ELSEVIER

Journal of Organometallic Chemistry 535 (1997) 77–79

Journal of Organometallic Chemistry

Palladium-catalysed mild transformation of non-activated terminal alkynes into acetals [1]

Christoph Scheffknecht, Paul Peringer *

Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Received 24 September 1996; revised 3 December 1996

Abstract

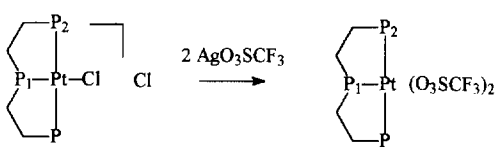
$Pd(pp_2)$ $(O_3SCF_3)_2$ (pp_2 = bis(2-diphenylphosphinoethyl)phenylphosphine) catalyses the transformation of non-activated terminal alkynes into acetals. The reaction proceeds fast, without the addition of heat and in quantitative yield. σ-Alkynyl-palladium complexes have been identified as intermediates. © 1997 Elsevier Science S.A.

1. Introduction

The transformation into acetals is a useful functionalization of alkynes, and a variety of catalysts for this reaction have been studied. We report here on a catalytic system for the rapid transformation of terminal non-activated alkynes into acetals, without the addition of heat and in quantitative yield. Previously reported catalysts are acids and bases, mercury(II)- and copper(I)-salts, $PtCl_2$, PtI_4, osmium- and rhodium-halides [1]. A recent report describes $NaAuCl_4$ as catalyst to be effective for non-activated alkynes [2]. The related intramolecular reactions of β, γ, and δ hydroxyalkynes leading to dihydrofuranes and dihydropyranes are catalysed by $PdCl_2$, $PdCl_2(PhCN)_2$ [3] and $PdCl_2(PPh_3)_2$–CuI [4].

2. Results and discussion

The catalyst $Pd(pp_2)(O_3SCF_3)_2$ (pp_2 = $PhP(CH_2CH_2PPh_2)_2$) was prepared according to Eq. (1) and in good yield.



(1)

* Corresponding author.

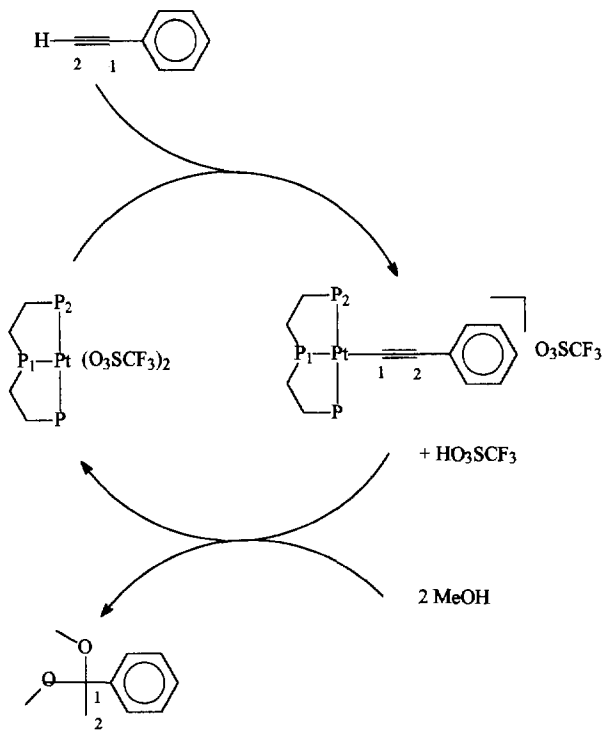
[1] Dedicated to Professor K.E. Schwarzhans on the occasion of his 60th birthday.

