cis-[Chlorotriphenylarsinopalladium(I)-(μ-carbonylo)chlorotriphenylarsinopalladium(I)] as a new arsenic-containing catalyst

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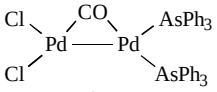
The title compound was synthesised and found to exhibit catalytic activity in acetylene alkoxycarbonylation.

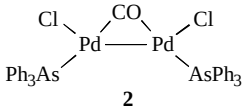
In contrast to tertiary phosphines, analogous arsenic derivatives are rarely used as ligands of homogeneous metal complex catalysts.[1,2] However, the synthesised *cis*-[chlorotriphenylarsinopalladium(I)-(μ-carbonylo)chlorotriphenylarsinopalladium(I)] [Pd($AsPh_3$)Cl](CO)[Pd($AsPh_3$)Cl] exhibits a reasonably high catalytic activity in acetylene alkoxycarbonylation even under mild conditions (at room temperature and atmospheric pressure).

It is well known that a number of products are formed in the course of acetylene alkoxycarbonylation. In particular, with the use of *n*-butanol as a reactant (in addition to acetylene and CO), corresponding mono- and diesters, primarily, butyl acrylate, butyl propionate, dibutyl maleate, dibutyl fumarate and dibutyl succinate, are formed. Coordination compounds of palladium(II) with phosphorus-donor ligands, in particular, phosphines, catalyse this reaction.[3] However, the experimental data on the kinetics of alkoxycarbonylation of acetylene in the presence of these compounds indicate that phosphine complexes of palladium(I) (which can be formed in the redox reaction $Pd^{II} \rightarrow Pd^{I}$ by the action of C_2H_2 or CO) rather than the above compounds actually serve as catalysts.[3] In this connection, it may be expected that not only arylphosphine complexes of palladium(I) but also coordination compounds of palladium(I) with arylarsines will be effective catalysts of acetylene alkoxycarbonylation. Complexes of the type [Pd(PPh_3)Cl]$_2$(μ-CO) can be postulated as intermediates in the course of acetylene alkoxycarbonylation with the participation of [Pd(PPh_3)$_2$Cl$_2$], one of the most effective catalysts of this reaction. Thus, it is of interest to synthesise the analogous arsenic-containing compounds [Pd($AsPh_3$)Cl]$_2$(CO) and to test them as catalysts of the above reaction.

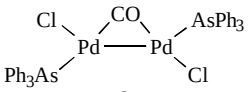
Theoretically, the compound [Pd($AsPh_3$)Cl]$_2$(CO) can exist in three isomeric forms as shown in structures **1**–**3** below where the arrangement of the $AsPh_3$ and Cl ligands differ:



1



2



3

The carbonyl chloride complex $H_2[Pd_2(CO)_2Cl_4]$ served as the starting compound for the synthesis of these isomers. This complex was prepared according to the reaction

$$2PdCl_2 + 3CO + H_2O \rightarrow H_2[Pd_2(CO)_2Cl_4] + CO_2.$$

In so doing, carbon monoxide was passed through a solution of 0.5 g of $PdCl_2$ in 20 ml of 36% HCl at 298–300 K and p = 1 atm for 8–10 h until the colour change of the solution from dark cherry to light green and the appearance of elemental palladium traces. The elemental palladium was separated from the solution by filtration through a glass filter in a mixed atmosphere of argon and CO. Isomers **1** and **2** were synthesised by partial replacement of acid ligands in $H_2[Pd_2(CO)_2Cl_4]$ by triphenylarsine (in the molar ratio 1:1.5) in an argon atmosphere at 20 °C and pressure p = 1 atm. The reaction was performed in hydrochloric acid or an equimolar mixture of hydrochloric and acetic acids to prepare **1** or **2**, respectively:

$$H_2[Pd_2(CO)_2Cl_4] + 2AsPh_3 \xrightarrow{HCl} \mathbf{1} + 2HCl + CO \quad (1)$$

$$H_2[Pd_2(CO)_2Cl_4] + 2AsPh_3 \xrightarrow{AcOH + HCl} \mathbf{2} + 2HCl + CO \quad (2)$$

