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Journal of Organometallic Chemistry 558 (1998) 235–237

Journal of Organometallic Chemistry

Preliminary communication

Supported organometallic complexes XVI[1]
A T-silyl functionalized dppp palladium complex as a precursor for catalysis in interphases

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Received 12 November 1997

Abstract

The dppp ligand **4(T^0)** being provided with a T-silylfunctionalized $(CH_2)_6$ spacer in the symmetric position of the C3 bridge is obtained by a simple three step reaction starting with 2-hydroxymethyl-1-hydroxy-7-octene (**1**) (Scheme 1). **1** is chlorinated to the dichloride **2** which can be hydrosilylated with $HSi(OMe)_3$ to give **3(T^0)**. Finally both chlorine atoms in **3(T^0)** are exchanged by PPh_2. Treatment of $(COD)PdCl_2$ with **4(T^0)** results in the formation of the T-silylfunctionalized palladium complex **5(T^0)**.

Keywords: Phosphines; Immobilized complex; Palladium

1. Introduction

The application of hybrid organometallic catalysts has recently attracted much interest, since they combine both the advantages of homogeneous and heterogeneous catalysis [1,2]. In the concept of interphases, which we have recently introduced [1], the catalytically active center is incorporated in a stationary phase consisting of a swellable polymer, a spacer unit and the reactive organometallic complex. To achieve high mobility it is of importance in which way the spacer is connected to the complex center and the matrix. In this communication we want to introduce a modified bis (diphenylphosphino)propane ligand (dppp) carrying a T-silylfunctionalized spacer fragment in the symmetric position of the C3 bridge. Diphos ligands play an important role in several catalytic processes like hydroformylation [3] and CO/alkene copolymerization [4]. The functionalized ligand was introduced in a palladium complex.

2. Results and discussion

A suitable starting compound for the generation of the T-silylfunctionalized ligand **4(T^0)** is the diol **1** [5], since it already contains the main building blocks of **4(T^0)** (**T** denotes alkoxylsilanes with three Si–O bonds, the superscript denotes the number of Si–O–Si bonds). It can easily be chlorinated with $SOCl_2$ to the dichloride **2** with preservation of the terminal double bond. In the following step the hydrosilylation is successfully carried out by using hexachloroplatinic(IV) acid as a catalyst. Although trichlorosilane generally leads to higher yields [6,7], trimethoxysilane was employed, because the necessary alkoholysis would substitute all chlorine atoms. The reaction can easily be monitored ^{1}H-NMR spectroscopically, in the course of which the signals of the allylic groups disappear. Due to its T-silylfunction com-

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[1] Part XV, see Ref. [1].

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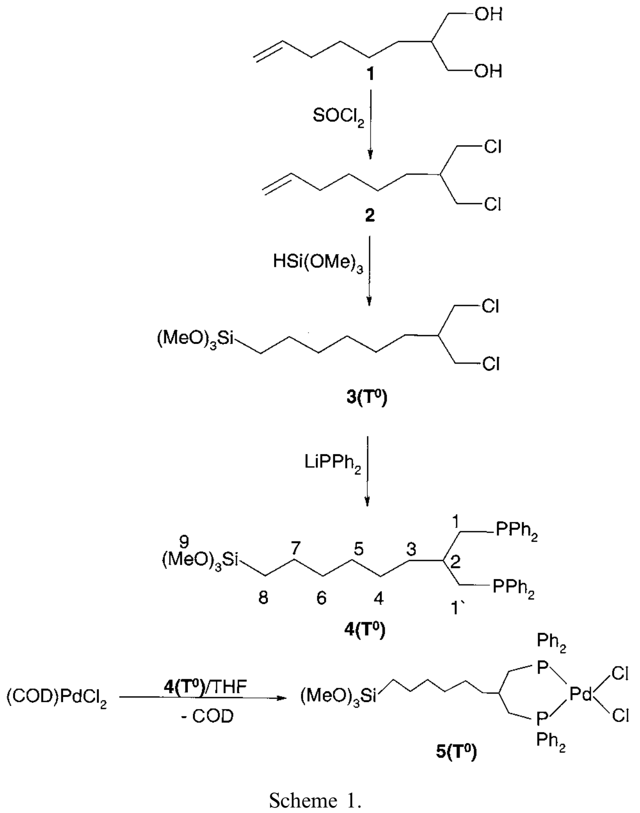
PII S0022-328X(98)00374-X

pound **3(T^0)** is sensitive toward moisture and must be handled under a dry inert gas atmosphere.

