

Water-soluble and Water-stable Gold(I), Gold(II) and Gold(III) Phosphine Complexes: the Early Years

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Abstract

This article briefly reviews the still rather limited knowledge of the chemistry, structures, reactions and applications of gold complexes containing water-soluble phosphine ligands sorted by gold oxidation state.

Introduction

Classical inorganic chemistry began with the use of water, both as solvent and as ligand for many coordination compounds. As this discipline of chemistry advanced, new ligands, complexes and reactions were discovered that required completely anhydrous reaction conditions as well as special apparatus and techniques to keep water out of reactions [1]. Today, the tide is turning and water is experiencing a renaissance as a solvent in inorganic and organometallic chemistry. This change is motivated largely by the advent of green chemistry (the development and design of environmentally benign chemical processes and reactions) and by the realization that nature herself has synthesized extremely complex and diverse molecules in water for millions of years! Furthermore, the ever increasing awareness of environmental concerns in the design of industrially important processes has been the driving force in the exploration of water-based reactions and water-soluble catalysis [2-9]. As a result, a key challenge for the chemistry community is the design and development of new complexes that are both soluble and stable in water. One important strategy for solubilising inorganic and organometallic compounds in water is by the use of water soluble phosphine ligands such as the sulfonated arylphosphines (abbreviated TPPMS, TPPDS, TPPTS), 1,3,5-triaza-7-phosphaadamantane (TPA)[10] or 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA)[11] as shown in Figure 1. The enormous industrial potential of aqueous catalysis using water-soluble and water-stable transition metal complexes is exemplified by the use of the rhodium complex $[\text{Rh}(\text{CO})(\text{TPPTS})_3]$ in the Ruhrchemie/Rhône-Poulenc hydroformylation process carried out on a scale of > 600,000 t/p. a. [5]. This article will review the current state of knowledge of water soluble gold phosphine complexes sorted according to the gold oxidation state.

Gold(I)

The photoluminescence properties and structures of a variety of gold complexes containing TPA and its *N*-alkylated derivatives as well as TPPTS have been studied in some detail by the group of Fackler Jr. in Texas. The gold(I) TPA complexes $[\text{AuX}(\text{TPA})]$ (X = Cl, Br, I, Me) were prepared and, in some cases, structurally characterized [12]. The complexes $[\text{AuX}(\text{TPA})]\cdot\text{CH}_3\text{CN}$ (X = Cl, Br) form dimers with short Au...Au contacts in the solid state, in contrast, unsolvated $[\text{AuCl}(\text{TPA})]$ is a chain polymer in the solid-state [13]. The coordinated TPA ligand can be protonated by acid to give the water-soluble derivative $[\text{AuCl}(\text{TPA-HCl})]$, which also forms dimers in the solid state. The photophysics of these complexes in aqueous solution and solid-state have been studied [14,15]. Various derivatives including some thiolato and aryl complexes were also synthesized and structurally characterized [16,17] but no information as to their solubility in water was provided.

