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Gold(I) complexes containing the cationic ylide ligand bis(methyldiphenylphosphonio)methylide

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Abstract

The ylide $Ph_2PCH=PPh_2Me$ can be selectively P-alkylated by MeI or MeO_3SCF_3 to form the bis(methyldiphenylphosphonio)methylide salts [MePPh_2CHPPh_2Me]A (A=I (1), CF_3SO_3 (2)). The ylidic carbon shows a weak nucleophilicity and does not give typical reactions with common organic electrophiles, including Wittig type reactions, but it is able to displace tetrahydrothiophene in [AuX(tht)] to give the corresponding C-coordinated gold(I) compounds [Au{CH(PPh_2Me)_2}X]CF_3SO_3 (X=CI (3), C_6F_5 (4)). The crystal structure of (4) displays a linear coordination for the gold atom, single P-C bond lengths and a PCP angle of 119.1(3)° for the ligand. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Gold(I) complexes; Cationic ylide ligand; Bis(methyldiphenylphosphonio)methylide salts; P-alkylation

1. Introduction

Carbodiphosphorane chemistry has attracted much attention not only because of the synthesis and geometry of the P=C=P fragment [1] but also for the synthesis of metallic complexes. Therefore several mononuclear copper, gold, silver [2,3], iridium [4], platinum [5,6], rhenium [7,8], tungsten [6,8,9], manganese, chromium, iron and nickel [8] or dinuclear gold [10] and iron [11] derivatives have been prepared.

On the contrary the mesomeric phosphonium ylides $R_3PCHPR_3^+$ have often been overlooked because of their intermediate position on the carbodiphosphoranes and not C_{ylidic} -bonded metallic complexes have been described so far. Some complexes containing the unit $-CH_2PR_2CHPR_2CH_2^-$ have been reported with the ligand acting as quelate through the CH₂ groups [10,12,13].

In this paper, the synthesis of the phosphoranium salts $[MePPh_2CHPPh_2Me]A$ (A=I, CF₃SO₃) and their first metallic complexes $[Au[CH(PPh_2Me)_2)X]CF_3SO_3$ (X=Cl, C₆F₅) are reported, which in spite of the weak nucleophilic character of the ylidic carbon are stable.

X-ray diffraction studies of the pentafluorophenyl derivative were carried out to fully characterize their geometry.

2. Experimental

All the reactions were carried out under a dry nitrogen atmosphere at room temperature (r.t.). IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm⁻¹, by using Nujol mulls between polyethylene sheets. ¹H, ¹⁹F and ³¹P{¹H} NMR spectra were recorded on a Varian UNITY 300 or Bruker ARX-300 apparatus in CDCl₃ solutions; chemical shifts are quoted relative to SiMe₄ (external, ¹H), CFCl₃ (external, ¹⁹F) and 85% H₃PO₄ (external, ³¹P). C, H, N and S analyses were performed with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec using LSIMS technique (with cesium gun) and 3-nitrobenzyl alcohol as matrix.

2.1. Preparation of the ligands

2.1.1. $[MePh_2PCHPPh_2Me]I$ (1)

To a diethyl ether suspension (10 ml) of [Ph₂PCH₂PPh₂Me]I [14] (0.54 g, 1 mmol) was added an

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excess of sodium hydride (1.2 g of a 60% paraffin suspension, 3 mmol). After stirring for 5 h, the excess of NaH and the formed NaI are filtered off, obtaining a yellow solution of the ylide. The addition of MeI (0.142 g, 1 mmol) immediately afforded a white solid which was filtered off and washed with diethyl ether (3 × 5 ml). Yield of 1: 55%. ¹H NMR: δ 7.8–7.2 (m, 20H, Ph), 2.13 (d, 6H, ²J_{HP} = 12.0, Me–P), 1.39 (t, 1H, ²J_{HP} = 4.6 Hz, P–CH–P); ³¹P{¹H} NMR: δ 16.5. Anal. Calc. C₂₇H₂₇IP₂: C, 60.0; H, 5.05. Found: C, 59.85; H, 4.9.

