Water-Soluble and Water-Stable Organometallic Gold(II) Complexes

Fabian Mohr,[†] Sergio Sanz,[†] Edward R. T. Tiekink,[‡] and Mariano Laguna*[,†]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, and Department of Chemistry,
University of Texas at San Antonio, San Antonio, Texas 78249-0698

Received March 17, 2006

The dicationic digold(II) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(P)_2](OTf)_2$, where P are the water-soluble phosphine ligands 1,3,5-triaza-7-phosphaadamantane (TPA), 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA), and mono-, di-, and trisulfonated triphenylphosphines (TPPMS, TPPDS, TPPTS), were prepared by a metathesis reaction from $[Au_2Cl_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with the silver(I) salts [Ag(OTf)(P)]. The complexes where fully characterized by spectroscopic methods and, in the case of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPA)_2](OTf)_2$, by X-ray diffraction. The complexes containing sulfonated triphenylphosphine ligands are very water soluble (up to 75 g/L) and also are stable in water. The catalytic activity of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPPDS)_2](OTf)_2$ in the addition of MeOH to phenyl acetylene in an aqueous medium was tested; however the complex was found to be a poor catalyst for this reaction under these conditions.

Introduction

Classical coordination chemistry began by using water both as solvent and as ligand for many 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 so as to keep water *out* of reactions.[1] Today, the tide has turned and water is experiencing a renaissance as a solvent in inorganic and organometallic chemistry. This change, motivated largely by the ever-increasing awareness of environmental concerns in the design of industrially important chemical processes has been the main driving force in the exploration of water-based reactions and water-soluble catalysts.[2−4] However, the vast majority of homogeneous catalysts available today are either insoluble or unstable in water; as a result, one key challenge for the inorganic/organometallic chemistry community today is the design and development of compounds that are both soluble and stable in aqueous medium. Our group has studied the addition of methanol to terminal alkynes catalyzed by various water-insoluble gold(I) and gold(III) complexes in aqueous medium,[5] and more recently, we reported the first examples of water-soluble and water-stable organometallic gold(I) and gold(III) compounds.[6] As a logical extension to this work, we were interested in trying to obtain water-soluble gold(II) derivatives and to study their catalytic activity in the addition of methanol to terminal alkynes.

The chemistry of binuclear gold(II) complexes containing gold−gold bonds has been studied in some detail by various groups over the last 40 years with significant contributions originating from the laboratories of Schmidbaur, Fackler, Jr., and Bennett[7] and also from our group.[8,9]

One commonly used strategy to impart water-solubility to a given metal complex involves the use of ligands possessing solubilizing groups or use of water-soluble ligands. Typical examples of such ligands are those selected for this study: TPA, DAPTA, TPPMS, TPPDS, and TPPTS.[10] All five phosphines are soluble in water and have previously been used as ligands in various metal complexes including some examples of gold(I) and gold(III).[11]

Results and Discussion

Treatment of the digold(II) bis(ylide) complex $[Au_2Cl_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with the silver(I) phosphine compounds

---

* To whom correspondence should be addressed. E-mail: mlaguna@unizar.es.

[†] Universidad de Zaragoza-CSIC.

[‡] University of Texas at San Antonio.

(1) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

(2) Cornils, B. *Org. Process Res. Dev.* **1998**, *2*, 121−127.

(3) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis Concepts and Applications*; Wiley-VCH: Weinheim, 1998.

(4) Joó, F. *Aqueous Organometallic Catalysis*; Kluwer Academic Publishers: Dordrecht, 2001.

(5) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925−11935.

(6) Mohr, F.; Cerrada, E.; Laguna, M. *Organometallics* **2006**, *25*, 644−648.

(7) See for example: (a) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Organogold chemistry. In *Gold Progress in Chemistry, Biochemistry and Technology*, Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; pp 647−746. (b) Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 1−17. (c) Mohr, F.; Privér, S. H.; Bhargava, S. K.; Bennett, M. A. *Coord. Chem. Rev.*, in press.

(8) Laguna, A.; Laguna, M. *Coord. Chem. Rev.* **1999**, *193−195*, 837−856.

