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A dimeric gold(I) triphospholyl complex

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Dedicated to professor Francois Mathey on the occasion of his 60th birthday

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Abstract

The reaction of 1-trimethylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphol with PPh_3AuCl affords [(1,2,4-triphospholyl)Au(PPh_3)] (**5**) in high yield. NMR spectra of **5** are indicative for a highly dynamic compound in solution. The molecular structure of **5** in the solid state is that of the dimer [(1,2,4-triphospholyl)Au(PPh_3)]$_2$. Its most striking feature is a remarkable range of different metal–triphospholyl ligand bonds which create a pronounced asymmetric core of the molecule. The central Au–Au distance of 3.14 Å indicates a weak interaction of the metal atoms. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NMR spectra; Triphospholyl; Ligand; Gold

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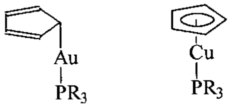
1. Introduction

Triorganylstannyl-1,2,4-triphosphol derivatives are excellent starting materials for a high yield transfer of the five membered heterocyclic ligand 1,2,4-triphospholyl onto various ML_n fragments [1]. Ease and reproducibility of this reaction encouraged us to investigate the specific contributions of the phosphorus atoms to the reactivity of this phosphorus-rich cyclopentadienyl (Cp) analogue. Principally, the phosphorus atoms supply three lone pairs to the triphospholyl ring and cause a decrease of the frontier π-orbital energies as well as a significant ring size expansion with respect to Cp. All three aspects contribute to the properties of compounds which contain a triphospholyl unit, aspecially if the rings are complexed to a metal atom. In case of their dominance, the triphospholyl ligand cannot be viewed as a Cp analogue any longer, where the phosphorus atoms just replace CR fragments as isovalent and isolobal building blocks [2]. Exceptions of that sort are [bis(1,2,4-triphospholyl)Mn], which exhibits a novel electronic ground state for manganocene derivatives [3], and new structural features have been observed for [(1,2,4-triphospholyl)NiLL′] derivatives, including the formation of an unpredictable σ-complex dimer [4].

When investigating the chemistry of [(1,2,4-triphospholyl)Cu(I)L] complexes [5], we found evidence for several coexisting species. Most of them exhibit a remarkable structural flexibility which causes a big manifold of spectroscopic parameters, aspecially in NMR spectroscopy. No unambiguous interpretation of the data was thus possible, even the reversible formation of dimers could not be ruled out. To get some insight into possible d^{10}-M(I)-1,2,4-triphospholyl dimer structures, we reacted triorganylstannyl-1,2,4-triphosphol with PPh_3AuCl, as Au(I) is more likely to form stable dimers than Cu(I).

Cp(PPh_3)Au(I) (**1**) is known since 1967 [6]. In contrast to its Cu(I) analogue **2**, **1** exhibits a fluxional η^1-bonded Cp ligand in solution (Scheme 1). In the solid state, however, a tendency towards η^3-co-ordination of Cp ligands of Au(I) has been observed, too [7].

Au–Au bonds are found regularly in Au(I) complex dimers [8], but no simple models have been developed



1 **2**

Scheme 1.

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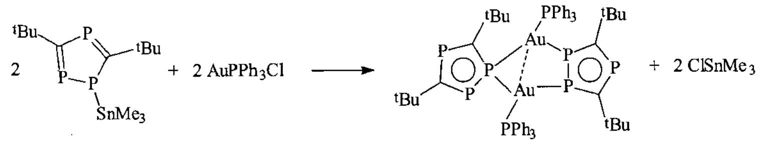

3 **4** **5**

Scheme 2.

yet to interpret the Au–Au interactions and the bonding angles around the metal atoms in the solid state [9]. Gold–gold distances for molecular species have been observed in the range of 2.50–4.00 Å. Values of more than 3 Å might be viewed as weak or even non-bonding interactions, while contacts below this are regarded as bonds. Theoretical studies revealed a complex bonding situation of oligonuclear gold compounds [10]. The aurophilic attraction of gold atoms is caused by a combination of correlation and relativistic effects [11].

2. Results

The reaction of 1-trimethylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphol (**3**) with PPh_3AuCl (**4**) results in the formation of the desired product **5** in 86% yield. According to the analytical data it contains the three components 1,2,4-triphospholyl, PPh_3, and gold in the ratio 1:1:1.

