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Note

Synthesis and X-ray crystal structure determination of the first structurally authenticated terphenyl gold complex

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Abstract

The synthesis and X-ray crystal structure determination of a novel metal-terphenyl derivative, namely DmpAuPPh₃ (1), is reported (Dmp = 2,6-dimesitylphenyl). Complex 1 is synthesized by the reaction of one equivalent of DmpLi with one equivalent of Ph₃PAuCl in tetrahydrofuran at room temperature in 70% yield. The molecular structure of monomeric 1 features a two-coordinate gold atom with an essentially linear arrangement of the two ligands with an interligand angle of 174.21(8)° as well as a slightly tilted terphenyl moiety. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is much current interest in the chemistry of terphenyl ligand systems because this type of sterically demanding ligands was found to be suitable for the stabilization of main group element complexes in unusual coordination geometries and unprecedented bonding situations [1]. While the vast majority of so far structurally characterized complexes are based on s and p block elements, relatively little information is available on terphenyl complexes of the d block elements. As a matter of fact, all of the few known examples are derived from late transition metals [1]. For example, terphenyl complexes have been reported for the elements copper [2-6] and silver [7]. However, to the best of our knowledge, so far there are no reports on structurally characterized terphenyl gold complexes. In general, organometallic complexes of the elements gold and silver have received considerably less attention as compared with organocopper(I) complexes. An observation which is most likely partially due to the signifi-

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cantly higher costs of the elements silver and gold, respectively. In this work the synthesis and structural characterization of the first terphenyl gold complex is reported.

2. Experimental

The compound described below was handled under nitrogen using Schlenk double manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. Ph₃PAuCl was purchased from Aldrich and used as received. DmpLi [8] was prepared according to the literature. NMR spectra were recorded on a JMN-GX 400 instrument. The ¹³C NMR spectrum, recorded in C₆D₆, was referenced to the solvent signal at 128.0 ppm.

2.1. $DmpAuPPh_3$ (1)

Addition of a freshly prepared solution of DmpLi (320 mg, 1.0 mmol) in 5 ml tetrahydrofuran to a colorless suspension of Ph_3PAuCl (500 mg, 1.0 mmol)

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in 5 ml tetrahydrofuran caused a color change to pale pink. The reaction mixture was stirred for 30 min at ambient temperature, followed by removal of all volatiles and washing of the residues with hexanes, which gave the title compound as a colorless powder. Crystallization of the obtained DmpAuPPh₃ from toluene + hexanes (1:1) at -30° C gave 1 as colorless crystals (544 mg, 70%), which are not light-sensitive and air-stable. Complex 1 is insoluble in hexanes, but well soluble in arene solvents and tetrahydrofuran. Anal. Calc. for C42H40AuP: C, 65.29; H, 5.22. Found: C, 65.11; H, 5.07%. ¹H NMR (C₆D₆, 400.0 MHz, 25°C): δ 2.22 (p-Me, 6H), 2.41 (o-Me, 12H) plus several signals in the aromatic region (from 6.8 to 7.4 ppm). ³¹P NMR (C₆D₆, 161.9 MHz, 25°C): δ 43.5. ¹³C NMR (C₆D₆, 100.4 MHz, 25°C): δ 21.3 (p-Me), 21.8 (o-Me), 127.9, 128.7, 128.8, 130.6 (d, $J_{C-P} = 3$ Hz), 131.4, 132.1, 134.4 (d, $J_{C-P} = 20$ Hz), 134.5, 136.5, 145.6 (d, $J_{C-P} = 3$ Hz), 150.2, 176.7 (ipso-C). IR (Nujol): 1306 w, 1180 m, 1098 s, 1026 m, 997 m, 845 m, 803 m, 782 w, 738 s, 708 m, 691 s, 618 w, 588 w, 574 w, 532 m, 502 s, 444 w, 431 w cm^{-1} . M.p. (dec.) = 233–235. Prior to decomposition complex 1 turns pink and then decomposes forming a red oil.

2.2. X-ray data collection, structure determination, and refinement for $DmpAuPPh_3$ (1)

Crystallographic data are collected in Table 1. A sample was mounted on a glass fibre under inert perfluoropolyether. No symmetry higher than triclinic was observed and the centrosymmetric option was selected

Table 1				
Crystallographic	data	for	DmpAuPPh ₃	(1) ^a

	1	
Formula	C42H40AuP	
$F_{\rm w}$	772.68	
Space group	$P\overline{1}$	
a (Å)	8.702(2)	
b (Å)	10.668(2)	
c (Å)	19.539(1)	
α (°)	85.55(1)	
β (°)	85.85(1)	
γ (°)	72.98(1)	
V (Å ³)	1726.8(5)	
Z	2	
D_{calc} (g cm ⁻³)	1.486	
Temperature (°C)	-125(2)	
Radiation, λ (Mo K α) (Å)	0.71073	
μ (Mo K α) (cm ⁻¹)	4.334	
R_1 (%)	2.33	
wR_2 (%)	5.86	

^a The quantity minimized was $wR_2 = \sum [w(F_o^2 - F_o^2)^2]/\Sigma [(wF_o^2)^2]^{1/2}$; $R_1 = \sum \Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o, 0]/3$.

