

Sodium tetraphenylborate as a phenylating agent for gold(I) complexes [☆]

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Abstract

Phenyl[tri(tert-butyl)phosphine]gold(I) has been prepared from tris[tri(tert-butyl)phosphine]gold(I)oxonium tetrafluoroborate and sodium tetraphenylborate in ethanol at ambient temperature. The compound is also available from chloro[tri(tert-butyl)phosphine]gold(I) and phenyllithium in tetrahydrofuran. 1,4-Bis([phenylgold(I)]diphenylphosphinomethyl)benzene has been generated from the chloro complex 1,4-[(ClAu)Ph₂PCH₂]₂C₆H₄ either with silver oxide and sodium tetraphenylborate or with phenyllithium. The compounds have been identified by their analytical and spectroscopic data, and their structures have been determined by single-crystal X-ray diffraction studies.

Keywords: Phenylgold(I) Complexes; Tetraphenylborates as phenylating agents; Phenylation

1. Introduction

Arylgold(I) complexes of the type Ar–Au–L (with Ar = aryl and L = donor ligand) have recently attracted considerable interest owing to their versatility in oxidative addition–reductive elimination reactions [1–3]. Attention has also been directed towards the supramolecular chemistry of arylgold complexes, which have flat paddle-like Ar–Au units amenable to phenyl stacking and supramolecular Au–Au contacts (“auriophilicity”) [4,5].

The substrate molecules Ar–Au–L for oxidative addition reactions have traditionally been obtained by treatment of gold(I) halide complexes X–Au–L (X = halogen) with standard organometallic reagents. These include mainly Grignard reagents, and organolithium, organomercury and organothallium compounds [6–10].

In attempts to build gold clusters at chalcogen (O, S and Se) or pnictogen centers (N, P and As) using strongly electrophilic gold(I) complex cations L–Au⁺ or (LAu)₃O⁺ (associated with tetrafluoroborate anions BF₄[−]) [11–14], a number of ionic products were ob-

tained which were difficult to crystallize. Exchange of the anion appeared to be the most promising move to improve the crystal quality of the clusters. During these studies it was observed that tetraphenylborate anions, introduced solely for the purpose of anion exchange, can act as phenylating agents towards gold(I) complexes even in protic solvents and under mild conditions. This method of preparation for Ar–Au–L species is thus easier and less costly in most cases, since no anaerobic and anhydrous conditions need to be maintained, and no expensive reagents are necessary.

The arylation products have been isolated and fully characterized by X-ray diffraction studies, and alternative synthetic pathways have been followed in order to confirm product identity. A few representative examples of these gold(I) phenylations employing BPh₄[−] anions are presented in this paper. Similar observations with different substrates were made in another laboratory [15].

2. Preparation of phenylgold(I) complexes using tetraphenylborates

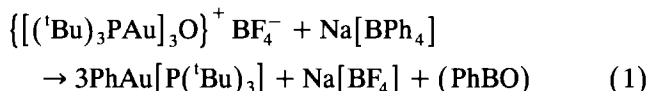
2.1. Phenyl[tri(tert-butyl)phosphine]gold(I)

The compound Ph–Au–P(^tBu)₃ was obtained in a slow reaction of tris[tri(tert-butyl)phosphine]gold(I)

[☆] Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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oxonium tetrafluoroborate (generated from $(^t\text{Bu})_3\text{P}-\text{Au}-\text{Cl}$ [16], Ag_2O , and NaBF_4 in tetrahydrofuran) with sodium tetraphenylborate in ethanol. After 15 days at room temperature there is complete conversion (100% yield):



The same product is formed in the metathesis of $[(^t\text{Bu})_3\text{P}]\text{AuCl}$ and phenyllithium in tetrahydrofuran (54% yield).



In both cases, colorless crystals are obtained (melting point (m.p.) 135°C), which decompose at 150°C . The composition has been confirmed by analytical, mass spectrometry (MS) and NMR spectroscopy data (see Section 3).

The compound crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with four molecules in the unit cell. There are no unusually short contacts between the molecular units. The configuration at the gold atom is linear ($\text{P}-\text{Au}-\text{C}$, $177.9(2)^\circ$), while phosphorus is in a tetrahedral array of nearest neighbors, with all angles at P very close to 109° , and $\text{P}-\text{C}$ and $\text{P}-\text{Au}$ bonds slightly longer than the standard reference values, probably owing to the steric congestion of the three tert-butyl groups (Fig. 1). These tert-butyl groups are in staggered conformations, and the plane of the phenyl ring is perpendicular to the plane defined by atoms C1, P and Au.

