bond distances (Å) and angles (deg) in **1** and **A**.

Bond distances	X-ray	DFT
Au(1)-Au(2)	2.9156(4)	3.1602
Au(1)-P(1)	2.231(2)	2.306
Au(2)-P(2)	2.233(2)	2.307
Au(1)-Cl(1)	2.289(2)	2.328
Au(2)-Cl(2)	2.302(2)	2.335
P(1)-C(1)	1.812(6)	1.854
P(2)-C(5)	1.823(6)	1.865
C(1)-C(5)	1.370(8)	1.369
Bond angles		
P(1)-Au(1)-Cl(1)	173.72(6)	170.76
P(2)-Au(2)-Cl(2)	172.69(6)	171.75
P(1)-Au(1)-Au(2)	83.37(4)	80.12
P(2)-Au(2)-Au(1)	100.46(4)	92.27
Cl(1)-Au(1)-Au(2)	101.55(4)	105.83
Cl(2)-Au(2)-Au(1)	86.85(4)	95.97
C(1)-P(1)-Au(1)	106.7(2)	103.1
C(5)-P(2)-Au(2)	117.2(2)	117.7
C(1)-C(5)-P(2)	129.7(4)	129.9
C(5)-C(1)-P(1)	125.3(5)	128.7

Table 3. Selected X-ray diffraction and DFT bond distances (Å) and angles (deg) in **2** (for one of the independent molecules) and **B**.

Bond distances	X-ray	DFT
Au(1)-Au(1A)	2.9810(5)	3.2061
Au(1)-P(1)	2.230(2)	2.299
Au(1)-Cl(1)	2.293(2)	2.331
P(1)-C(2A)	1.825(7)	1.856
C(2A)-C(2AA)	1.343(13)	1.355
Bond angles		
P(1)-Au(1)-Cl(1)	173.93(6)	173.13
P(1)-Au(1)-Au(1A)	85.93(4)	84.58
Cl(1)-Au(1)-Au(1A)	99.66(4)	102.24
C(2A)-P(1)-Au(1)	113.3(2)	113.6
C(2AA)-C(2A)-P(1)	130.1(1)	131.5

Figure 1. Thermal ellipsoid plot of the molecular structure of **1** at the 50% probability level (left) and the optimized B3LYP structure of **A** (right).

Figure 3. (top) DFT-optimized structures and free energy surface energy for the interconversion between the staggered structures **B** and **C** via **TSBC**. The quoted energies are in kcal/mol relative to species **B**. (bottom) Newman-type projections looking down the Au-Au vector that depict the “scissoring” motion of the phosphine and chloride ligands.