The precipitated products were separated on a glass filter in an argon atmosphere and washed with fivefold volumes of HCl or AcOH + HCl (in the case of **1** or **2**, respectively) to remove triphenylarsine and with twice distilled water to remove acid ions. The yields of the target products were 85 and 90%, respectively. We failed to obtain isomer **3**, and this compound was not described in the literature. According to the data of cryoscopy (in benzene solutions) and mass spectrometry, the molecular weights of **1** and **2** are 930–940; these values are close to 930 calculated for [Pd($AsPh_3$)Cl]$_2$(CO). Indeed, the chemical analysis data suggest that the empirical formula of **1** and **2** is $Pd_2As_2C_{37}H_{30}OCl_2$.† These compounds are diamagnetic and exhibit no EPR signals at both room temperature and 77 K. The IR spectra of **1** and **2** exhibit bands at (1855, 1895) and (1860, 1890) cm^{-1} associated with ν(CO) for the bridging carbonyl group. The XPS spectrum of **1** exhibits two lines at 337.1 and 338.1 eV, which correspond to the Pd $3d_{5/2}$ signals for Pd^0 and Pd^{II}, respectively, whereas the spectrum of **2** exhibits a symmetrical line at 337.7 eV, which correspond to the Pd $3d_{5/2}$ signal for Pd^I (according to the published data,[4–6] the Pd $3d_{5/2}$ signal is observed at 335.8–337.2, 337.5–337.9 and 338.1–338.9 eV in the presence of Pd^0, Pd^I and Pd^{II}, respectively). Thus, the palladium atoms in **1** are non-equivalent, whereas the palladium atoms in **2** are equivalent to one another. According to ^{75}As NMR data, compound **1** shows two separate signals while compound **2** shows one. This fact indicates that the arsenic atoms in the former compound are non-equivalent to one another, whereas in the latter, they are equivalent. Thus, the above data suggest that in **1** both of the triphenylarsine molecules are coordinated to one palladium atom, whereas the triphenylarsine molecules are coordinated to both of the palladium atoms in **2**. The electric dipole moments for **1**, **2** and **3** can be theoretically predicted to be approximately equal to 8–10, 4–5 and 1–2 D, respectively. We found that the electric dipole moments for **1** and **2** in benzene are 9.5 and 4.8 D, respectively. In this connection, we can suggest that **1** is triphenylarsinopalladium(0)-(μ-carbonylo)-dichloropalladium(II) [Pd($AsPh_3$)$_2$](CO)[$PdCl_2$], whereas **2** is *cis*-[chlorotriphenylarsinopalladium(I)-(μ-carbonylo)-chlorotriphenylarsinopalladium(I)] [Pd($AsPh_3$)Cl](CO)[Pd($AsPh_3$)Cl]. Unfortunately, we failed to prepare **1** and **2** as single crystals suitable for X-ray diffraction analysis. Moreover, the compounds were rapidly decomposed under exposure to X-rays. Therefore, we cannot determine the crystal and molecular structure of compounds **1** and **2**.

Compounds **1** and **2** were tested as acetylene alkoxycarbonylation catalysts in a well-stirred reactor thermostatically controlled with the use of a UR-20 thermostat. A required amount of the test complex, 3.35 ml of DMF and 1.65 ml of a 0.4 M HCl solution in butan-1-ol were added to the reactor in an argon flow, and the reaction mixture was stirred for 5 min at a constant temperature (298, 323 or 343 K). A gas mixture containing

† For **1** found (%): Pd, 22.6; C, 49.0; As, 16.3; H, 3.1; Cl, 7.8. For **2** found (%): Pd, 22.8; C, 48.9; As, 16.0; H, 3.2; Cl, 7.6. Calc. for $Pd_2As_2C_{37}H_{30}OCl_2$ (%): Pd, 23.02; C, 49.10; As, 16.23; H, 3.23; Cl, 7.68.

equimolar amounts of C_2H_2 and CO (p = 1 atm) was fed into the reactor. The reaction products were analysed by gas chromatography. Table 1 summarises the experimental results.