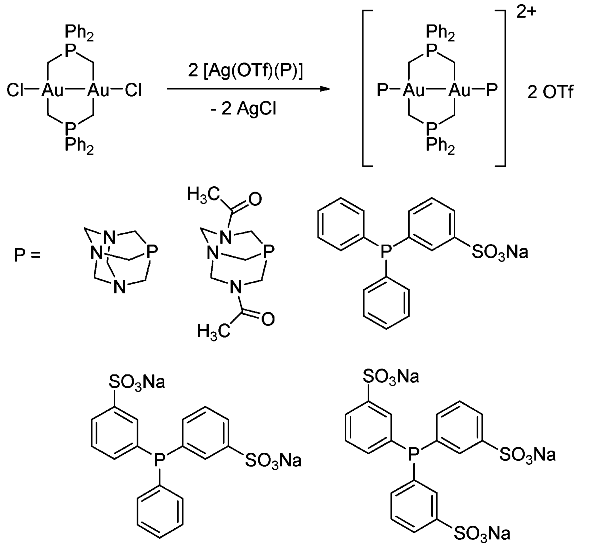
(9) Méndez, L. A.; Jiménez, J.; Cerrada, E.; Mohr, F.; Laguna, M. *J. Am. Chem. Soc.* **2005**, *127*, 852−853.

(10) Abbreviations: TPA, 1,3,5-triaza-7-phosphaadamantane; DAPTA, 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; TPPMS, monosulfonated triphenylphosphine; TPPDS, disulfonated triphenylphosphine; TPPTS, trisulfonated triphenylphosphine. All the sulfonates used here were used as their sodium salts.

(11) See for example: (a) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955−993. (b) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177−186. (c) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1−25. (d) Katti, K. V.; Hariprasad, G.; Smith, C. J.; Berning, D. E. *Acc. Chem. Res.* **1999**, *32*, 9−17, and references therein. (e) Assefa, Z.; Forward, J. M.; Grant, T. A.; Staples, R. J.; Hanson, B. E.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2003**, *352*, 31.

10.1021/om0602456 CCC: $33.50

Scheme 1



$[Ag(OTf)(P)]$ (P = TPA, DAPTA, TPPMS, TPPDS, TPPTS), prepared from AgOTf and the phosphines, affords the orange or yellow, dicationic gold(II) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(P)_2](OTf)_2$ in high yields (Scheme 1).

The structures of the complexes were deduced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and, in the case of the TPA derivative, X-ray diffraction. The ^1H NMR spectra display one doublet resonance due to the ylide methylene groups, signals due to the bis(ylide) phenyl groups, and signals of the coordinated P ligands, consistent with a symmetric structure. The $^{31}P\{^1H\}$ NMR spectra consist of two triplet resonances ($^3J_{PP} \approx 33$ Hz) due to coupling between the phosphorus atoms of the ylide and the coordinated P ligands, respectively. In case of the DAPTA complex, the P resonance due to the DAPTA phosphorus atoms appears as two overlapping triplets due to the presence of a mixture of *syn* and *anti* conformations of the acyl groups in the DAPTA unit.[12] The solid-state structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPA)_2](OTf)_2$, isolated as a tetra-acetone solvate, is shown in Figure 1; selected bond lengths and angles are collected in Table 1. The complex consists of two gold atoms with an Au−Au bond length of 2.6275(4) Å, which are bridged by two bis(ylide) units, forming a twisted eight-membered ring.

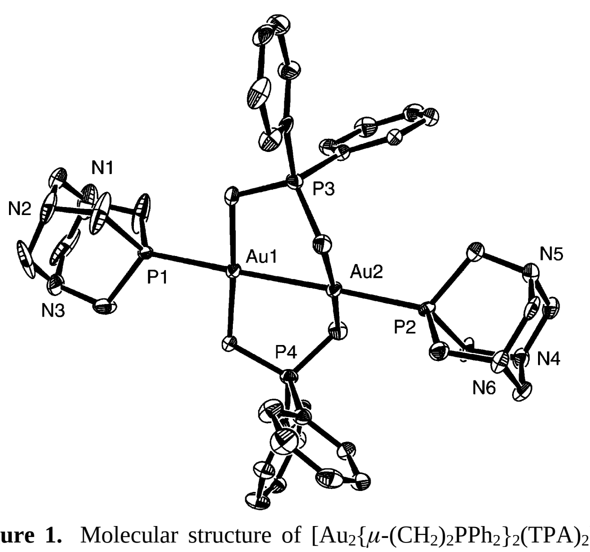


Figure 1. Molecular structure of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPA)_2](OTf)_2$. Acetone molecules of solvation, OTf anions, and hydrogen atoms have been omitted for clarity. Ellipsoids show 50% probability levels.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPA)_2](OTf)_2$

