

Gold Is Smaller than Silver. Crystal Structures of [Bis(trimesitylphosphine)gold(I)] and [Bis(trimesitylphosphine)silver(I)] Tetrafluoroborate

Angela Bayler,[†] Annette Schier,[‡]
Graham A. Bowmaker,[‡] and Hubert Schmidbaur^{*,†}

Anorganisch-chemisches Institut der
Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching, Germany
Department of Chemistry
The University of Auckland, Private Bag 92109
Auckland, New Zealand

Received April 25, 1996

Although it may have gone largely unnoticed, there is considerable confusion in handbooks of physical data as well as in chemistry textbooks and periodic tables concerning the relative sizes of silver and gold atoms. Values quoted for the ionic or covalent radii for the most common oxidation state +1 are either approximately equal for the two metals or larger for gold than for silver.^{1–4} The Pauling covalent radii for the two metals are essentially equal, which is due to the fact that the “metallic radius” in the close-packed cubic lattices happens to be virtually the same [the lattice constants are 4.0862 (Ag) and 4.07825 Å (Au),⁵ and the nearest-neighbor interatomic distances are 2.889 (Ag–Ag) and 2.884 Å (Au–Au) for coordination number 12].⁶

On the other hand, recent theoretical calculations including relativistic and correlation effects consistently predict that gold should be significantly smaller than silver, a phenomenon which is generally referred to as the “relativistic contraction”.^{7–9} In more qualitative terms, the concept of the “Lanthanide contraction”,^{7,8} employed successfully for other radius discontinuities in the periodic table, also points in the same direction.¹⁰ It appears, however, that no attempt has been made to settle this simple question by an experiment which can give unambiguous results.

The most straightforward approach to this problem would be a comparison of metal-to-ligand bond lengths in a set of complexes involving (a) the same ligands and counterions, (b) the same coordination number and geometry, (c) an isomorphous crystal lattice, and (d) equal experimental conditions. More often than not these conditions are not fulfilled, since Ag(I) and Au(I) cations form compounds which differ significantly in their basic structure,^{11,12} such that a direct comparison is not meaningful.

Table 1. Crystal Data for [(Mes₃P)₂M]BF₄ with M = Ag, Au (Both at –68 °C)

formula	[Mes ₃ P-Au-PMes ₃] ⁺ BF ₄ [–]	[Mes ₃ P-Ag-PMes ₃] ⁺ BF ₄ [–]
crystal system	trigonal	trigonal
space group	P3 ₁ 21	P3 ₁ 21
Z	3	3
a, b, Å	15.942(1)	15.900(2)
c, Å	18.206(2)	18.269(2)
V, Å ³	4006.7(4)	3999.9(9)

We have now discovered that the pair of title compounds meets all criteria on which to base the desired direct comparison, and from accurate single-crystal work we find that gold(I) is indeed much smaller than silver(I), by almost 0.1 Å.¹²

The two reference complexes are readily prepared from AgBF₄ and two equiv of Mes₃P in dichloromethane (95% yield, mp 193 °C) or from equimolar quantities of (Mes₃P)AuCl, Mes₃P, and AgBF₄ in CH₂Cl₂ (98% yield, mp 232 °C), respectively. The products can be obtained as large, transparent, isomorphous crystals (trigonal, space group P3₁21, Z = 3), which are stable to air, moisture, and light at ambient temperature.¹³ Their analytical and spectroscopic data are in full agreement with the proposed compositions.¹⁴

Selected crystal data for [(Mes₃P)₂M]BF₄ presented in Table 1 show the close crystallographic resemblance of the two unit cells, which suggest a very similar crystal field environment for the individual components. Both compounds are ionic in the crystal with no significant sub-van der Waals contacts between the ions. The cations have a crystallographically imposed 2-fold axis passing through the metal atom perpendicular to the P–M–P axis and relating the two phosphine ligand propellers, which thus have the same directionality (left- or right-handed propellers).¹⁴ The metal atoms are essentially linearly two-coordinate with bond angles which deviate from perfect collinearity by less than 0.3°. Selected distances and angles are compared in Table 2.

The structure of the cation of the gold complex is shown in Figure 1, and Figure 2 offers a superposition of the structures of the gold and silver complexes. It is obvious from this diagram that there is almost perfect agreement of all details except for the M–P distance, which is smaller for M = Au than for M = Ag by 0.09(1) Å. Assuming a covalent radius of