2.2. 1,4-Bis{[phenylgold(I)](diphenyl)phosphinomethyl}benzene

The compound $1,4\text{-}[\text{PhAu}(\text{Ph})_2\text{PCH}_2]_2\text{C}_6\text{H}_4$ was prepared from the bis(chloro) precursor [17] by treat-

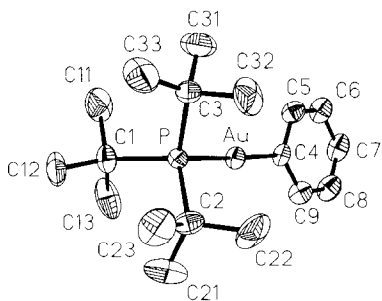


Fig. 1. Molecular structure of $(^t\text{Bu})_3\text{P}-\text{Au}-\text{Ph}$ with atomic numbering (ORTEP, 50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected distances and angles are as follows: $\text{Au}-\text{P}$, $2.305(1)$ Å; $\text{Au}-\text{C}(4)$, $2.055(6)$ Å; $\text{P}-\text{C}(1)$, $1.890(7)$ Å; $\text{P}-\text{C}(2)$, $1.894(8)$ Å; $\text{P}-\text{C}(3)$, $1.886(6)$ Å; $\text{P}-\text{Au}-\text{C}(4)$, $177.9(2)^\circ$; $\text{Au}-\text{P}-\text{C}(1)$, $108.8(2)^\circ$; $\text{Au}-\text{P}-\text{C}(2)$, $110.2(2)^\circ$; $\text{Au}-\text{P}-\text{C}(3)$, $109.1(2)^\circ$.

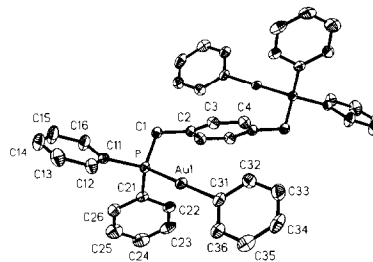
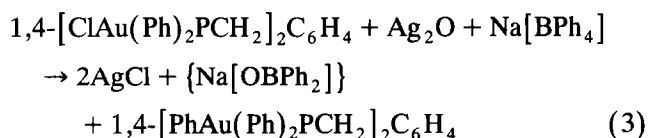
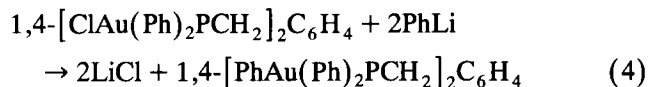


Fig. 2. Molecular structure of $1,4\text{-}[(\text{PhAu})\text{Ph}_2\text{PCH}_2]_2\text{C}_6\text{H}_4$ with atomic numbering (ORTEP, 50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected distances and an angle are as follows: $\text{Au}-\text{P}$, $2.284(1)$ Å; $\text{Au}-\text{C}(31)$, $2.044(4)$ Å; $\text{Au}-\text{P}-\text{C}(1)$, $114.1(1)^\circ$.

ment with silver oxide and sodium tetraphenylborate in tetrahydrofuran at ambient temperature (75% yield):



The alternative route using phenyllithium in dichloromethane gives the same product (88% yield):



Colorless crystals are obtained, which are stable in air. Elemental analyses and MS–NMR data are in agreement with the proposed formula (see Section 3).

The compound crystallizes from chloroform–pentane in the triclinic space group $P\bar{1}$ (No. 2) with one formula unit in the unit cell. The lattice is composed of independent molecules, which have a crystallographic center of inversion at the center of the bridging *p*-xylylene ring (Fig. 2). The gold atoms are two-coordinated with a $\text{P}-\text{Au}-\text{C}$ angle of $174.8(2)^\circ$. With none of the structural parameters outside the range of standard reference data, the structure represents a largely strain-free binuclear complex molecule. The ligands shield the gold atoms very effectively, and it is therefore not surprising that no intramolecular or supramolecular $\text{Au}-\text{Au}$ contacts can be detected. Even with smaller ligands the supramolecular chemistry may not be very pronounced, however, since it has been predicted from theoretical studies [18], that $\text{Au}-\text{Au}$ interactions should be relatively weak for arylgold(I) complexes. Some intermolecular phenyl stacking occurs with the aryl groups of the Ph_2P groups (Fig. 3).