Au(1)−Au(2)	2.6275(4)	Au(1)−P(3)	2.3678(18)
Au(2)−P(4)	2.4019(19)	Au(1)−C(1)	2.120(8)
Au(1)−C(3)	2.137(9)	Au(2)−C(2)	2.146(9)
Au(2)−C(4)	2.119(8)	Au(2)−Au(1)−P(3)	178.18(5)
Au(2)−Au(1)−C(1)	91.0(2)	Au(2)−Au(1)−C3	92.3(2)
Au(1)−Au(2)−P(4)	177.26(5)	Au(1)−Au(2)−C(2)	87.8(2)
Au(1)−Au(2)−C(4)	87.4(2)	P(3)−Au(1)−C(1)	89.3(2)
P(4)−Au(2)−C(2)	93.5(2)	P(4)−Au(2)−C(4)	91.3(2)
P(4)−Au(2)−C(4)	91.3(2)	C(2)−Au(2)−C(4)	175.2(3)
P(3)−Au(1)−C(3)	87.5(2)	C(1)−Au(1)−C(3)	176.0(3)

Furthermore, two TPA ligands coordinate to the gold centers through the P atom linearly along the Au−Au axis. The overall coordination about the gold(II) atoms is square planar. The Au−Au bond is slightly longer than that of the starting dichloro complex [2.600(1) Å][13] and also longer than that observed in the PPh_3 analogue $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(PPh_3)_2](ClO_4)_2$ [2.579(3) Å].[14] In general, the gold−gold bond length observed here is longer than most reported Au−Au bond distances for binuclear bis(ylide) complexes; only the CF_3, CN, and C_6F_5 derivatives have longer metal−metal bonds of ca. 2.6 Å.[15] The Au−P distances of 2.3678(18) and 2.4019(19) Å are longer than those in $[Au(TPA)_2][Au(CN)_2]$ [2.302(5) Å][16] and but similar to those in $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(PPh_3)_2](ClO_4)_2$ [2.365(6) and 2.384(6) Å].[14]

Our aim of producing water-soluble and water-stable gold(II) complexes was indeed realized. Of the five compounds reported here, the DAPTA, TPPMS, TPPDS, and TPPTS derivatives are all soluble and stable in water. Solubility in water ranges from ca. 4 g/L for the DAPTA and TPPMS complexes to ca. 75 g/L for the TPPTS complex! Aqueous solutions of the compounds remain unchanged for at least 7 days with no sign of decomposition. This last result is particularly significant and perhaps surprising, given that other known digold(II) complexes undergo various isomerization processes in nonaqueous media or polar solvents, as shown in Figure 2.

For example, the digold(II)dichloro precursor used in this work, $[Au_2Cl_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$, isomerizes to a mixed-valence Au(I)/Au(III) complex in polar solvents such as nitromethane and acetone.[17] Similarly, binuclear gold(II) compounds containing *ortho*-metalated phosphine ligands undergo isomerization reactions resulting in the formation of a new C−C bond.[18] If there are Me substituents on the cyclometalated phosphine *ortho* to the gold centers, the digold(II) complexes are stable in solution only below −20 °C; upon warming, isomerization to Au(I)/Au(III) complexes occurs.[19]

To test the catalytic activity of these gold(II) complexes, we examined the addition of MeOH to phenyl acetylene in the presence of 10 mol % H_2SO_4 and 1 mol % of $[Au_2\{\mu\text{-}(CH_2)_2\text{-}$

---

(12) Darensbourg, D. J.; Ortiz, C. G.; Kamplain, J. W. *Organometallics* **2004**, *23*, 1747−1754.

(13) Murray, H. H.; Fackler, J. P., Jr.; Porter, L. C.; Mazany, A. M. *J. Chem. Soc., Chem. Commun.* **1986**, 321−322.

(14) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1361−1365.

(15) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Gold, Progress in Chemistry, Biochemistry and Technology. In *Gold, Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; p 747, and references therein.

(16) Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 6274−6280.

(17) Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics* **1985**, *4*, 1891−1893.

(18) Bennett, M. A.; Bhargava, S. K.; Hockless, D. C. R.; Welling, L. L.; Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 10469−10478.

(19) Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. *Organometallics* **2000**, *19*, 5628−5636.