Table 1

Details of data collection and	structure	refinement fo	r complex 4
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Compound	4
Chemical formula	C34H27AuF8O3P2S
Crystal habit	colourless needle
Crystal size (mm)	$0.65 \times 0.20 \times 0.10$
Crystal system	triclinic
Space group	$P\overline{1}$
a (Å)	9.641(2)
b (Å)	11.538(2)
c (Å)	16.696(3)
α (°)	77.91(3)
β (°)	77.69(3)
γ (°)	81.05(3)
U (Å ³)	1762.3(6)
Ζ	2
D_{calc} (Mg m ⁻³)	1.746
M	926.52
<i>F</i> (000)	904
$T(^{\circ}C)$	25
$2\theta_{\max}$ (°)	50
μ (Mo K α) (mm ⁻¹)	4.400
Transmission	0.649-0.970
Number of reflections measured	7767
Number of unique reflections	6179
R _{int}	0.023
$R^{a}(F, F > 4\sigma(F))$	0.040
$wR^{\rm b}$ (F^2 , all reflections)	0.098
Number of parameters	442
Number of restraints	0
S [°]	0.959
Max. $\Delta \rho$ (eÅ ⁻³)	1.81

^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b wR $(F^2) = [\Sigma \{w(F_o^2 - F_o^2)2\}/\Sigma \{w(F_o^2)^2\}]^{0.5};$ $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_o^2]/3$ and *a* and *b* are constants adjusted by the program.

^c $S = [\Sigma \{w(F_o^2 - F_o^2)^2\}/(n-p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.



2.1.2. $[MePh_2PCHPPh_2Me]CF_3SO_3$ (2)

As stated for (1) but adding drop by drop MeO₃SCF₃ instead of MeI till all the white solid has precipitated. Yield of 2: 65%. ¹H NMR: 8 7.8–7.2 (m, 20H, Ph), 2.04 (d, 6H, ${}^{2}J_{HP} = 12.3$, Me–P), 1.30 (t, 1H, ${}^{2}J_{HP} = 5.6$ Hz, P–CH–P); ${}^{31}P{}^{1}H{}$ NMR: δ 16.5. Anal. Calc. C₂₈H₂₇F₃O₃P₂S: C, 59.8; H, 4.85;S, 5.7. Found: C, 60.0; H, 4.65; S, 5.55.

2.2. Preparation of the gold(I) complexes

2.2.1. $[Au{CH(PPh_2Me)_2}X]CF_3SO_3; X=Cl (3), C_6F_5$ (4)

To a dichloromethane solution (20 ml) of 2 (0.11 g, 0.2 mmol) was added 0.2 mmol of [AuX(tht)] (X=Cl 0.064 g, C6F5 0.09 9) [15,16]. The mixture was stirred for 90 min, then concentrated to ca. 5 ml and the addition of diethyl ether (15 ml) afforded complexes 3-4 as white solids, which were washed with diethyl ether $(3 \times 5 \text{ ml})$. Yield of (3): 88%. ¹H NMR: 67.8–7.2 (m, 20H, Ph), 4.66 (t, 1H, ${}^{2}J_{HP} = 16.8$, P–CH–P), 2.14 (d, 6H, ${}^{2}J_{HP} = 12.4$ Hz, Me–P); ${}^{31}P{}^{1}H}$ NMR: δ 22.1. Anal. Calc. C₂₈H₂₇CIF₃O₃P₂SAu: C, 42.3; H, 3.4; S, 4.05. Found: C, 42.35; H, 3.75; S, 4.0. Yield of (4): 87%. ¹H NMR: δ 7.8–7.2 (m, 20H, Ph), 4.28 (t, 1H, ${}^{2}J_{\text{HP}} = 16.7, \text{ P-CH-P}, 2.22 \text{ (d, 6H, } {}^{2}J_{\text{HP}} = 11.9 \text{ Hz},$ Me–P); ¹⁹F NMR: δ – 78.0 (s, 3F, CF₃), –117.0 (m, $2F_{o}$), -161.3 (t, $1F_{p}$), -164.8 (m, $2F_{m}$); ${}^{31}P{}^{1}H$ NMR: δ 22.7. Anal. Calc. C₃₄H₂₇F₈O₃P₂SAu: C, 44.1; H, 2.95; S, 3.45. Found: C, 44.35; H, 3.0; S, 3.3.

2.3. X-ray crystallography

The crystal was mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an Oxford low temperature attachment. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$). Scan type theta-2theta. Absorption correction was applied based on Ψ -scans. The structure was solved by the heavyatom method, and refined on F² using the program SHELXL-93 [17]. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table 1.

3. Results and discussion

3.1. Ligand synthesis

The phosphoranium salts were prepared following the Scheme 1. First it was carried out the reaction of bis(diphenylphosphino)methane (dppm) with MeI to give the monomethylated product. This compound was deprotonated in the presence of an excess of sodium hydride to afford a yellow solution of the mono-ylide



Scheme 2.