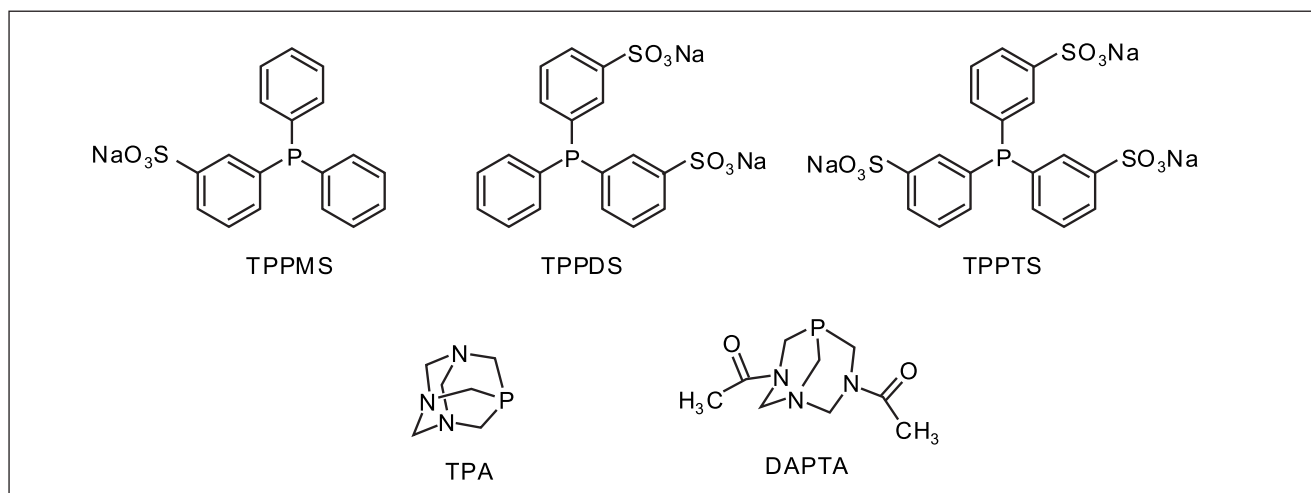


Figure 1

Interest has also focused on the luminescence properties of three- and four-coordinate gold(I) complexes including $[\text{Au}(\text{TPA-Et})_3]_4$, $[\text{AuCl}(\text{TPA})_2]$, $[\text{Au}(\text{TPA})_3]^+$, $[\text{Au}(\text{TPA})_4]^+$ and $[\text{Au}(\text{TPA-Me})_4]^+$ [18-20]. The luminescent, water-soluble, three-coordinate gold complex $\text{Cs}_8[\text{Au}(\text{TPPTS})_3]$ has been characterized by X-ray diffraction, and represents the only example of a gold complex containing TPPTS that has been structurally characterized.

The tetranuclear gold(I) complex $[\text{Au}_2\{\mu\text{-S}_2\text{C}_2(\text{CN})_2\}]_2\{\text{Au}(\text{TPA})_3\}_2$ (Fig. 2), obtained by the reaction of $\text{K}_2[\text{S}_2\text{C}_2(\text{CN})_2]$ with $[\text{Au}(\text{TPA})_3]\text{Cl}$, represents a rare example of a non-linear chain of gold(I) atoms. The separation between the two gold atoms in the central, dimeric unit is 2.799(1) Å, while the Au...Au contacts between the two $\text{Au}(\text{TPA})_3$ units and the $[\text{Au}_2\{\mu\text{-S}_2\text{C}_2(\text{CN})_2\}]_2$ dimer are ca. 3.11 Å [21].

Our group has prepared an extensive collection of alkynyl and thiolato complexes of gold(I) containing TPPMS, TPPDS, TPPTS, TPA and DAPTA as shown in Schemes 1 and 2. Some of these complexes are highly water soluble (up to 125 g/L) and, furthermore, the organometallic alkynyl gold(I) complexes are also stable in water for a period of at least one week [22-25]. The gold(I) TPPTS complexes containing $^1\text{BuC}\equiv\text{CH}$ and 3-ethenylthiophene are highly efficient catalysts for the hydration of phenylacetylene in water, giving the highest ever reported turnover frequencies for this reaction. Furthermore, the process can be carried out using water as the solvent, which allows the catalyst to be recycled [24]. The cytotoxicity of TPA and DAPTA

gold(I) complexes containing various thiol derivatives has been evaluated against a panel of seven human cancer cell lines. It was found that some complexes display similar cytotoxicity to *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ “cisplatin” against renal and colon cancer cell lines [25]. The same thiolatogold(I) complexes have also been patented for the decoration of ceramics [26].

The Burrows group has studied the assembly of hydrogen bonded networks of guanidinium sulfonate derivatives and have reported the X-ray crystal structure of $[\text{C}(\text{NH}_2)_3][\text{AuCl}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{SO}_3)\}]$, the only structurally characterized gold complex containing TPPMS [27].