In a final step the colorless diphos ligand **4(T^0)** is obtained by treatment of **3(T^0)** with $LiPPh_2$ in THF. Because of the high boiling point (> 220°C in a vacuum of 0.5 mbar) and the presence of a T-silylfunction it is not possible to purify **4(T^0)** by distillation or chromatography. Therefore the crude product was extracted with *n*-pentane from the reaction mixture leading to a wax-like compound, which is sensitive toward air and moisture.

The substitution of the chlorines for diphenylphosphino groups leads to a splitting of the ^{13}C signals in the $^{13}C\{^1H\}$ NMR spectrum caused by the interaction of carbon atoms C1–C3 and those of the aromatic skeleton with the phosphorus nuclei. The C1 methylene groups and the ipso carbon atoms of the phenyl rings are magnetically inequivalent and give rise to AXX′ multiplet patterns.

The presented synthesis of diphos with a T-silylfunctionalized spacer unit is not only limited to obtain the ligand **4(T^0)**, it also allows several modifications, which we are currently working on: according to Scheme 1 it is possible to realize a general route for the access to diphos ligands with different spacer lengths and organophosphines. A variation of the substituents at both phosphorus atoms enables to select an electronic and stereochemical environment corresponding to the chosen transition metal complex. The chelating effect of the two phosphorus atoms reduces leaching and catalyst deactivation. In contrast to our previous work [1,2], the spacer unit was not attached directly to both phosphorus atoms. By connecting it with the symmetric position of the C3 bridge, the highest possible mobility of the ligand is guaranteed, since flexibility in the interphase strongly controls the catalytic activity of the reactive center.



Scheme 1.

Since cationic palladium dppp complexes play an important role in the alkene/CO copolymerization [4] the diphos ligand **4(T^0)** was reacted with $(COD)PdCl_2$ in THF. After a short time the T-silylfunctionalized palladium complex **5(T^0)** was obtained as a yellow highly viscous oil. The $^{31}P\{^1H\}$ NMR spectrum of **5(T^0)** displays the expected resonance at δ 18.7. The chemical shift corresponds well with that one of $(dppp)PdCl_2$ [8].

Further investigations are devoted to the catalytic activity of a cationic variant of complex **5(T^0)** in interphases and will be published elsewhere.

3. Experimental section

3.1. General remarks

All experiments were carried out under an atmosphere of argon, if not stated otherwise. Tetrahydrofuran, diethyl ether and *n*-pentane were distilled from sodium benzophenone ketyl. $PdCl_2$ was a gift from Degussa AG. $HSi(OCH_3)_3$ was obtained from Fluka. $(COD)PdCl_2$ [9] and the starting compound **1** [5] were prepared according to the literature. Elemental analyses were carried out on a Carlo Erba analyzer, model 1106; Cl analyses were carried out according to Dirschel and Erne [10] and Schöniger [11]. The high resolution $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 296 K. Frequencies and standards are as follows: $^{29}Si\{^1H\}$ NMR (DEPT45 pulse sequence): 49.69 MHz, $^{31}P\{^1H\}$ NMR: 101.25 MHz, and $^{13}C\{^1H\}$ NMR 62.90 MHz. Chemical shifts in the $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to DMS. Mass spectra were acquired on a Finnigan MAT 711A modified by AMD 'Meß- und Datensysteme' (8 kV, 303 K) and reported as mass/charge (*m*/*z*). The IR spectrum was measured on a Bruker IFS 48 instrument.

3.2. 2-chloromethyl-1-chloro-7-octene (*2*)

Under ambient atmosphere an excess of $SOCl_2$ (22.2 g, 186.8 mmol) was added dropwise at 0°C to 11.8 g (74.7 mmol) of 2-hydroxymethyl-1-hydroxy-7-octene (**1**). After stirring the solution over night at room temperature unreacted $SOCl_2$ was removed in vacuo. Distillation under vacuum gave 9.5 g (65.1%) of **2**; b.p.

54–60°C (0.5 mbar). Anal. Found: C, 55.37; H, 8.18; Cl, 36.38. $C_9H_{16}Cl_2$ (195.13) Calc.: C, 55.40; H, 8.27; Cl, 36.34%. MS (EI) m/z 193.4 [M^+]. IR (film): $\nu(CH_2=)$ 3077 (m), $\nu(-CH=)$ 2934 (m), $\nu(CH_2)$ 2861 (w), $\nu(C=C)$ 1640 (m), $\delta(CH_2)$ 1463 (m) cm^{-1}. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.8 (C7), 113.8 (C8), 44.7 (C1), 41.6 (C2), 32.7 (C6), 28.6, 28.0 (C3, C5), 25.3 (C4).