Fig. 1. Structure of the cation of complex 4 in the crystal with the numbering scheme. Radii are arbitrary; hydrogen atoms except at C1 are omitted for clarity.

Ph₂PCH=PPh₂Me, air and moisture sensitive, which had been already prepared by a transylidation reaction [14]. Ylides can be easily alkylated although a mixture of the C-alkylated and the P-alkylated derivatives are usually obtained [18,19]. The alkylation of our ylide affords purely the P-alkylated derivative, by using MeI or methyl triflate as reagents, which is probably due to the stability of the bisphosphonium fragment. Even by adding 100% excess of MeI the P-alkylated derivative was the only compound obtained. However the addition of methyltriflate to the ylide in a 2:1 molar ratio leads mainly to a mixture of the P-alkylated derivative (**2**) and the phosphonium salt PPh₂Me₂⁺ coming from the cleavage of (**2**).

These derivatives are air- and moisture-stable white solids at room temperature. The IR spectrum of (2) shows absorptions at 1266, 1222 and 638 cm⁻¹ from the triflate anion [20]. The ¹H NMR spectra of (1) and (2) are very similar showing a doublet around 2 ppm for the methyl group and a higher field triplet (about 1.35 ppm) for the methylide bridge. In the ³¹P{¹H} NMR spectra it can be observed, in both cases, a singlet at 16.5 ppm as expected for two equivalent phosphorus atoms.

These phosphoranium salts are very stable, which has been explained by the very weak nucleophilicity of the ylidic carbon which prevents nucleophilic substitution or addition reactions. In fact, typical Wittig reactions for these ylides are only known if hydrogen is replaced by fluor in the carbanion, that has been explained because fluor destabilizes negative charges in an alfa position [21,22]. That is why to our knowledge there is no metallic complexes containing the ligand $R_3P=CH-PR_3^+$. On the contrary and as stated before for the corresponding carbodiphosphorane ligands $R_3P=C=PR_3$, of which the ylidic carbon is a stronger nucleophile, coordination compounds are well known, although most of them are only mononuclear C-coordinated complexes. Reactions of ylides with electrophiles such as benzaldehyde, acetyl chloride, benzoyl chloride, benzyl chloride and carbon disulfide gave no reaction.

3.2. Gold(I) complexes synthesis

We have previously reported several gold(I) complexes with C-coordination to ylides coming from the dppm [23]. For instance we have prepared the corresponding C-bonded gold complexes by coordination to $[Au(C_6F_5)SPPh_2CH(PPh_2Me)]$ [24] or to $[Au(C_6F_5)-PPh_2CH(PPh_2Me)]$ [25] which are very close to ligands **1–2** (equals by substituting the P- or S-coordinated gold(I) fragment for methyl) and they also are very stable ylides. Therefore we carried out the same reactions between the phosphoranium salts **1–2** and gold(I) complexes (see Scheme 2). The reactions evolve with displacement of tetrahydrothiophene (tht) to afford complexes **3–4** as white solids air and moisture stable.

Their IR spectra show absorptions at 335 cm⁻¹ (3) due to v(Au-Cl) [26], 955 and 797 cm⁻¹ from the pentafluorophenyl groups (4) [27], and 1265, 1222, 638 (3), 1250,1224 and 638 cm⁻¹ (4) from triflate anions. The ¹H NMR spectra show an almost unchanged doublet around 2.1 ppm for the methyl group and a triplet at 4.66 ppm for (3) and 4.28 ppm for (4) due to the methylide bridge, clearly low-field shifted from (2) ($\Delta\delta$ is 3.36 ppm for (3) and 2.98 ppm for (4)). The ${}^{31}P{}^{1}H{}$ NMR spectra show a singlet around 22 ppm and again about 6 ppm low-field shifted after gold coordination. The ¹⁹F NMR spectrum of (4) shows the pattern of a pentafluorophenyl group besides of the triflate counterion. The LSIMS mass spectra show the base peak at m/z = 413 due to the bis(phosphonium)methylide ligand and at 645 (20%, for (3)) and at 777 (65%, for (4)) corresponding to $[M-CF_3SO_3]^+$.