3. Results and discussion

 $DmpAuPPh_3$ (1) is synthesized by reaction of equimolar amounts of DmpLi and Ph_3PAuCl in tetrahydrofuran at room temperature in 70% yield. Colorless crystals of air-stable 1 suitable for an X-ray diffraction study were grown by slow evaporation of a toluene solution at ambient temperature.

The molecular structure of complex 1 (Fig. 1) features an almost linear C(*ipso*)-Au-P arrangement. As was previously observed in the molecular structure of Ph₃PAuPh [9,10], there is no intermolecular Au···Au interaction in complex 1 (Fig. 2). The Au-C distance of 2.046(3) Å, the Au-P distance of 2.2799(8) Å, as well as the C-Au-P angle of 174.21(8)° in complex 1 can favorably be compared with the corresponding distances in Ph₃PAuPh [Au-C = 2.045(6) Å; Au-P = 2.296(2) Å; P-Au-C = 175.5(2)°] [9,10]. Besides the gold-*ipso* carbon distance in 1, there are weak secondary interactions between the metal atom and the



Fig. 1. ORTEP diagram and numbering scheme of DmpAuPPh₃ (1) drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected intatomic distances (Å) and angles (°): Au(1)–C(41) = 2.046(3), Au(1)···C(51) = 3.166(3), Au(1)···C(61) = 3.271(3), Au(1)-P(1) = 2.2799(8), P(1)-C(11) = 1.825(3), P(1)-C(21) = 1.816(3), P(1)-C(31) = 1.814(3) Å; C(41)-Au(1)-P(1) = 174.21(8), Au(1)-C(41)-C(42) = 119.0(2), Au(1)-C(41)-C(46) = 122.6(2), Au(1)-P(1)-C(11) = 113.64(9), Au(1)-P(1)-C(21) = 114.77(10), Au(1)-P(1)-C(31) = 111.30(10), C(41)-C(42)-C(51) = 119.2(2), C(41)-C(46)-C(61) = 119.3(2)°.



Fig. 2. Packing diagram of the molecular structure of complex 1.

ipso carbon atoms of the mesityl rings at a distance of 3.166(3) Å [C(51)] and 3.271(3) Å [C(61)] in complex 1. Further comparison of the Au–C(*ipso*) distance in complex 1 can be made with the corresponding distances in two anionic bis(terphenyl) silver complexes, namely [Li(THF)₄][Ag(Triph)₂]·THF [av. 2.097(9) Å] and [Li(THF)₄][Ag(C₆H₃-2,6-Mes)₂]·1/8 OEt₂ [av. 2.09(3) Å] [7]. Both complexes show almost linear coordination of the silver(I) cation. The Dmp ligand in complex 1 is slightly tilted, as can be seen by inspecting the Au(1)–C(*ipso*)–C(*ortho*) angles [Au(1)–C(41)–C(42) = 119.0(2); Au(1)–C(41)–C(46) = 122.6(2)].

It is interesting to note that the average Ag-C(ipso)distances in both diorgano argentates mentioned above are clearly longer than the Au-C(ipso) distance in the neutral complex 1, an observation which can most likely be attributed to increased steric crowding around the metal center in both silver complexes. Another possible explanation is based on previously reported experimental evidence for the ionic radius of gold(I) being actually smaller than that of silver(I) for a given coordination number due to relativistic effects [11]. It is also to be noted that the observed Au-C(ipso) distance in complex 1 is approximately 0.10-0.15 Å longer than was found for the corresponding distances in related terphenyl copper complexes [7]. On the other hand, based on Shannon's ion radii [12] two-coordinate silver(I) ions are expected to be approximately 0.2 Å larger than two-coordinate copper(I) ions.

4. Conclusion

The results presented in our work provide more insight into structural aspects of so far relatively rare terphenyl complexes of the coinage metals. Bonding parameters for the first terphenyl gold complex are provided. Our work also allows for a detailed comparison of complex **1** with other aryl gold(I) complexes as well as terphenyl complexes of the late transition metals. Further investigations in this particular area of chemistry are clearly warranted. For example, the synthesis and X-ray structural characterization of the silver analogue of complex **1** is still to be accomplished and might give further corroboration to the experimentally evidenced observation of gold(I) being smaller than silver(I) ions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 116984. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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