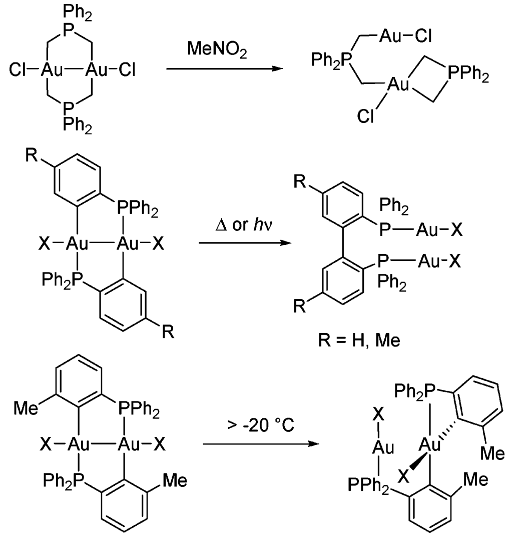


Figure 2. Isomerization reactions of various gold(II) complexes.

PPh$_2$}$_2$(TPPDS)$_2$](OTf)$_2$ in an aqueous medium as described in ref 5. After 30 min reflux only a 1% conversion to acetophenone was observed, which increased to 46% after 5 h of reflux. In comparison, the gold(I) alkynyl complex [Au(C≡C^{t}Bu)-(TPPDS)] gives a quantitative yield of acetophenone in 30 min under the same conditions.[20] This catalytic inactivity may also be ascribed to the rather high stability of the binuclear gold(II) bis(ylide) system. We, and others, have shown that in order for a gold species to be catalytically active in this reaction, a cationic [PAu]$^+$ unit needs to be generated.[5,21] In case of gold alkynyl or gold alkyl complexes such a species is easily formed by acid cleavage of the gold−carbon σ-bond. However, our results of the bis(ylide) system here suggest that acid cleavage of the gold dimer is very slow under these conditions, thus explaining the poor catalytic activity in this reaction. It is unfortunate that the advantage gained by an increase in availability of the gold species in solution (due to its greater solubility in the aqueous reaction medium) is offset by the poor catalytic activity due to the high stability of the system. Clearly what is needed are gold species that are soluble in an aqueous medium but at the same time are labile enough that the necessary "activation" process to begin the catalytic cycle is still possible. Further work to design such a complex is currently ongoing.

In summary we have show that by judicious choice of ligands, even normally unstable organometallic species in labile oxidation states can be solubilized and stabilized in water. The general implications of these findings are that it can indeed be possible to do chemistry with metal complexes in any attainable oxidation state in water just as easily as in nonaqueous solvents. We hope to illustrate here that by using water as solvent there are no stability-imposed limitations to the type of complexes and metal oxidation states that can be studied. It is hoped that these findings will inspire further work in this field of aqueous organometallic chemistry.

Experimental Section

General Procedures. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer. Chemical shifts are quoted relative to external TMS (^{1}H) and 85% H_3PO_4 (^{31}P); coupling constants are reported in Hz. FAB mass spectra were measured on a VG Autospec spectrometer in positive ion mode using NBA as matrix. TPA,[22] DAPTA,[12] TPPMS,[23] TPPDS,[24] and [Au_2Cl_2{μ-$(CH_2)_2PPh_2$}][25] were prepared by published procedures. A sample of TPPTS was kindly provided by European Oxo GmbH. The silver(I) phosphine complexes were prepared by the reaction of equimolar amounts of [AgOTf] with the respective phosphines in MeOH. The catalytic experiments were carried out as described in ref 5.

Preparation of [$Au_2(P)_2${μ-$(CH_2)_2PPh_2$}](OTf)$_2$ Complexes. To a solution of [Au_2Cl_2{μ-$(CH_2)_2PPh_2$}] (0.050 g, 0.056 mmol) in MeOH (10 mL) was added the silver(I) phosphine complexes (0.056 mmol). After stirring for ca. 18 h the mixture was filtered through Celite and the orange solution was concentrated in a vacuum. Addition of Et_2O precipitated the complexes, which were isolated by filtration and dried in a vacuum.