3. Experimental part

3.1. General

All experiments were carried out under dry purified nitrogen. Samples and solutions were protected against

direct incandescent light. Solvents were dried, distilled and saturated with nitrogen. Glassware was oven dried and filled with nitrogen. $[(^t\text{Bu}_3\text{P})\text{Au}]_3\text{O}^+ \text{BF}_4^-$ was prepared according to a literature method [19]. The instruments used were as follows: MS, Varian MAT 311A; NMR, JEOL GX 400 spectrometer, CDCl_3 , with tetramethylsilane as an internal standard, and H_3PO_4 as external standard.

3.2. Phenyl[tri(tert-butyl)phosphine]gold(I)

3.2.1. Procedure I

0.50 g of tris[tri(tert-butyl)phosphine]gold(I)oxonium tetrafluoroborate (0.38 mmol) is dissolved in 25 ml of ethanol and an excess of sodium tetraphenylborate in ethanol is added with stirring. After 15 days at room temperature, colorless crystals are isolated (yield, 0.18 g (100%)).

3.2.2. Procedure II

The same product is formed from the reaction of 0.10 g of chloro[tri(tert-butyl)phosphine]gold(I) (0.23 mmol) with 0.02 g of phenyllithium (0.23 mmol) in 10 ml of tetrahydrofuran. After stirring for 12 h at room temperature, evaporation of the mixture to dryness in a vacuum and recrystallization from dichloromethane–diethyl ether (yield, 0.06 g (54%); m.p., 135°C; decomposition temperature, 150°C). ^1H NMR: δ 1.54 (d, $^3J_{\text{HP}} = 12.82$ Hz, CH_3), 7.03 (m, Ph-*para*), 7.24 (m, Ph-*meta*), 7.50 (m, Ph-*ortho*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 32.50 (d, $^2J_{\text{CP}} = 4.78$ Hz, CH_3), 38.58 (d, $^1J_{\text{CP}} = 31.47$ Hz, CP), 125.33 (s, Ph-*para*), 127.44 (s, Ph-*ortho*), 139.46 (s, Ph-*meta*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 93.14 (s, PPh_3) ppm. MS (CI): m/z (%) 476.5 (23.31) [M^+], 399.4 (100) [(M-Ph) $^+$].

Anal. Found: C, 44.99%; H, 6.68%; Au, 40.90%, P, 6.67%. $\text{C}_{18}\text{H}_{32}\text{AuP}$ (476.39) calc.: C, 45.38%; H, 6.77%, Au, 41.35; P, 6.50%.

Table 1
Crystallographic data for phenyl[tri(tert-butyl)phosphine]gold(I) and 1,4-bis[(phenylgold(I))(diphenyl)phosphinomethyl]benzene

Empirical formula	$\text{C}_{18}\text{H}_{32}\text{AuP}$	$\text{C}_{44}\text{H}_{38}\text{Au}_2\text{P}_2$
Formula weight	476.37	1022.62
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.570(1)	6.030(1)
b (Å)	18.500(1)	10.544(1)
c (Å)	12.497(1)	15.707(1)
α (°)	90	109.50(1)
β (°)	90.56(1)	97.58(1)
γ (°)	90	93.34(1)
V (Å ³)	1981.24	927.5(2)
ρ_{calc} (g cm ⁻³)	1.597	1.831
Z	4	1
$F(000)$ (electrons)	936	490
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	75.00	80.16
Crystal dimensions (mm)	0.25 × 0.35 × 0.50	0.20 × 0.30 × 0.35
T (°C)	+22	-56
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Scan	θ – θ	ω
hkl range	$0 \leq h \leq 10, -23 \leq k \leq 0, -15 \leq l \leq 15$	$-7 \leq h \leq 7, -13 \leq k \leq 12, -20 \leq l \leq 12$
Number of measured reflections	4432	4048
Number of unique reflections	3844	3983
Number of observed reflections	3159	3817
R_{int}	0.1151	0.0036
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$
Number of refined parameters	181	217
H atoms (found; calc.)	—; 32	—; 38
Absorption correction	Empirical	Empirical
$T_{\text{min}}/T_{\text{max}}$	0.5873/0.9995	0.5189/1.0000
R^a	0.033	0.028
R_w^b	0.037	0.032
Weighting scheme ^c	$1 = 1.0000/k = 0.001215$	$1 = 1.0000/k = 0.002583$
ρ_{fin} (maximum) (electrons Å ⁻³);	+0.67; -1.10	+1.47; -3.58
ρ_{fin} (minimum) (electrons Å ⁻³)		

^a $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$.

^b $R_w = [\sum w(\|F_o\| - \|F_c\|)^2 / \sum wF_o^2]^{1/2}$.

^c $w = 1/\sigma^2(F_o) + kF_c^2$.