3.3. 2-chloromethyl-1-chloro-8-trimethoxysilyloctane [3(T⁰)]

A solution of 6.0 g (30.7 mmol) of **2** in 20 ml of THF was treated with 4.2 g (34.1 mmol) of trimethoxysilane. Then a suspension of 20 mg (0.039 mmol) of chloroplatinic acid in 20 ml of THF was added and the reaction mixture was stirred for 3d. After evaportion of the solvent and distillation under vacuo 5.6 g (57.3%) of **3**(**T**^{0}) were obtained as a colorless liquid; b.p. 111–120°C (0.5 mbar). Anal. Found: C, 45.42; H, 8.26; Cl, 22.34. $C_{12}H_{26}Cl_2O_3Si$ (317.33) Calc.: C, 45.70; H, 8.06; Cl, 22.08%. MS (EI) m/z 317.0 [M^+]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.94 (C9), 45.91 (C1), 42.84 (C2), 33.29, 29.92, 29.59, 26.95, 22.96 (C2 to C6), 9.55 (C8).

3.4. 2-(diphenylphosphinomethyl)-1-diphenylphosphine-8-trimethoxysilyloctane [4(T⁰)]

A solution of n-BuLi in n-hexane (18.8 ml of a 1.6 M solution) was added dropwise to a solution of 5.6 g (30.1 mmol) of $HPPh_2$ in 30 ml of THF at 0°C. After stirring the reaction mixture for 30 min 4.8 g (15.0 mmol) of **3**(**T**^{0}) was added dropwise. The solution was stirred over night and became almost colorless. 5 ml of methanol was added and **4**(**T**^{0}) was extracted three times with 30 ml of n-pentane. After removal of n-pentane in vacuo 5.8 g (62.4%) of **4**(**T**^{0}) were obtained. Anal. Found: C, 70.10; H, 7.52. $C_{36}H_{46}O_3P_2Si$ (616.80) Calc.: C, 70.03; H, 7.40%. MS (FD) m/z 616.1 [M^+]. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -41.00. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.5 (m, *ipso*-C-phenyl), 133.3 (d, $^2J(PC)$ 19.2 Hz, *o*-C-phenyl), 128.9 (d, $^3J(PC)$ 1.42 Hz, *m*-C-phenyl), 128.8 (d, $^4J(PC)$ 1.42 Hz, *p*-C-phenyl), 51.0 (C9), 36.3 (t, $^3J(PC)$ 9.3 Hz, C3), 35.6 (A part of an AXX′ pattern, $|^1J(PC) + {}^3J(PC)| = 22.05$ Hz, C1), 33.0 (t, $^2J(PC)$ 12.8 Hz, C2), 33.6, 29.9, 29.6, 26.2, 23.0 (C4–C7), 9.6 (C8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -21.0.

3.5. 2-dichloro-(2-diphenylphosphinomethyl-1-diphenylphosphine-8-trimethoxysily loctane) palladium(II) [5(T⁰)]

A solution of 1.3 g (2.17 mmol) of **4**(**T**^{0}) in 5 ml of THF was added dropwise to a suspension of 0.62 g (2.17 mmol) of (COD)$PdCl_2$ in 10 ml of THF. The mixture was stirred for 3 h at ambient temperature. Subsequently THF was removed in vacuo and the reaction mixture was treated with 10 ml of a n-pentane/diethyl ether mixture (1/3) over night. After drying the product for 3 h in vacuo a yellow viscous oil was obtained. Anal. Found: C, 53.38 [12]; H, 5.97; Cl, 9.07. $C_{36}H_{46}Cl_2O_3P_2PdSi$ (794.1) Calc.: C, 54.48; H, 5.84; Cl, 8.93%. MS (FD) m/z 793.7 [M^+]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.0–128.9 (m, C-phenyl), 51.0 (OCH_3), 34.1 (C1), 31.6 (C2), 9.5 (C8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.7.

Acknowledgements

The support of this research by the Deutsche Forschungsgemeinschaft (Forschergruppe, Grant No. 154/41-3) Bonn/Bad Godesberg, and by the Fonds der Chemischen Industrie, Frankfurt/Main is gratefully acknowledged. We are grateful to Degussa AG, Germany, for a generous gift of $PdCl_2$. The authors wish to thank Priv.-Doz. Dr H.A. Mayer for the helpful discussion of the NMR spectra.

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