Gold(II)

The +2 oxidation state is very rare in mononuclear complexes but quite common in binuclear compounds containing a formal gold-gold bond [28,29]. To date, the only known water-soluble gold(II) species are those derived from halide methathesis of the bis(ylide) dimer $[\text{Au}_2\text{Cl}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$ with the silver(I) salts $[\text{Ag}(\text{OTf})\text{P}]$ (P = TPPMS, TPPDS, TPPTS, TPA, DAPTA) as shown in Scheme 3 [30].

The TPA derivative has been characterized crystallographically and the Au-Au bond length was determined to be 2.6275(4) Å [30]. Remarkably, these gold(II) complexes are not only soluble but also stable in water for up to one week before deposition of a gold mirror is observed. In many other cases, water-insoluble binuclear gold(II) complexes undergo various isomerization or C-C coupling reactions in solution [31-33].

Gold(III)

There are only very few examples of gold(III) compounds containing water-soluble phosphine ligands. The dimethylgold(III) derivatives *cis*- $[\text{Au}(\text{Me})_2\text{P}]$ and *cis*- $[\text{Au}(\text{Me}_2)\text{P}_2]\text{I}$ [P = TPPMS, TPPTS, and $\text{P}(\text{CH}_2\text{OH})_3$] have been prepared by the group of Komiya [34]. Although these complexes are soluble in water, they undergo reductive

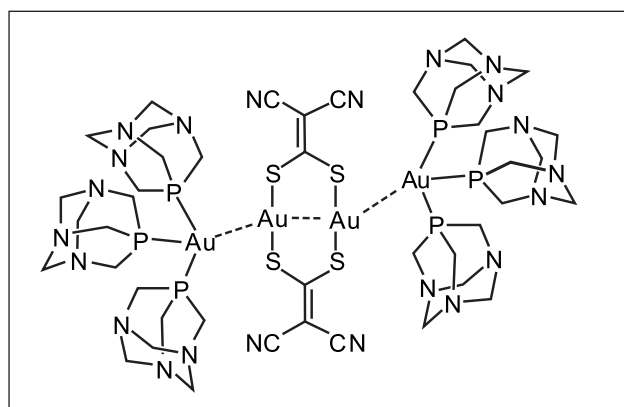
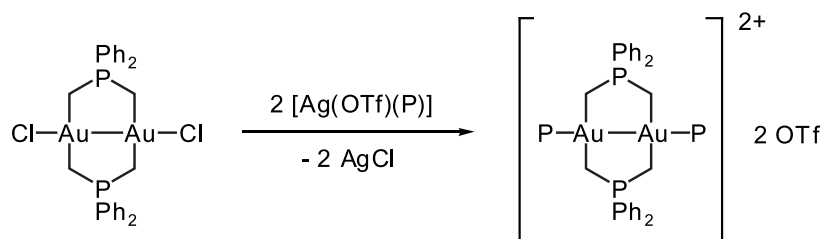


