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Complex of tris(*Z*-styryl)phosphine with PdCl₂ as a new catalyst for the Sonogashira reaction

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The complex [(*Z*-PhCH=CH)₃P]₂PdCl₂ synthesized from tris(*Z*-styryl)phosphine and PdCl₂ (DMF, 90 °C, 15 min, yield 50%) is an active catalyst in the Sonogashira reaction (coupling between 1-ethynyl-4-nitrobenzene and 1-iodoanthra-9,10-quinone) and its activity is comparable with that of the complex [Ph₃P]₂PdCl₂, the most common catalyst for this type of reactions.

The Pd–Cu-promoted coupling (the Sonogashira reaction) of terminal acetylenes with haloaromatics and haloheteroaromatics has become a powerful tool in modern organic synthesis.¹ Now, it is a common place that the outcome of the reactions (yield, chemo-, regio- and stereodirection, *etc.*) depends strongly on the ligand structure of the catalytic complexes.^{1(b),2} Consequently, special efforts are currently focused on the search for new ligands, particularly bulky ones³ allowing more efficient and available catalysts for the Sonogashira coupling to be designed.

The most common catalyst for this reaction remains the complex of triphenylphosphine with PdCl₂.^{1,2(a)} Preparation of this ligand is usually based on hazardous PCl₃ or POCl₃ and sodium metal or corresponding organomagnesium derivatives under an inert atmosphere. Therefore, alternative more accessible and save in preparation tertiary phosphines, particularly those having new possibilities to be employed as ligands for catalyst design, are always desirable.

Previously, we have developed a one-pot stereoselective synthesis of tris(*Z*-styryl)phosphine **1** directly from elemental phosphorus and acetylene in the superbase system KOH–HMPA, the yield being up to 55%.⁴ Later,⁵ phosphine **1** was synthesized by the addition of phosphine gas (easily generated from phosphorus red and KOH in the H₂O–toluene system) to phenylacetylene in the superbase system KOH–HMPA in 80% yield. Thus, tris(*Z*-styryl)phosphine is now one of the most available tertiary phosphine, vinyllog of triphenylphosphine, the most applicable ligand in the Sonogashira coupling. The vinyllog

suggests a close likeness in properties of both ligands. One may just wonder why tris(*Z*-styryl)phosphine waited so long to be tried as a ligand to prepare catalysts for the Sonogashira type reaction.

In this work, we synthesized complex **2** of tris(*Z*-styryl)phosphine with PdCl₂ and checked its activity in the Sonogashira coupling. The preparation of complex **2** was carried out by heating (90 °C, 15 min) phosphine **1** with PdCl₂ in DMF, the molar ratio PdCl₂:phosphine **1** being 1:2 (Scheme 1).[†]

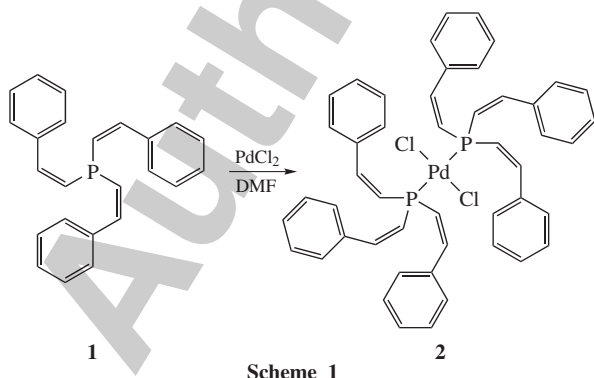
According to X-ray analysis[‡] (Figure 1), complex **2** has the structure of *trans*-bis[tris(*Z*-styryl)phosphino]palladium dichloride. The coordination surroundings and geometry of the complex are usual. The styryl moieties are non-planar, the torsion angles between the double bond and benzene ring planes are 22.6–60.9°.

Previously,⁶ the reaction of phosphine **1** with PdCl₂[–] in aqueous alcohol in the presence of HCl was reported to afford a complex having the composition similar to that of complex **2**; however, no X-ray structure was given. The complex was characterized only by IR and ¹H NMR (200 MHz) spectra and elemental analysis, mp (166 °C) being significantly different from that of complex **2**.

[†] *trans*-[Tris(*Z*-styryl)phosphino]palladium dichloride **2**. A mixture of PdCl₂ (0.25 mmol) and tris(*Z*-styryl)phosphine (0.5 mmol) in 2 ml of DMF was stirred at 90 °C for 15 min until PdCl₂ was dissolved. Hot solution was filtered through dense funnel. After cooling, yellow precipitate was washed with benzene to give complex **2**, yield 50%, mp 188.5–189.5 °C. ¹H NMR (Bruker AV-300, 300.13 MHz, CDCl₃) δ: 6.26 (dt, 6H, =CHPh, ³J_{HH} 13.0 Hz, ³J_{HP} 10.1 Hz, virtual coupling⁷), 6.82 (dt, 6H, =CH–P, ³J_{HH} 13.0 Hz, ²J_{HP} 18.4 Hz, virtual coupling⁷), 7.13–7.22 (m, 18H, *m*-H_{Ph}, *m'*-H_{Ph}, *p*-H_{Ph}), 7.33 (m, 12H, *o*-H_{Ph}, *o'*-H_{Ph}). IR (Bruker Vector-22, KBr pellets, ν/cm^{–1}): 1443, 1490, 1592 [C=C(Ph)], 1610 (C=C), 2996, 3025 [=CH(Ph)], 3050 (=CH).