5 is a stable orange compound. NMR spectra are dominated by dynamic effects. At room temperature ^1H- and ^{13}C-NMR spectra indicate a symmetric chemical situation for the triphospholyl ligand. The ^{31}P-NMR lines are slightly broadened, but close to a fast exchange limit case and form three lines in the ratio 1:1:2. No coupling between the different phosphorus atoms of **5** is observable. The room temperature NMR data are in line with a σ-complexed anionic triphospholyl ligand. Because of the broadening of all NMR lines at low temperature, the compound is regarded to undergo rapid exchange process which simplify the spectra. This dynamic situation is in contrast to the only known example of a dimeric σ-complex of this ligand $[(1,2,4\text{-triphospholyl})(PPh_3)(NO)Ni]_2$ [4]. The ^{31}P-NMR signals of **5** not only broaden, but split to form several new ones. No slow-exchange limit spectrum could be obtained, however. This indicates a low-activated equilibrium between different triphospholyl–Au bonding modes. As for the Cu(I) triphospholyl complexes, the dynamic NMR spectra do not reveal details of the dynamic processes or the involved species. FD MS spectra exhibit peaks, which represent $(\text{triphospholyl})Au(PPh_3)$ as well as its dimer $[(\text{triphospholyl})Au(PPh_3)]_2$. Crystals suitable for X-ray structural analysis could be obtained from a solution in *n*-hexane–THF. The molecular structure in the solid state is that of the dimer $[(\text{triphospholyl})Au(PPh_3)]_2$ only (Scheme 2, Fig. 1, Tables 1 and 2).

The most striking feature of dimer **5** is a remarkable range of different metal–triphospholyl ligand interactions. One of the ligands bridges the Au–Au unit by one P atom (P(3)), whereas the other one fulfils the same function by the two adjacent phosphorus atoms P(5) and P(6). P–Au bonds of different lengths as well as a warped orientation of the ligand planes with respect to the Au–Au vector creates a distinctly asymmetric core of the molecule. When compared to the literature values, the distance Au(1)–Au(2) = 3.14 Å indicates a weak interaction of the metal atoms in the range of 6 kcal mol^{-1} [12].

In spite of their different interactions with the two metal atoms, both triphospholyl ligands of **5** form almost identical delocalized π-systems which are characterized by constant P–C bonding distances. They appear all in the small range of 1.74–1.76 Å. Likewise, the P–P bonds of the ligands have the same length as well (2.09 Å). The observed π-electron delocalization is in line with the solution NMR data at room tempera-

Table 1
Selected bond length (Å) and angles (°) for **5**

Bond lengths		*Bond angles*	
Au(1)–Au(2)	3.1395(9)	Au(1)–P(3)–C(1)	133.5(3)
Au(1)–P(5)	2.335(2)	Au(1)–P(3)–P(2)	85.41(10)
Au(1)–P(7)	2.300(2)	Au(1)–P(3)–Au(2)	74.00(7)
Au(1)–P(3)	2.836(2)	P(2)–P(3)–C(1)	104.1(3)
Au(2)–P(3)	2.339(2)	Au(1)–Au(2)–P(8)	125.57(6)
Au(2)–P(6)	2.730(2)	Au(2)–Au(1)–P(7)	126.68(6)
Au(2)–P(8)	2.295(2)	P(3)–Au(2)–P(8)	147.41(8)
P(5)–P(6)	2.090(3)	P(3)–Au(2)–P(6)	99.80(7)
P(2)–P(3)	2.092(3)	P(6)–Au(2)–P(8)	112.76(7)
P(5)–C(4)	1.741(9)	P(7)–Au(1)–P(3)	111.79(8)
P(6)–C(3)	1.725(9)	P(3)–Au(1)–P(5)	98.97(8)
P(4)–C(4)	1.732(9)	P(7)–Au(1)–P(5)	148.97(9)
P(4)–C(3)	1.764(9)	Au(2)–P(6)–P(5)	85.83(10)
P(3)–C(1)	1.732(9)	Au(1)–P(5)–P(6)	116.41(12)
P(2)–C(2)	1.732(9)	Au(2)–P(6)–C(3)	129.4(3)
P(1)–C(1)	1.737(9)	P(5)–P(6)–C(3)	97.8(3)
P(1)–C(2)	1.763((9)	P(6)–P(5)–C(4)	103.5(3)
		Au(1)–P(5)–C(4)	130.1(3)
		Au(1)–Au(2)–P(3)	60.26(6)
		Au(2)–Au(1)–P(3)	45.73(5)
		Au(2)–Au(1)–P(5)	72.89(6)
		Au(2)–P(3)–C(1)	128.3(3)