Figure 2



P = TPPMS, TPPDS, TPPTS, TPA, DAPTA

Scheme 3

- 3 F. Joó and A. Kathó, *J. Mol. Cat. A*, 1997, **116**, 3
- 4 B. Cornils, W.A. Herrmann and R.W. Eckl, *J. Mol. Cat. A*, 1997, **116**, 27
- 5 B. Cornils, *Org. Process Res. Dev.*, 1998, **2**, 121
- 6 F. Joó, *Aqueous organometallic catalysis*, 2001, Kluwer Academic Publishers, Dordrecht
- 7 N. Pinault and D.W. Bruce, *Coord. Chem. Rev.*, 2003, **241**, 1
- 8 B. Cornils and W.A. Herrmann, *Aqueous-phase organometallic catalysis*, 2004, Wiley-VCH, Weinheim
- 9 B. Cornils, W.A. Herrmann, I.T. Horvath, W. Leitner, S. Mecking, H. Olivier-Bourbigou and D. Vogt, *Multiphase Homogeneous Catalysis*, 2005, Wiley-VCH, Weinheim
- 10 D.J. Daigle, A.B. Pepperman Jr. and S.L. Vail, *J. Heterocyclic Chem.*, 1974, **11**, 407
- 11 D.J. Darensbourg, C.G. Ortiz and J.W. Kamplain, *Organometallics*, 2004, **23**, 1747
- 12 Z. Assefa, B.G. McBurnett, R.J. Staples, J.P. Fackler, Jr., B. Assmann, K. Angermaier and H. Schmidbauer, *Inorg. Chem.*, 1995, **34**, 75
- 13 Z. Assefa, M.A. Omary, B.G. McBurnett, A.A. Mohamed, H.H. Patterson, R.J. Staples and J.P. Fackler, Jr., *Inorg. Chem.*, 2002, **41**, 6274
- 14 Z. Assefa, B.G. McBurnett, R.J. Staples and J.P. Fackler, Jr., *Inorg. Chem.*, 1995, **34**, 4965
- 15 J. Forward, Z. Assefa and J.P. Fackler Jr., *J. Am. Chem. Soc.*, 1995, **117**, 9103
- 16 J.M. Forward, D. Bohmann, J.P. Fackler, Jr. and R.J. Staples, *Inorg. Chem.*, 1995, **34**, 6330
- 17 J.M. Forward, J.P. Fackler, Jr. and R.J. Staples, *Organometallics*, 1995, **14**, 4194
- 18 J. Forward, R.J. Staples, C.W. Liu and J.P. Fackler Jr., *Acta Cryst.*, 1997, **C53**, 195
- 19 J.M. Forward, Z. Assefa, R.J. Staples and J.P. Fackler, Jr., *Inorg. Chem.*, 1996, **35**, 16
- 20 Z. Assefa, J.M. Forward, T.A. Grant, R.J. Staples, B.E. Hanson, A.A. Mohamed and J.P. Fackler, Jr., *Inorg. Chim. Acta*, 2003, **352**, 31
- 21 J.P. Fackler, Jr., R.J. Staples and Z. Assefa, *J. Chem. Soc., Chem. Commun.*, 1994, 431
- 22 F. Mohr, E. Cerrada and M. Laguna, *Organometallics*, 2006, **25**, 644
- 23 F. Mohr, E. Vergara, E. Cerrada, E.R.T. Tiekink and M. Laguna, *Eur. J. Inorg. Chem.*, to be published
- 24 S. Sanz, L.A. Jones, F. Mohr and M. Laguna, *Organometallics*, **in press**
- 25 F. Mohr, S. Miranda, A. Mendia, E. Vergara, E. Cerrada and M. Laguna, *Inorg. Chem.*, submitted
- 26 M. Laguna, F. Mohr, E. Vergara and E. Cerrada, Spanish patent assigned to ICMA, 2004
- 27 A.D. Burrows, R.W. Harrington, M.F. Mahon and S.J. Teat, *Eur. J. Inorg. Chem.*, 2003, 1433
- 28 A. Laguna and M. Laguna, *Coord. Chem. Rev.*, 1999, **193-195**, 837
- 29 M. Laguna and E. Cerrada, in *Metal Clusters in Chemistry*, Vol. I (Eds.: P. Braunstein, L.A. Oro, P.R. Raithby), Wiley-VCH, Weinheim, **1999**, p. 459 and references therein
- 30 F. Mohr, S. Sanz, E.R.T. Tiekink and M. Laguna, *Organometallics*, 2006, **25**, 3084
- 31 M.A. Bennett, S.K. Bhargava, K.D. Griffiths and G.B. Robertson, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 260
- 32 J.P. Fackler, Jr. and B. Trzcinska-Bancroft, *Organometallics*, 1985, **4**, 1891
- 33 S.K. Bhargava, F. Mohr, M.A. Bennett, L.L. Welling and A.C. Willis, *Organometallics*, 2000, **19**, 5628
- 34 N. Komine, K. Ichikawa, A. Mori, M. Hirano and S. Komiya, *Chem. Lett.*, 2005, **34**, 1704
- 35 S. Komiya, JP2004035498, assigned to Koei Chemical Co. Ltd. Japan, 2004