(13) **Crystal Structure Determination.** The samples were mounted in glass capillaries on an Enraf-Nonius CAD4 diffractometer and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Graphite-monochromated Mo Kα radiation was used. Both structures were solved by Patterson methods and refined by full matrix least-squares calculations on F². **Crystal Data for C₅₄H₆₆P₂AuBF₄.** M_r = 1060.85, colorless crystals of dimensions 0.25 × 0.30 × 0.50 mm, trigonal, a, b = 15.942(1) Å, c = 18.206(2) Å, space group P3₁21, Z = 3, V = 4006.7(4) Å³, ρ_{calc} = 1.319 g cm^{–3}, F(000) = 1620; T = –68 °C. Data were corrected for Lorentz, polarization, and absorption effects [μ(Mo Kα) = 28.47 cm^{–1}]. 11 882 measured [(sin θ/λ)_{max} = 0.62 Å^{–1}] reflections, 5682 independent reflections; 295 refined parameters, wR2 = 0.0764, R = 0.0288 for 5645 reflections with F_o ≥ 4σ(F_o). Residual electron densities: +1.68/–0.76 eÅ^{–3}. Absolute structure parameter: –0.019(7). **Crystal Data for C₅₄H₆₆P₂AgBF₄.** M_r = 971.69, colorless crystals of dimensions 0.35 × 0.35 × 0.45 mm, trigonal, a, b = 15.900(2) Å, c = 18.269(2) Å, space group P3₁21, Z = 3, V = 3999.8(9) Å³, ρ_{calc} = 1.210 g cm^{–3}, F(000) = 1524; T = –68 °C. Data were corrected for Lorentz and polarization but not for absorption effects [μ(Mo Kα) = 4.84 cm^{–1}]. 5815 measured [(sin θ/λ)_{max} = 0.62 Å^{–1}] reflections, 2914 independent reflections; 295 refined parameters, wR2 = 0.0835, R = 0.0320 for 2895 reflections with F_o ≥ 4σ(F_o). Residual electron densities: +0.66/–0.31 eÅ^{–3}. Absolute structure parameter: –0.07(3). All hydrogen atoms in both structures were calculated and allowed to ride on their corresponding C atoms with fixed isotropic contributions [U_{iso(fix)} = 0.08 Å²]; all non-H atoms were refined with anisotropic displacement parameters. The BF₄ counterions were disordered on a 2-fold axis. Refinement of both structures in the enantiomorphic space group P3₂21 led to significantly worse R and GOF values and to absolute structure parameters of 1.0.

(14) Bayler, A.; Bowmaker, G. A.; Schmidbaur, H. *Inorg. Chem.*, in press.

[†] Technische Universität München.

[‡] The University of Auckland.

(1) Emsley, J. *The Elements*, 2nd ed.; Clarendon: Oxford, 1991.

(2) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; p 1368.

(3) Huheey, J.; Keiter, E.; Keiter, R. *Inorganic Chemistry*; Harper Collins College: New York, 1993.

(4) (a) *VCH Periodic Table of the Elements*; VCH: Weinheim, 1980.

(b) *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: New York, 1995–96. Based on: Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

(5) Wyckhoff, R. G. *Crystal Structures*, 2nd ed.; Interscience Publishers: New York, 1958; Vol. 1, p 10.

(6) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1980; p 403.

(7) Pyykkö, P. *Chem. Rev.* **1988**, 88, 563.

(8) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, 91, 1762.

(9) Schwerdtfeger, P.; Boyd, P. D. W.; Burrell, A. K.; Robinson, W. T.; Taylor, M. J. *Inorg. Chem.* **1990**, 29, 3593.

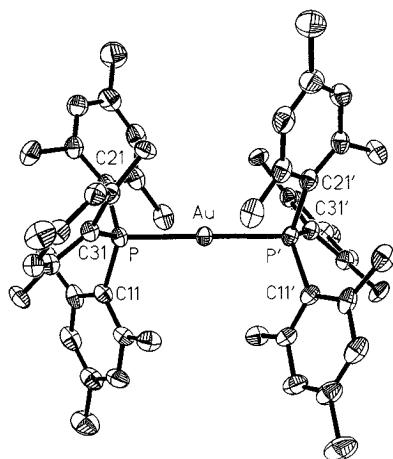
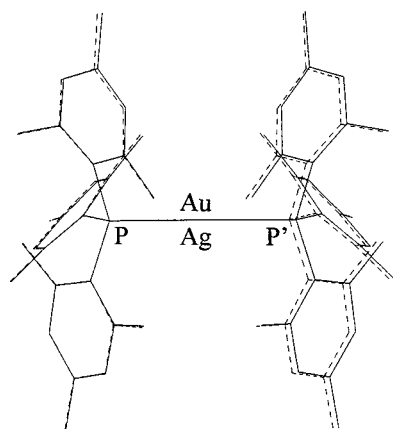
(10) Liao, M. S.; Schwarz, W. H. E. *Acta Crystallogr.* **1994**, B50, 9.

(11) Lancashire, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 5, p 775.