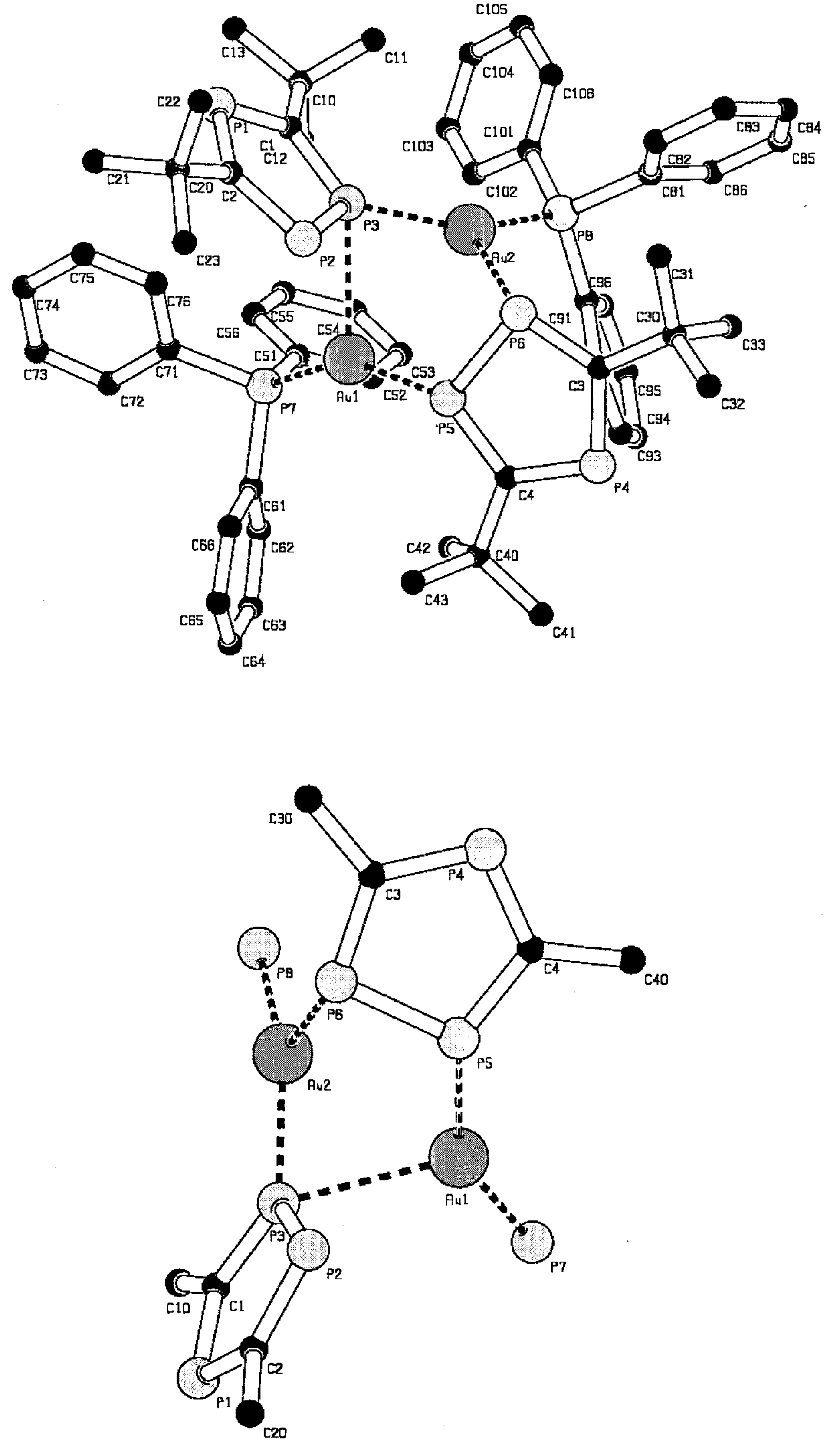

Fig. 1. (A) Molecular structure of **5** in the solid state; hydrogen atoms are omitted for clarity; (B) core of **5**.