3.3. Crystal structure of $[Au{CH(PPh_2Me)_2}(C_6F_5)]CF_3SO_3$

The structure of the cation is shown in Fig. 1, with selected bond lengths and angles in Table 2. It consists of a gold(I) center bonded to two kinds of carbon atoms, one coming from a pentafluorophenyl group and the other from an ylidic ligand. Both distances Au–C are very different; Au^I–C₆F₅ is 2.029(6), which is of the same order as that found in related complexes such as $[Au(C_6F_5)_2{(PPh_2)_2CH}Au(C_6F_5)]$ (2.048(8) Å)

Table 2 Selected bond lengths (Å) and angles (°) for complex ${\bf 4}$

Au(1)–C(2)	2.029(6)	P(1)-C(21)	1.795(6)
Au(1)–C(1)	2.112(6)	P(1)-C(11)	1.799(7)
C(1)–P(2)	1.781(6)	P(2)-C(9)	1.794(7)
C(1)–P(1)	1.792(6)	P(2)-C(41)	1.794(7)
P(1)-C(8)	1.788(7)	P(2)-C(31)	1.797(7)
C(2)-Au(1)-C(1)	175.9(2)	C(1)-P(2)-C(31)	106.6(3)
P(2)-C(1)-P(1)	119.1(3)	C(9)–P(2)–C(31)	106.6(3)
P(2)-C(1)-Au(1)	109.1(3)	C(41)–P(2)–C(31)	110.4(3)
P(1)-C(1)-Au(1)	105.7(3)	C(16)–C(11)–P(1)	121.2(5)
C(8) - P(1) - C(1)	111.4(3)	C(12)-C(11)-P(1)	119.9(7)
C(8)–P(1)–C(21)	108.5(3)	C(22)–C(21)–P(1)	123.2(5)
C(1)–P(1)–C(21)	112.6(3)	C(26)–C(21)–P(1)	118.1(5)
C(8)–P(1)–C(11)	108.9(4)	C(36)-C(31)-P(2)	119.7(5)
C(1)–P(1)–C(11)	108.4(3)	C(32)-C(31)-P(2)	121.3(6)
C(21)–P(1)–C(11)	107.0(3)	C(42)-C(41)-P(2)	120.7(5)
C(1)–P(2)–C(9)	112.3(3)	C(46)-C(41)-P(2)	119.9(5)
C(1)–P(2)–C(41)	111.8(3)	C(3)-C(2)-Au(1)	125.9(5)
C(9)-P(2)-C(41)	109.0(4)	C(7)–C(2)–Au(1)	120.3(5)

[(F₅C₆)AuCH(PPh₂AuPPh₂)₂CHAu(C₆F₅)] [28] or (2.012(13) Å) [29] or to the one for the Au–C₆F₅ group trans to the ylidic carbon in [(F₅C₆)AuPPh₂CH- $(PPh_2Me)Au(C_6F_5)$] (2.011(11) Å) [25]. In the latter the Au– C_6F_5 distance *trans* to the phosphorus ligand is longer, 2.053(15) Å, as corresponds to the higher trans influence of the phosphine ligand. The Au-C_{vlidic} bond length is 2.112(6) Å and the value agrees well with those in the complexes mentioned. The gold atom displays an almost linear coordination (175.9(2)°). There are not short gold-gold interactions presumably because steric effects of the bulky ligand prevent the intimate approach required for metal-metal contacts, as have been observed for other complexes with crowded ligands [30].

The P–C_{ylidic} bond lengths are 1.781(6) and 1.792(6) Å, far from those found in MePPh₂P=C=PPh₂Me (1.645 Å) [31,32] or in [Au(C₆F₅)PPh₂CH(PPh₂Me)] [25] (1.692 Å), as expected because of the absence of double bond character in complex **4**. In fact the distances compare well with the other P–C single bond lengths found in the ligand (from 1.788(7) to 1.799(7) Å), although they are shorter than those reported in [PPh₃CH₂PPh₃]-[FeCl₄] (1.822(4) and 1.816(4) Å) [33].

The P–C–P angle is 119.1(3)°, slightly smaller than that found in MePPh₂P=C=PPh₂Me (121.8°) or [Au(C₆F₅)PPh₂CH(PPh₂Me)] (126.0(4)°) due to hybridization state, also smaller than that found in [PPh₃CH₂PPh₃][FeC1₄] (123.4(2)°), probably because of electrostatic repulsion in the latter [33] but bigger than that in [(F₅C₆)AuPPh₂CH(PPh₂Me)AuC₆F₅] 114.9(6)° presumably because the major steric repulsion of an Au– C_6F_5 unit compared to a methyl group. The P–C–Au angles, 109.1(3) and 105.7(3)°, are close to a tetrahedral disposition.

4. Supplementary material

Crystallographic data for complex **4** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 141436. Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1123-336033; e-mail: deposit @ccdc. cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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