Treatment of phenylacetylene with $Pd(pp_2)(O_3SCF_3)_2$ in a ratio of 429/1 in MeOH or MeOH–$CHCl_3$ produces acetophenone dimethylacetal. The reaction proceeds fast (approximately 30 min), without addition of heat and in quantitative yield. After this, the catalyst is still active and may be used for repeat batches of phenylacetylene. In a solution of the catalyst in MeOH–$CHCl_3$ the catalytically inactive complex $[Pt(pp_2)Cl]^+$ is partially formed within a few days. $[Pt(pp_2)Cl]^+$ was identified according to its ^{31}P NMR data [5] and may be converted to the catalyst by use of AgO_3SCF_3. According to ^{31}P NMR spectroscopy, a σ-alkynyl complex is formed as intermediate as shown in Scheme 1. This complex is transformed into acetophenone dimethylacetal under the conditions mentioned above, but is stable when the reaction is carried out in acetone. The σ-alkynyl complex was isolated as tetraphenylborate and characterized by elemental analysis and NMR spectroscopy. The most characteristic features are the multiplicities of the acetylenic carbon atoms being split into doublets of triplets by the phosphorus atoms of the pp_2 ligand.

Along with the σ-alkynyl complex equimolar amounts of trifluoromethanesulfonic acid are formed, as indicated in Scheme 1. This acid is essential for the transformation of phenylacetylene into acetophenone dimethylacetal because the σ-alkynyl complex is stable in MeOH–$CHCl_3$ when trifluoromethanesulfonic acid is absent.

Since the trifluoromethanesulfonic acid is formed along with the σ-alkynyl complex and consumed during

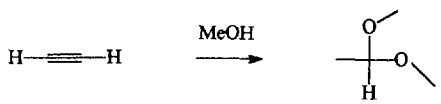
PII S0022-328X(96)06955-0



Scheme 1.

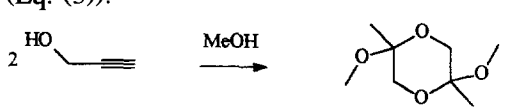
the regeneration of the catalyst, the appearance of the acid is limited in time to the actual reaction. Treatment of phenylacetylene in MeOH with trifluoromethanesulfonic acid instead of the catalyst in the same ratio of 429/1 showed no effect. Higher concentrations of trifluoromethanesulfonic acid caused a mixture of products, which was not identified. The reaction of $Pd(pp_2)(OAc)_2$ with phenylacetylene results in the σ-alkynyl complex $[Pd(pp_2)(C_2Ph)](OAc)$ which is however not converted into acetophenone dimethylacetal. This indicates that acetic acid which is formed along with the σ-alkynyl complex does not mediate the transformation.

Similarly, acetaldehyde dimethylacetal is formed, when acetylene is absorbed in a solution of the catalyst in MeOH–$CHCl_3$ (Eq. (2)).



(2)

Propynol is quantitatively transformed under similar conditions into 2,5-dimethoxy-2,5-dimethyl-1,4-dioxane (Eq. (3)).



(3)

Reactions with 0.2 mol% of the catalyst are finished within a few minutes. Only one species seems to be present according to NMR spectroscopy (see Section 3), but it has not been determined whether the cis- or trans-species is formed. In pure MeOH hydroxyacetone dimethylacetal is formed in a 1/1 mixture with the dioxane. Removal of the methanol left the pure dioxane.

The dioxane was previously synthesized with HgO–$BF_3 \cdot Et_2O$ as catalyst [6].

The catalyst $Pd(pp_2)(O_3SCF_3)_2$ appears to be ineffective for the transformation of 1,2-disubstituted acetylenes because 1,2-diphenylacetylene is recovered unchanged. This is in keeping with the mechanism proposed in Scheme 1, because it is impossible for the trifluoromethanesulfonic acid and the σ-alkynyl complex to be formed.

3. Experimental section

The NMR spectra were recorded on a Bruker AC 200 instrument. MS data were recorded on a Varian Mat CH7. Elemental analyses were performed by the Institut für analytische Chemie, Universität Wien. $Pd(pp_2)Cl_2$ was prepared according to the literature [7].