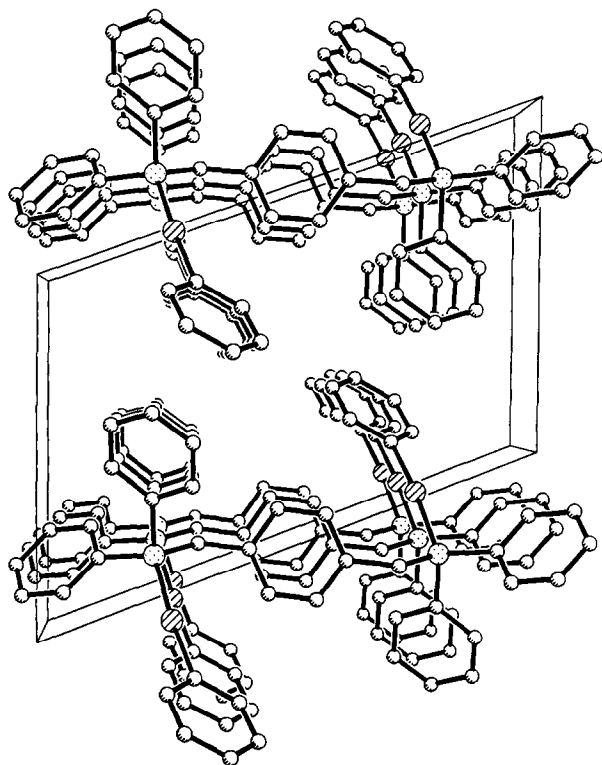


Fig. 3. Stacking of the molecules 1,4-[(PhAu)Ph₂P]₂C₆H₄ in the unit cell (Schakal, arbitrary radii).

3.3. 1,4-Bis{[phenylgold(I)](diphenyl)phosphinomethyl}benzene

3.3.1. Procedure I

A solution of 51.3 mg of sodium tetraphenylborate (0.15 mmol) in 10 ml of tetrahydrofuran is added dropwise to a suspension of 141 mg of 1,4-bis{[chlorogold(I)](diphenyl)phosphinomethyl}benzene (0.15 mmol) and freshly prepared silver oxide (from 0.50 g of silver nitrate (3.0 mmol) and 0.17 g of KOH in 40 ml of water) in 30 ml of tetrahydrofuran. After stirring for 90 min at room temperature the solvent is evaporated in a vacuum and the residue extracted with 2 × 15 ml of dichloromethane. The filtered solution is evaporated to dryness and recrystallized from chloroform–pentane (yield, 144 mg (94%)).

3.3.2. Procedure II

188 mg of 1,4-bis{[chlorogold(I)](diphenyl)phosphinomethyl}benzene (0.20 mmol) is dissolved in 50 ml of dichloromethane and cooled to –78°C. A solution of 33 mg of phenyllithium (0.40 mmol) in cyclohexane–diethyl ether is added dropwise and the mixture is allowed to warm to room temperature. After stirring for 4 h at ambient temperature, evaporation to dryness in a vacuum and extraction with 2 × 50 ml of benzene leads to the product (yield, 179 mg (88%); m.p., 196°C (decomposition)), ¹H NMR: δ 3.69 (d, ²J_{HP} = 10 Hz,

CH₂), 6.89–7.82 (m, aryl-H), ppm. ¹³C{¹H} NMR: δ 35.6 (d, ²J_{CP} = 25 Hz, C1), 125.8 (s, C34), 127.4 (d, ³J_{CP} = 16 Hz, C32/36), 128.5 (d, ¹J_{CP} = 28 Hz, C11/21), 130.7 (d, ⁴J_{CP} = 7 Hz, C14/24), 131.3 (s, C3/4), 131.7 (s, C2), 133.6 (m, C12/16/22/26), 139.5 (s, C33), 173.0 (d, ²J_{CP} = 119 Hz, C31) (atomic numbering as in Fig. 2) ppm. ³¹P{¹H} NMR: δ 41.61 (s) ppm. MS (fast atom bombardment): m/z (%) 945.5 (100) [M⁺ – Ph], 869.4 (3) [(M – 2 × Ph)⁺], 671.3 (42) [M⁺ – AuPh – Ph]. Anal. C₄₄H₃₈Au₂P₂ (1022.67) calc. C, 51.68; H, 3.74; Au, 38.52. Found: C, 51.72, H, 3.88; Au, 36.90.

3.4. Crystal structure determination

The samples were mounted in glass capillaries. Graphite-monochromated Mo K_α radiation was used. The structures were solved by direct methods (SHELXTL-PC). The final cell parameters and specific data collection parameters are summarized in Table 1. Further details of the X-ray structure determinations have been deposited at Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation and the CSD number XXXXX.

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