Table 2
Crystal data and structure refinement of compound **5**

Empirical formula	$C_{56}H_{66}Au_2P_8$
Formula weight	1380.78
Solvent	*n*-hexane–THF
Crystal habit	Orange prism
Temperature (K)	200
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.661(2)
b (Å)	14.426(3)
c (Å)	14.426(3)
α (°)	80.03(2)
β (°)	85.92(1)
γ (°)	69.22(1)
V (Å^3)	2852.5(9)
Z	2
D_{calc} (g cm^{-3})	1.608
Absorption coefficient (mm^{-1})	5.396
F(000)	1360
Crystal size (mm)	0.38 × 0.20 × 0.10
Theta range for data collection (°)	1.97–27.00
Index ranges	$-13 \leq h \leq 1$ $-18 \leq k \leq 17$ $-25 \leq l \leq 25$
Reflections collected	14 078
Reflections with $I > 2\sigma(I)$	8209
Independent reflections	12 428 [$R_{int} = 0.0457$]
Completeness to θ	27.00°: 99.7%
Absorption correction	ψ-scan
Max/min transmission	0.163, 0.086
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	12428/0/607
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0563$, $wR_2 = 0.1182$
R indices (all data)	$R_1 = 0.1010$, $wR_2 = 0.1395$
Goodness-of-fit on F^2	1.013
Largest difference peak and hole (e nm^{-3})	1639 and −2528

ture and a hint on aromatic π^6-systems. The heterocycles are thus anionic and compensate the charge of the Au(I) cations.

Besides the weak Au–Au interaction, both gold centres exhibit planar co-ordination spheres, which are occupied by three phosphorus atoms (sum of angles: 359.7 and 360.0°, respectively). In contrast to a [tris(diphosphanylmethane)Au$_2$]$^{2+}$ (Au–Au = 3.04 Å) derivative, however [13], the central P–Au–P bond angles differ significantly from the symmetrical case 120°. The P–Au–P angles of **5** cover the range of ca. 99–150° for Au(1) as well as for Au(2).

As indicated by the asymmetric core of the dimer, the metal to ligand distances of the doubly bridging ligand Au(1)–P(5) = 2.335 Å and Au(2)–P(6) = 2.730 Å differ by remarkable 17%. This big difference leads to the assumption that the shorter one contributes the main part of the bonding energy Au(1)–triphospholyl. This opens the possibility to view the co-ordination sphere of Au(1) as a perturbed linear unit. The corresponding angle triphospholyl–Au–PPh$_3$=P(5)–Au(1)–P(7) equals 149°, thus the deviation from linearity is ca. 31°. The interaction of P(3) with Au(1) and Au(2) can be viewed as a bridging bonding mode, where the lone pair is oriented towards the space between the two Au atoms. Again, the bridge is asymmetric, as the Au–P bonds P(3)–Au(1) and P(3)–Au(2) differ in their length by 21%. The short one, P(3)–Au(2) = 2.339 Å is almost the same as Au(1)–P(5). As the central angle P(3)–Au(2)–P(8) = 147.4°, Au(2) appears as a perturbed linear coordinate metal atom as well.

Because of the aromaticity of the triphospholyl anions, the ligand to metal interaction is dominated by the P lone pairs. Taking a high s-character of the P lone pairs [14] and the empty gold orbitals into consideration, their overlap should not be very sensitive towards tilting of such σ-bonds. Such a non-directional bonding mode has been observed for the ligand properties of bis(phospholyl)Fe derivatives with respect to Pd(0) [15] and Ag(I) [16], already. The same effect may contribute to the weaker Au–triphospholyl interactions as well and promote the asymmetry of dimer **5**.

3. Conclusions

Besides of the pronounced s-character of the P and Au atom orbitals which create the bonding molecular orbitals of **5**, they are somewhat diffuse and allow significant deviations from the optimal arrangement of gold atoms and triphospholyl ligands without too much loss of interaction energy. As a consequence, the equilibrium structure of **5** is supposed to form a shallow energetic minimum, thus packing effects may influence the observed molecular structure in the solid state significantly and create the pronounced asymmetry of the co-ordination core. The low activation energy for the dynamic effects in solution is completely in line with this interpretation, however, the data do not allow to distinguish unambiguously between intramolecular rearrangement processes or the participation of a monomer–dimer equilibrium.