The transformations of the alkynes into the corresponding acetals were monitored by NMR spectroscopy. After the reaction times stated, no alkynes could be detected and the acetals were the sole products present. All products have previously been described in the literature and, except for 2,5-dimethoxy-2,5-dimethyl-1,4-dioxane, the products were not isolated. The identity of the products has been established by ^1H and ^{13}C NMR spectroscopy. The recovery of the catalyst had been performed in the case of acetaldehyde dimethylacetal by removing the solvent and the product under reduced pressure.

3.1. Synthesis of the catalyst $Pd(pp_2)(O_3SCF_3)_2$

A sample of $Pd(pp_2)Cl_2$ (711.9 mg, 1.0 mmol) dissolved in $CHCl_3$ (2 ml) is added to a solution of AgO_3SCF_3 (514.0 mg, 2.0 mmol) in MeOH (0.5 ml). The resulting suspension is stirred for 5 min. The solid (AgCl) is removed and the solution is evaporated to dryness and the product residue is recrystallized from MeOH to yield colourless crystals in ca. 80% yield. Anal. calcd. for $C_{36}H_{33}F_6O_6P_3PdS_2$: C, 46.1; H, 3.54. Found: C, 46.4; H, 3.40. $^{31}P\{^1H\}$ NMR (81.015 MHz, $CDCl_3$–MeOH = 2:1): δ 116.0 (P_1, t, J(PP) 6.9), 52.0 ppm (P_2, d).

3.2. Synthesis of $[Pd(pp_2)(C_2Ph)]BPh_4$

Phenylacetylene (7.7 μl, 0.07 mmol) is added to a solution of $Pd(pp_2)(O_3SCF_3)_2$ (65.7 mg, 0.07 mmol) in 0.5 ml of dry acetone. After stirring for 5 min, 0.2 ml of water is added to precipitate $[Pd(pp_2)(C_2Ph)]O_3SCF_3$.

The solid is separated, washed with H_2O, dried in vacuo, and is redissolved in MeOH (0.4 ml) and added to a solution of $NaBPh_4$ (34.5 mg, 0.105 mmol) in MeOH (0.4 ml) to precipitate $[Pd(pp_2)(C_2Ph)]BPh_4$ which is separated, washed with H_2O and dried in vacuo. Pale yellow powder, yield almost quantitative.

Anal. calcd. for $C_{66}H_{58}BP_3Pd$: C, 72.6; H, 5.52. Found: C, 73.0; H, 5.47. ^{13}C NMR (50.328 MHz, $CDCl_3$): δ 106.8 (C_1, dt, $J(P_1C_1)$ 130.9, $J(P_2C_1)$ 13.8 Hz), 118.8 ppm (C_2, dt, $J(P_1C_2)$ 29.1 Hz, $J(P_2C_2)$ 3.2 Hz). $^{31}P\{^1H\}$ NMR (81.015 MHz, $CDCl_3$): δ 102.4 (P_1, t, J(PP) 16.9 Hz), δ 45.9 (P_2, d).

3.3. Synthesis of $[Pd(pp_2)(C_2Ph)]OAc$

A mixture of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol pp_2 (26.7 mg, 0.05 mmol) and $CHCl_3$ (0.5 ml) is stirred at ambient temperature for 5 min giving a dark red solution of $Pd(pp_2)(OAc)_2$. $^{31}P\{^1H\}$ NMR (81.015 MHz,): δ 108 (P_1, t, J(PP) 11 Hz), δ 49 (P_2, d). Methanol (0.5 ml) and phenylacetylene (5.5 µl, 0.05 mmol) is added and the solution is stirred for 5 min. The ^{31}P NMR data of $[Pd(pp_2)(C_2Ph)]$ (OAc) are essentially the same as of $[Pd(pp_2)(C_2Ph)]BPh_4$. According to ^{31}P NMR $Pd(pp_2)(OAc)_2$ and $[Pd(pp_2)(C_2Ph)](OAc)$ are formed quantitatively. The products were not isolated.