[Au_2{μ-$(CH_2)_2PPh_2$}$_2$(TPA)$_2$](OTf)$_2$: orange solid, 84% yield; ^{1}H NMR ($CDCl_3$) δ 1.88 (dt, $J = 12.2$, 4.4 Hz, 8 H, CH_2), 4.10 (s, 12 H, NCH_2P), 4.40 (s, 12 H, NCH_2N), 7.55−7.83 (m, 20 H, PPh$_2$); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −47.52 (t, $J = 37.2$ Hz, TPA-*P*), 45.08 (t, $J = 37.2$ Hz, Ph$_2$P); FAB-MS 1134 [M]$^+$, 977 [M − TPA]$^+$, 820 [M − 2 TPA]$^+$. Anal. Calcd for $C_{42}H_{52}N_6O_6P_4S_2Au_2F_6$ (1432.9): C 35.21, H 3.66, N 5.87. Found: C 35.27, H 3.44, N 5.55. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into an acetone solution of the compound.

[Au_2{μ-$(CH_2)_2PPh_2$}$_2$(DAPTA)$_2$](OTf)$_2$: orange solid, 85% yield; ^{1}H NMR ($CDCl_3$) δ 1.92−2.20 (m, 20 H, Me, CH_2), 3.51 (d, $J = 12.1$ Hz, 2 H, DAPTA), 3.67 (d, $J = 12.1$ Hz, 2 H, DAPTA), 3.79−4.00 (m, 6 H, DAPTA), 4.33 (br s, 2 H, DAPTA), 4.54 (d, $J = 14.4$ Hz, 2 H, DAPTA), 4.84 (d, $J = 13.4$ Hz, 2 H, DAPTA), 5.34 (d, $J = 14.7$ Hz, 2 H, DAPTA), 5.67 (d, $J = 13.4$ Hz, 2 H, DAPTA6), 7.55−7.86 (m, 20 H, PPh$_2$); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −31.26 (t, $J = 35.2$ Hz, DAPTA-*P*), −31.12 (t, $J = 35.2$ Hz, DAPTA-*P*), 45.86 (t, $J = 35.4$ Hz, Ph$_2$P); FAB-MS 820 [M − 2 DAPTA]$^+$. Anal. Calcd for $C_{48}H_{60}N_6O_{10}P_4S_2Au_2F_6$ (1576.9): C 36.56, H 3.83, N 5.33. Found: C 36.64, H 3.53, N 5.19.

[Au_2{μ-$(CH_2)_2PPh_2$}$_2$(TPPMS)$_2$](OTf)$_2$: yellow solid, 84% yield; ^{1}H NMR (CD_3OD) δ 1.72 (d, $J = 11.8$ Hz, 8 H, CH_2), 7.14−7.62 (m, 44 H, PPh$_2$, TPPMS), 8.07 (d, $J = 7.8$ Hz, 2 H, *o*-$C_6H_4SO_3Na$), 8.15 (t, $J = 5.8$ Hz, 2 H, *p*-$C_6H_4SO_3Na$); ^{31}P{^{1}H} NMR (CD_3OD) δ 28.81 (t, $J = 33.5$ Hz, TPPMS-*P*), 45.78 (t, $J = 33.5$ Hz, Ph$_2$P); FAB-MS 1534 [M − 2 Na]$^+$, 1161 [M − Na − TPPMS]$^+$, 820 [M − 2 TPPMS]$^+$.

[Au_2{μ-$(CH_2)_2PPh_2$}$_2$(TPPDS)$_2$](OTf)$_2$: orange solid, 81% yield; ^{1}H NMR (D_2O) δ 1.60 (br s, 8 H, CH_2), 6.92−7.96 (m, 46 H, PPh$_2$, TPPDS); ^{31}P{^{1}H} NMR (D_2O) δ 28.29 (t, $J = 31.6$ Hz, TPPDS-*P*), 44.23 (t, $J = 31.6$ Hz, Ph$_2$P); FAB-MS 1707 [M − 2 Na]$^+$, 1263 [M − Na − TPPDS]$^+$, 820 [M − 2 TPPDS]$^+$.

[Au_2{μ-$(CH_2)_2PPh_2$}$_2$(TPPTS)$_2$](OTf)$_2$: yellow solid, 90% yield; ^{1}H NMR (D_2O) δ 1.70 (d, $J = 11.6$ Hz, 8 H, CH_2), 7.15−7.89 (m, 44 H, PPh$_2$, TPPTS); ^{31}P{^{1}H} NMR (D_2O) δ 28.24 (t, $J = 33.5$ Hz, TPPTS-*P*), 44.19 (t, $J = 33.5$ Hz, Ph$_2$P); FAB-MS 1903 [M − Ph + Na]$^+$, 1811 [M − 3 Na − Ph]$^+$, 820 [M − 2 TPPTS]$^+$.