Note that isomer **2** exhibits a reasonably high catalytic activity in acetylene alkoxycarbonylation, whereas isomer **1**, as well as all known arsenic compounds, inhibits this reaction to some extent. In this case, the catalytic activity of *cis*-[Pd($AsPh_3$)Cl](CO)[Pd($AsPh_3$)Cl] is pronounced even under mild conditions (298 K, 1 atm), and it somewhat decreased with increasing temperature. It should be noted that the acetylene alkoxycarbonylation catalysed by compound **2** at 298 K is highly selective for *n*-butyl acrylate (80%), whereas diesters were not formed at all. The surprising thing is that the catalytic activity of **2** in this reaction is much higher than that of the phosphorus-containing analogue *cis*-[Pd(PPh_3)Cl](CO)[Pd(PPh_3)Cl]. In this connection, we can suggest the following. It is well known that the phenyl fragment can coordinate to the Pd–Pd bond as a π-ligand[3] (as evidenced by a considerable broadening of the band due to phenyl protons in the ^{1}H NMR spectra of **1** and **2** to 1.0 ppm as compared with uncoordinated $AsPh_3$). Thus, two phenyl fragments can be coordinated to the Pd–Pd bond in isomers **1** and **3**, whereas only one phenyl fragment can be coordinated in **2**. Because of this, we can expect that the Pd–Pd bonds in compounds **1** and **3** will be completely blocked by phenyl groups; however, the corresponding bond in **2** will be accessible to the coordination of other molecules. It is also well known[3] that the coordination of acetylene molecules to the Pd–Pd bond takes place in the alkoxycarbonylation of acetylene with the participation of Pd^I and Pd^0 compounds, and this process is responsible for the catalytic activity. Thus, we may expect that compound **1**, as well as hypothetical compound **3**, will be inactive in this reaction, whereas **2** will exhibit somewhat activity. In the case of arsenic-containing ligands, the coordination of the C_2H_2 molecule during a nucleophilic attack on the Pd–Pd unit is more favourable than that in the case of analogous phosphorus-containing ligands because the electron pair in As^{III} is more diffuse[1,2] and, as a consequence, the Pd–As distance is longer than the Pd–P bond length; thus, the catalytic activity of arsenic-containing palladium complexes is higher than that of phosphorus-containing palladium complexes. However, this explanation is only a hypothesis, which needs further investigation.

Table 1 Catalytic activity of phosphinic and arsinic palladium complexes.

Compound	Reaction temperature/K	Rate of formation/ mol dm^{-3} h^{-1}	
		Monoesters	Diesters
cis-[Pd($AsPh_3$)Cl](CO)[Pd($AsPh_3$)Cl] **2**	298	0.170	0.000
	323	0.120	0.010
	343	0.106	0.035
[Pd($AsPh_3$)$_2$](CO)[$PdCl_2$] **1**	298	0.001	0.000
	323	0.000	0.000
	343	0.000	0.000
cis-[Pd(PPh_3)Cl](CO)[Pd(PPh_3)Cl]	298	0.120	0.003
	323	0.115	0.008
	343	0.108	0.015
[Pd(PPh_3)$_2$$Cl_2$]	298	0.024	0.061
	323	0.110	0.104
	343	0.152	0.129
[Pd($AsPh_3$)$_2$$Cl_2$]	298	0.004	0.000
	323	0.002	0.000
	343	0.000	0.000

In all cases, the catalyst concentration was 0.05 mol dm^{-3}.

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