4. Experimental

4.1. General considerations

The experiments were conducted under a N_2 atmosphere by using standard Schlenk and cannula techniques. Solvents were dried according to described procedures and used freshly distilled from the drying agent. PPh_3AuCl (**4**) and $(H_3C)_3Sn(P_3C_2^tBu_2)$ (**3**) were prepared according to the literature [5,17].

4.2. $[Au(P_3C^t_2Bu_2)(PPh_3)]_2$ (**5**)

0.841 g (1.7 mmol) of $Au(PPh_3)Cl$ is suspended in 25 ml of THF 0.673 g (1.7 mmol) of 1-trimethylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphol (**3**) in 25 ml of THF is added at a temperature of − 50 °C. The reaction mixture is then stirred and allowed to warm up to room temperature (r.t.) over night. The THF is removed in vacuo. The residue is suspended in *n*-hexane, filtered, washed with *n*-hexane, dried in vacuo, and the resulting orange–red powder is dissolved in 10 ml of THF and a few drops of *n*-hexane. Crystallization occurs over night at − 18 °C to yield 1.012 g (1.465 mmol, 86.2%) of the target product **5**.

4.3. Spectroscopic data for (**5**)

^{1}H-NMR (399.65 MHz, CD_2Cl_2, 20.1 °C): $\delta = 1.44$ (s, 18H, CH_3), 7.23–7.39 (m, 15H, C_6H_5). $^{13}C\{^1H\}$-NMR (100.40 MHz, CD_2Cl_2, 20.3 °C): $\delta = 204.9$ (dpt = doublet of pseudo triplets, $^1J(^{31}P(3)^{13}C) = 32.2$ Hz; $\Sigma\ ^1J(^{31}P(1)^{13}C) + {}^2J(^{31}P(2)^{13}C) = 54.5$ Hz, C_{Ring}); 134.34 (d, $^2J(^{31}P^{13}C) = 14.9$ Hz, *o*-Ph–C); 131.62 (s, *p*-Ph–C); 131.08 (d, $^1J(^{31}P^{13}C) = 46.3$ Hz, *i*-Ph–C); 129.50 (d, $^3J(^{31}P^{13}C) = 10.7$ Hz, *m*-Ph–C); 40.95 (dpt, $^2J(^{31}P(3)^{13}C) = 19.8$ Hz; $\Sigma\ ^2J(^{31}P(1)^{13}C) + {}^3J(^{31}P(2)^{13}C) = 5.8$ Hz, $C(CH_3)$); 37.12 (dpt, $^3J(^{31}P(3)^{13}C) = 5.8$ Hz; $\Sigma^3\ J(^{31}P(1)^{13}C) + {}^4J(^{31}P(2)^{13}C) = 4.9$ Hz, $C(CH_3)$). $^{31}P\{^1H\}$-NMR (161.70 MHz, CD_2Cl_2, 20.7 °C): $\delta =$ 251.54 (br, 1P, P_{Ring}); 194.72 (br, 2P, P_{Ring}); 36.98 (br, 1P, PPh_3). MS (FD^+, THF): *m*/*z* (%): 262 (100) $[P(C_6H_5)_3]^+$; 464 (48) $[(t\text{-}Bu_2C_2P_3)_2]^+$; 690 (4) $[Au(P_3C^t_2Bu_2)(PPh_3)]^+$; 1381 (2) $\{Au(P_3C^t_2Bu_2)(PPh_3)]_2\}^+$. m.p.: 169 °C.

Anal. Calc. for $(C_{25}H_{33}AuP_4)_n$: C, 48.71; H, 4.82. Found: C, 48.63; H, 4.70%.

4.4. Crystal structure determination of **5**

Intensity data of **5** were collected on a Siemens P4 diffractometer (ω scan technique, 4.0° min^{-1}, Mo–K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å) using the XSCAnS 2.31 software (Bruker AXS, 1999). The structure was solved by direct methods and refined by full-matrix least-squares procedures against F^2 with all reflections using SHELXTL-NT 5.1 (Bruker AXS 1998) programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **5** are geometrically positioned with an isotropic displacement parameter corresponding to 1.2- or 1.5-times of the equivalent isotropic displacement parameter of its carrying carbon atoms. Crystal data and experimental details are listed in Table 2.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167423 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: www:http://ccdc.cam.ac.uk).

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