Samples of the sulfonated triphenylphosphine derivatives consistently gave bad elemental analyses perhaps due to incomplete combustion or absorption of moisture.

X-ray Crystallography. A yellow needle was mounted in oil on a glass fiber, and data were collected on an Oxford Diffraction XCalibur 2 CCD diffractometer at 100 K. Data were reduced and

---

(20) Sanz, S.; Laguna, M. Unpublished results.

(21) Teles, J. H.; Brode, S.; Chabanas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1415−1418.

(22) Daigle, D. J. *Inorg. Synth.* **1998**, *32*, 40−45.

(23) Joó, F.; Kovács, J.; Kathó, A.; Bényei, A. C.; Decuir, T.; Darensbourg, D. J. *Inorg. Synth.* **1998**, *32*, 1−8.

(24) Thorpe, T.; Brown, S. M.; Crosby, J. S. F.; Muxworthy, J. P.; Williams, J. M. J. *Tetrahedron Lett.* **2000**, *41*, 4503−4505.

(25) Schmidbaur, H.; Wohlleben, A.; Wagner, F. E.; van de Vondel, D. F.; van der Kelen, G. P. *Chem. Ber.* **1977**, *110*, 2758−2764.

Table 2. Details of Crystal Data and Structure Refinement for $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(TPA)_2](OTf)_2\cdot(Me_2CO)_4$

empirical formula	$C_{54}H_{76}Au_2F_6N_6O_{10}P_4S_2$
fw	1665.14
temp/K	100
wavelength/Å	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
a/Å	11.6241(3)
b/Å	13.5892(4)
c/Å	21.9393(4)
α/deg	82.340(2)
β/deg	81.252(2)
γ/deg	67.190(3)
V/Å^3	3146.87(14)
Z	2
density(calcd)/(Mg/m^3)	1.757
abs coeff/mm^{-1}	4.902
F(000)	1652
cryst habit	yellow needle
cryst size/mm	0.06 × 0.07 × 0.16
θ range for data collecn/deg	3.70−31.80
index ranges	$-16 \leq h \leq 15$, $-19 \leq k \leq 19$, $-30 \leq l \leq 31$
no. of reflns collected	16 414
no. of indep reflns	11 060 (R(int) = 0.057)
no. of data/restraints/params	16 414/617/42
R_1 ($I > 2\sigma(I)$)[a]	0.057
wR_2 (all data)[b]	0.166
S (all data)[c]	1.07
largest diff peak, hole/(e Å^{-3})	3.29, −2.94

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$. [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of refined parameters.

absorption corrections applied using CrysalisRED[26] and SADABS.[27] The structure was solved by heavy-atom methods[28] and refined[29] on F^2 with non-hydrogen atoms modeled with anisotropic displacement parameters, with hydrogen atoms in the riding model approximation and using a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.085P)^2 + 9.437P]$ where $P = (F_o^2 + 2F_c^2)/3)$. Disorder was detected and modeled in the refinement. Significant satellite peaks were observed for both the Au1 and Au2 atoms, i.e., labeled Au1′ and Au2′, and from fractional refinement, these had site occupancy values of 0.05 and were refined isotropically; the maximum residual electron density peak in the final difference map of 3.29 e Å^{-3} was located 0.68 Å from the Au1 atom. The anions and solvent acetone molecules were refined with soft constraints so that S−C was 1.81, S−O 1.44, C−F 1.32, C−O 1.21, and C−C 1.45 Å. The atoms comprising these groups were refined isotropically. High thermal motion for the N and C atoms of the P2-phosphine could not be resolved into two positions, however. Crystallographic and refinement details are summarized in Table 2.

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología Spain for financial support (CTQ2005-08099-C03-01) and for research grants to F.M. (SB2003-0235) and S.S. (BES2003-2259).

Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0602456

---

(26) *CrysAlis CCD* and *CrysAlis RED, V 1.171.27p8*; Oxford Diffraction, Ltd., 1995−2005.

(27) Sheldrick, G. M. *SADABS version 2.03*; Universiät Göttingen, 2002.

(28) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY: The DIRDIF Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(29) Sheldrick, G. M. *SHELXTL-NT 6.1*; Universität Göttingen, 1998.