[‡] *Crystallographic data for 2*: C₄₈H₄₂Cl₂P₂Pd, *M* = 858.06. Bruker P4 diffractometer [graphite monochromator, λ(MoKα) = 0.71073 Å, 296 K, ω-scanning, 2θ < 52°]. Orthorhombic system, space group *P*2₁2₁2₁, *a* = 12.204(2), *b* = 12.625(2), and *c* = 26.877(5) Å, *V* = 4141(1) Å³, *Z* = 4, *d*_{calc} = 1.376 g cm^{–3}, μ = 0.687 mm^{–1}, *R*₁ = 0.0654 [2221 reflections with *I* ≥ 2σ(*I*)], *wR*₂ = 0.1123 (all 4539 reflections), *S* = 0.998. All H atoms were positioned geometrically and refined in riding model. Empirical absorption correction was applied (transmission 0.89–0.99).

CCDC 706178 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.



Scheme 1

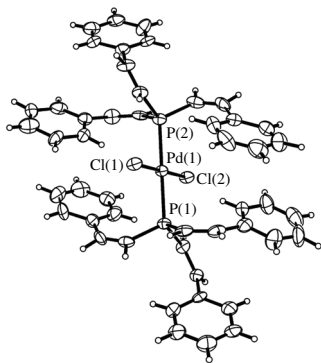
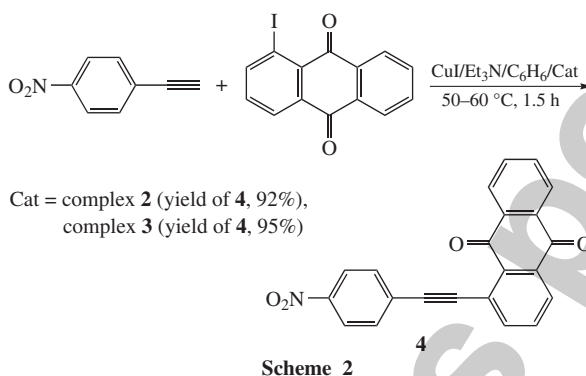


Figure 1 Molecular structure of complex **2** in a crystal (thermal ellipsoids are drawn at 30% probability level). Selected bond lengths (Å): Pd–Cl 2.309(2), 2.311(2), Pd–P 2.336(2), 2.347(2), P–C 1.802(8)–1.831(9); selected bond angles (°): Cl–Pd–Cl 179.86(9), P–Pd–P 179.72(8), Pd–P–C 111.6(3)–115.3(3), C–P–C 99.7(3)–108.3(4).

The Sonogashira reaction has been performed using the published results^{1(b)} concerning the coupling between 1-ethynyl-4-nitrobenzene and 1-iodoantra-9,10-quinone in the presence of complex **2** and complex $[\text{Ph}_3\text{P}]_2\text{PdCl}_2$ **3** leading to 1-[2-(4-nitrophenyl)ethynyl]antra-9,10-quinone **4** (Scheme 2).[§]

Addition of triphenylphosphine to the reaction mixture often favors the Sonogashira coupling.^{1(b)} In the case of complex **2**, the response to such an addition turned out to be much more pronounced than in the reaction with complex **3**: the synthesis was more than six times faster, as compared to that using a traditional catalyst.[¶] The substitution of triphenylphosphine for phosphine **1** is unreasonable since this decreases the efficiency of the reaction studied.



[§] Coupling of 1-ethynyl-4-nitrobenzene with 1-iodoantra-9,10-quinone in the system $\text{CuI}/\text{Et}_3\text{N}/\text{Cat}$. A mixture of 1-ethynyl-4-nitrobenzene (2.5 mmol), 1-iodoantra-9,10-quinone (2.5 mmol), CuI (0.015 mmol), Et_3N (7 mmol) and Cat (0.007 mmol of complex **2** or **3**) in 7 ml of benzene was stirred under an argon atmosphere at 50 °C (1 h) and at 60 °C (0.5 h). The reaction mixture was cooled and filtered through alumina (2.5×10 mm), eluted with toluene (40 ml). The solvents were evaporated under reduced pressure, and residue was recrystallized from toluene to give compound **4** in 92% (when complex **2** was used) and 95% (in the case of complex **3**) yields, mp 214–215 °C (lit.,⁸ 214–215 °C).

As follows from the results obtained, complex **2** when applied as a catalyst in the Sonogashira reaction has exhibited a very similar activity compared to that of complex **3**.

In conclusion, the Pd complex with tris(*Z*-styryl)phosphine, $[(\text{Z}-\text{PhCH}=\text{CH})_3\text{P}]_2\text{PdCl}_2$ was for the first time shown to be a promising catalyst for the Sonogashira coupling. Its easy accessibility makes this complex a probable alternative to the traditional catalyst $[\text{Ph}_3\text{P}]_2\text{PdCl}_2$ for this type of reactions.

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[¶] Coupling of 1-ethynyl-4-nitrobenzene with 1-iodoantra-9,10-quinone in the system $\text{CuI}/\text{Et}_3\text{N}/\text{Ph}_3\text{P}/\text{Cat}$. The coupling reaction in the presence of Ph_3P (0.014 mmol) was carried out according to the procedure described above,[§] the yields of compound **4** being 95% when complex **2** was used [at 50 °C (1 h) and at 60 °C (0.5 h)] and 90% in the case of complex **3** [at 50 °C (1 h) and at 60 °C (8 h)].