References

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- ¹ (a) C.M. Friend, A.S.K. Hashmi, *Acc. Chem. Res.* 47 (2014) 729. (b) M.F. Espada, J. Campos, J. López-Serrano, M.L. Poveda, E. Carmona, *Angew. Chem. Int. Ed.* 54 (2015) 15379. (c) T.J. Brown, M. Dickens, R.A. Widenhoefer, *J. Am. Chem. Soc.* 131 (2009) 6350. (d) S. Handa, L.M. Slaughter, *Angew. Chem. Int. Ed.* 51 (2012) 2912.
- ² (a) H. Schmidbaur, *Chem. Soc. Rev.* 24 (1995) 11. (b) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* 41 (2012) 370.
- ³ For example, see: (a) S. Bhargava, K. Kitadai, T. Masahi, D.W. Drumm, S.P. Russo, V.W.-W. Yam, T.K.-M. Lee, J. Wagler, N. Mirzadeh, *Dalton Trans.* 41 (2012) 4789. (b) J.B. Foley, A. Herring, B. Li, E.V. Dikarev, *Inorg. Chim. Acta* 392 (2012) 300.
- ⁴ (a) D.V. Partyka, T.S. Teets, M. Zeller, J.B. Updegraff, III, A.D. Hunter, T.G. Gray, *Chem. Eur. J.* 18 (2012) 2100. (b) C. Sarcher, A. Lühl, F.C. Falk, S. Lebedkin, M. Kühn, C. Wang, J. Paradies, M.M. Kappes, W. Kloppe, P.W. Roesky, *Eur. J. Inorg. Chem.* (2012) 5033.
- ⁵ W. Yu, O. Fuhr, D. Fenske, *J. Clust. Sci.* 23 (2012) 753.
- ⁶ (a) D. Fenske, H.J. Becher, *Chem. Ber.* 107 (1974) 117; 108 (1975) 2115. (b) D. Fenske, *Chem. Ber.* 112 (1979) 363.
- ⁷ (a) F. Mao, D.R. Tyler, M.R.M. Bruce, A.E. Bruce, A.L. Rieger, P.H. Rieger, *J. Am. Chem. Soc.* 114 (1992) 6418. (b) D.M. Schut, K.J. Keana, D.R. Tyler, P.H. Rieger, *J. Am. Chem. Soc.* 117 (1995) 8939. (c) F. Mao, C.E. Philbin, T.J.R. Weakley, D.R. Tyler, *Organometallics* 9 (1990) 1510.
- ⁸ (a) K. Yang, J.M. Smith, S.G. Bott, M.G. Richmond, *Organometallics* 12 (1993) 4779. (b) S.G. Bott, K. Yang, J.C. Wang, M.G. Richmond, *Inorg. Chem.* 39 (2000) 6051. (c) S.G. Bott, K. Yang, M.G. Richmond, *J. Organomet. Chem.* 690 (2005) 3067; 691 (2006) 3771.
- ⁹ K. Yang, J.A. Martin, S.G. Bott, M.G. Richmond, *Organometallics* 15 (1996) 2227.
- ¹⁰ W.H. Watson, B. Poola, M.G. Richmond, *J. Organomet. Chem.* 691 (2006) 4676.
- ¹¹ R. Uson, A. Laguna, M. Laguna, *Inorg. Synth.* 26 (1989) 86.
- ¹² *Handbook of Preparative Inorganic Chemistry*, G. Brauer, Ed., Vol 1, 2nd edition, Academic Press, London, pp. 1052-1053, 1963.
- ¹³ D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969.
- ¹⁴ Bruker APEX2, Bruker Advanced Analytical X-ray Systems, Inc. Copyright 2007, Madison, WI.
- ¹⁵ Bruker Saint; Bruker Advanced Analytical X-ray Systems, Inc. Copyright 2007, Madison, WI.

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- ¹⁶ Bruker SADABS; Bruker Advanced Analytical X-ray Systems, Inc. Copyright 2007, Madison, WI.
- ¹⁷ A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, Utrecht University, 456 Utrecht, The Netherlands, 2006.
- ¹⁸ SHELXTL Version 6.14, Bruker Advanced Analytical X-ray Systems, Inc. Copyright 2003, Madison, WI.
- ¹⁹ M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
- ²⁰ A.D. Becke, *J. Chem. Phys.* **98** (1993) 5648.
- ²¹ C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* **37** (1988) 785.
- ²² (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. (b) Walch, S. P.; Bauschlicher, C. W. *J. Chem. Phys.* **1983**, *78*, 4597-4605.
- ²³ (a) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193-2218. (b) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081-6090.
- ²⁴ Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
- ²⁵ Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.
- ²⁶ (a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall, R.F. Fenske, *Inorg. Chem.* **11** (1972) 768. (b) J. Manson, C.E. Webster, M.B. Hall, Texas A&M University, College Station, TX, 2006: <http://www.chem.tamu.edu/jimp2/index.html>.
- ²⁷ N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1990.
- ²⁸ A. Bondi, *J. Phys. Chem.* **68** (1964) 441.

²⁹ (a) P. Pyykkö, *Chem. Rev.* 97 (1997) 597. (b) X.-G. Xiong, P. Pyykkö, *Chem. Commun.* 49 (2013) 2103.

³⁰ For a recent compilation of Au-Au bond distances in digold compounds, see: C. Ganesamoorthy, M.S. Balakrishna, J.T. Mague, H.M. Tuononen, *Inorg. Chem.* 47 (2008) 2764.

³¹ S. Bhargava, K. Kitadai, T. Masashi, D.W. Drumm, S.P. Russo, V.W.-W. Yam, T.K.-M. Lee, J. Wagler, N. Mirzadeh, *Dalton Trans.* 41 (2012) 4789.

³² N. Yoshinari, N. Kitani, T. Tsukuda, T. Konno, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 67 (2011) m121.

³³ For reports on the orbital properties of related diphosphines, see: (a) K. Yang, S.G. Bott, M.G. Richmond, *Organometallics* 14 (1995) 2387. (b) N.W. Duffy, R.R. Nelson, M.G. Richmond, A.L. Rieger, P.H. Rieger, B.H. Robinson, D.R. Tyler, J.C. Wang, K. Yang, *Inorg. Chem.* 37 (1998) 4849.