3.4. Transformation of phenylacetylene into acetophenone dimethylacetal

A sample of 0.5 ml (4.56 mmol, 429 meq) is syringed within 1 min into a solution of $Pd(pp_2)(O_3SCF_3)_2$ (10 mg, 0.0106 mmol) in MeOH (1 ml). The reaction is complete within 30 min. ^1H NMR (200.13 MHz, MeOH): δ 1.40 (CH_3), δ 3.05 (OCH_3), δ 7.05-7.40 (Ar). ^{13}C NMR (50.328 MHz, MeOH): δ 25.4 (CH_3), δ 48.0 (OCH_3), δ 101.2 (C_{quart}), δ 125.9, δ 127.1, δ 127.6 (C_{ar}), δ 142.1 (C_i).

3.5. Transformation of phenylacetylene into acetaldehyde dimethylacetal

A solution of $Pd(pp_2)(O_3SCF_3)_2$ (10 mg, 0.0106 mmol) in MeOH (1 ml) is stirred in a Schlenk tube under an atmosphere of acetylene. Within 8 h ca. 200 mol product are formed per mole of catalyst as estimated by the integration of the ^1H NMR spectra. The reaction times depend on the contact of the acetylene with the solution and were not optimized. ^1H NMR (200.13 MHz, MeOH): δ 1.20 (d, CH_3), δ 3.25 (OCH_3), δ 4.50 (q, CH). ^{13}C NMR (50.328 MHz, MeOH): δ 18.0 (CH_3), δ 52.0 (OCH_3), δ 101.0 (C_{quart}).

3.6. Transformation of 1-propinol into 2,5-dimethoxy-2,5-dimethyl-1,4-dioxane

A sample of 1-propinol (0.5 ml, 6.27 mmol, 592 meq) is syringed within 5 min into a solution of $Pd(pp_2)(O_3SCF_3)_2$ (10 mg, 0.0106 mmol) in a mixture of MeOH (0.2 ml) and $CHCl_3$ (0.3 ml). The reaction is complete within 10 min. The product precipitates as colourless crystals. M.p. 135 °C (m.p. 125-128 °C [6]) after sublimation. MS (m/z 70 eV) 176 (M^+), ^{13}C NMR (50.328 MHz, $CDCl_3$): δ 93.9 (C_q), δ 65.4 (CH_2), δ 47.8 (CH_3O), δ 18.8 (CH_3). ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.03 (s, 6H, CH_3), δ 3.07 s, 6H, CH_3O), δ 3.21 (d, 1H, CH_2, J(HH) 11.5 Hz, diastereotopic), δ 3.46 (d, 1H, CH, diastereotopic).

3.7. Formation of hydroxyacetone dimethylacetal

A sample 58 ml propinol (1.0 mmol, 20 meq) is added to a solution of $Pd(pp_2)(O_3SCF_3)_2$ (47 mg, 0.05 mmol) in MeOH. After 10 min ^{13}C NMR shows the presence of ca. 50% hydroxyacetone dimethylacetal besides 2,5-dimethoxy-2,5-dimethyl-1,4-dioxane. ^{13}C NMR (50.328 MHz, MeOH): δ 101.1 (C_q), δ 63.3 (CH_2OH), δ 47.6 (CH_3O), δ 18.9 (CH_3).

References

[1] H. Hagemann and D. Klamann, *Houben / Weyl, Methoden der Organischen Chemie*, Vol. E 14a, Thieme, Stuttgart, 1991, Part 1, p. 470ff.
[2] Y. Fukuda and K. Utimoto, *J. Org. Chem., 56* (1991) 3729.
[3] K. Utimoto, *Pure Appl. Chem., 55* (1983) 1845.
[4] S. Torii, L.H. Xu and H. Okumoto, *Synlett*, (1992) 515.
[5] R.B. King and J.C. Cloyd, *Inorg. Chem., 14* (1975) 1550.
[6] W. Reppe, *Justus Liebigs Ann. Chem., 596* (1955) 62.
[7] L.R. Gray, D.J. Gulliver, W. Levason and M. Webster, *J. Chem. Soc. Dalton Trans.*, (1983) 133.