(12) (a) Puddephatt, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 5, p 861. (b) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Title Compounds

parameter	M = Ag	M = Au
M–P	2.4409(9)	2.3525(10)
P–C11	1.827(4)	1.820(5)
P–C21	1.829(4)	1.829(5)
P–C31	1.833(4)	1.834(4)
P–Au–P'	179.80(6)	179.72(7)
Au–P–C11	107.22(13)	107.5(2)
Au–P–C21	105.74(12)	105.85(13)
Au–P–C31	107.50(12)	107.82(13)
C11–P–C21	113.8(2)	113.3(2)
C21–P–C31	111.6(2)	111.5(2)
C31–P–C11	111.6(2)	111.5(2)

**Figure 1.** Molecular structure of the cation of $[(\text{Mes}_3\text{P})_2\text{Au}]\text{BF}_4$ (ORTEP, 50% probability ellipsoids) with atomic numbering. The cation has a crystallographic 2-fold axis passing through the Au atom.**Figure 2.** Superposition of the structures of the cations of $[(\text{Mes}_3\text{P})_2\text{M}]\text{BF}_4$ with $M = \text{Ag}, \text{Au}$, drawn with coinciding phosphorus positions in the left part of the molecules.

tetracoordinate phosphorus as $r(\text{P})_{\text{cov}} = 1.11 \text{ \AA}$,¹⁵ the covalent radii of two-coordinate Ag and Au are estimated as 1.33 and 1.25 Å, respectively, a reduction in radius of as much as 6% from Ag to Au.

Possible sources of error to be considered are steric interactions of the two bulky Mes_3P ligands. Inspection of Figure 1

(15) Corbridge, D. E. C. *Phosphorus. An Outline of its Chemistry, Biochemistry, and Technology*; Elsevier: Amsterdam, 1978; pp 440–442.

and Table 2 reveals that the two ligands are in a strain-free staggered conformation with deviations in their geometrical parameters within the limits of experimental error. The positions of the BF_4 anions relative to the cations are also virtually unchanged for $M = \text{Ag}$ and Au . Thus the internal and external force fields in the lattice exerting influences on the P–M–P units should be comparable.

It should be noted that Ag/Au– PR_3 distances are found to be smaller in most other complexes of these metals than in the title compounds, depending on the size and electronic structure of the substituents R.^{16,17}

However, for small ligands there is generally also a growing interference of the “third party” in the coordination sphere of the metals (the counterions becoming ligands), such that the structural characteristics become fundamentally different; e.g., $[(\text{Ph}_3\text{P})_2\text{AuCl}]$ features trigonal planar tricoordinate gold centers, while the corresponding silver complex is dimeric, with tetra-coordinate silver.^{18,19}

Unfortunately, crystals of $[(\text{Mes}_3\text{P})_2\text{Cu}]\text{BF}_4$ obtained from various solvents are *not* isomorphous with the Ag and Au analogues and were always found to contain solvent. Notwithstanding, the structure (of a CH_2Cl_2 solvate) was also solved and gave an average Cu–P distance of 2.242(2) Å, placing copper even smaller than gold with a radius of 1.13 Å. These data refer to a different crystal environment and are therefore not considered any further in this account, except to remark that the shorter Cu–P distance supports the claim made above that steric effects between the two Mes_3P ligands in the silver and gold complexes are not important in determining the M–P bond lengths.

The results presented here are in full agreement with data obtained from theoretical calculations for the coinage metals, which predict an increase of the atomic radii on going from copper to silver, but a decrease on continuing from silver to gold.^{7–10} Strictly speaking, the values are only valid for the +1 oxidation state, but it is likely that gold should now be taken as smaller than silver in most of its chemistry. For two-coordinate M(I) compounds, radii of 1.13 (Cu), 1.33 (Ag), and 1.25 (Au) Å could be tabulated.

Acknowledgment. This work was supported by DFG, FCI, and the Alexander von Humboldt Foundation (G.A.B.) and—through the donation of chemicals—by Degussa AG and Heraeus GmbH. The authors are grateful to Mr. J. Riede for determining the X-ray data sets.

Supporting Information Available: Tables of crystal data, bond lengths, atomic coordinates, and thermal parameters for both compounds (16 pages). See any current masthead page for ordering and Internet access instructions. The same material has also been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen and is available on request on quoting CSD 405279/405280.

JA961363V

(16) Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steigelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656. Baker, L.-J.; Bott, R. C.; Bowmaker, G. A.; Healy, P. C.; Skelton, B. W.; Schwerdtfeger, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 1341.

(17) Berners-Price, S. J.; Colquhoun, L. A.; Healy, P. C.; Byriel, K. A.; Hanna, J. V. *J. Chem. Soc., Dalton Trans.* **1992**, 3357.

(18) Bowmaker, G. A.; Dyason, J. C.; Healy, L. A.; Engelhardt, L. M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1089.

(19) Bowmaker, G. A.; Effendy; Hanna, J. H.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1387. Cassel, A. *Acta Crystallogr., Sect. B* **1979**, *35*, 174.