Inorganica Chimica Acta 375 (2011) 324–328

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Note

First microwave-assisted synthesis of an electron-rich phosphane and its coordination chemistry with platinum(II) and palladium(II)

Barbara Trettenbrein [a], Markus Fessler [a], Martin Ruggenthaler [a], Stephan Haringer [a], Dennis Oberhuber [a], Georg Czermak [a], Peter Brüggeller [a,*], Werner Oberhauser [b,*]

[a] *Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck, Innrain 52a, 6020 Innsbruck, Austria*

[b] *Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area di Ricerca di Firenze, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*

ARTICLE INFO

Article history:
Received 18 February 2011
Received in revised form 12 May 2011
Accepted 20 May 2011
Available online 30 May 2011

Keywords:
Microwave-assisted synthesis
Phosphane
Palladium
Platinum
X-ray structure

ABSTRACT

The P–O ligand 3-(di(2-methoxyphenyl)phosphanyl)propionic acid (**HL**) was synthesized by a microwave-assisted reaction of a secondary phosphane. The coordination of **HL** to Pt^{II} yielded the neutral mononuclear complex *trans*-[PtCl(κ^2-*P*,*O*-**L**)(κ-P-**HL**)] (**1**), while the reaction of PdClMe(η^4-COD) (COD = 1,4-cyclooctadiene) with **HL** in the presence of NEt_3 gave the anionic Pd^{II} compound of the formula ($HNEt_3$)[PdClMe(κ^2-*P*,*O*-**L**)] (**2**). Upon crystallization of the latter compound the neutral chloride-bridged dimetallic compound *cis*-[Pd(μ-Cl)Me(**HL**)]$_2$ (**3**) was obtained. **HL**, **1** and **3**·CH_2Cl_2 have been characterized by single crystal X-ray structure analyses.

1. Introduction

The organometallic chemistry of functionalized phosphanes modified with an additional (non-phosphane) donor group has revealed a great deal of applications in homogeneous catalysis [1]. Among these non-phosphane donors, sulfonate [2] and carboxylate [3] groups have gained particular interest in the Ni(P-O)-catalyzed olefin oligomerization (SHOP) [4] as well as in the Pd(P-O)-catalyzed non-strictly CO olefin copolymerization reaction [2]. In particular, the presence of the 2-methoxyphenyl moiety in the ligand scaffold has shown to confer high stability to the ligand against phosphane oxide formation, which is the most encountered deactivation process occurring in metal-phosphane catalyzed reactions [5]. In order to contribute to the field of synthesis of new phosphanyl-carboxylate ligands, we report here a microwave-assisted synthesis of 3-(di(2-methoxyphenyl)phosphanyl)propionic acid (**HL**) and its coordination chemistry with Pt^{II} and Pd^{II}.

2. Experimental

2.1. Methods and materials

All synthetic reactions and manipulations were carried out under an argon atmosphere by using standard Schlenk techniques. Reagents were used as received from Aldrich, unless stated otherwise. Bis-(di(2-methoxy)phenyl)phosphane [6] and [PdClMe(η^4-COD)] [7] were prepared according to literature methods. The microwave synthesis was carried out with an Anton Paar Synthos 3000 (1400 W unpulsed microwave) dual magnetron system, with an operation volume of 60 mL and reaction vessels of PTFE–TFM. Deuterated solvents for routine NMR measurements were dried with activated molecular sieves. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained with a Bruker Avance DRX-400 spectrometer acquiring spectra at 400.13, 100.62 and 161.98 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to TMS (^1H and ^{13}C NMR spectra) or 85% H_3PO_4. IR spectra were acquired on a Nicolet 5700 ATR FT-IR spectrometer. Microanalyses were performed using a Carlo-Erba Model 1106 elemental analyzer. FAB mass spectrometric measurements were carried out on a Finnigan MAT-95 spectrometer, using 3-nitrobenzylalcohol (NOBA) as matrix.

2.2. Synthesis of *HL*

Deaerated ethyl 3-chloropropionate (12 mL, 88.0 mmol) was added to a teflon vessel, which was sealed after

---

* Corresponding authors. Tel.: +43 512 5075115; fax: +43 512 5072934 (Peter Brueggeller); tel.: +39 055 5225284; fax: +39 055 5225203 (Werner Oberhauser).

E-mail addresses: Peter.Brueggeller@uibk.ac.at (P. Brüggeller), werner.oberhauser@iccom.cnr.it (W. Oberhauser).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.05.020

bis-(di(2-methoxy)phenyl)phosphane (200.3 mg, 0.813 mmol) had been added. The reaction vessel was heated by microwave irradiation at 100 °C for 2 h. Afterwards, deaerated water (50 mL) was added to the reaction mixture. The water phase was separated, concentrated to dryness and the viscous residue was dissolved in deaerated EtOH (20 mL). Then $NaOCH_3$ (7.0 g, 130.1 mmol) was added to the reaction solution, which was stirred at 80 °C for 4 h. The reaction solvent was then completely removed and the crude residue was dissolved in deaerated water (20 mL) and HCl was added at room temperature, causing the precipitation of the desired product as an off-white product, which was then separated from solution by filtration and dried by vacuum. Yield 106.2 mg (41%). Mp 145–148 °C. *Anal.* Calc. for $C_{17}H_{19}O_4P$ (318.29): C, 64.15; H, 6.02. Found: C, 63.99; H, 6.04%. ^1H NMR (DMSO-d_6, 21 °C): δ 2.21–2.22 (s, 4H, CH_2CH_2COO), 3.73 (s, 6H, OCH_3), 6.91–7.37 (m, 8H, Ar-*H*), 12.17 (s, 1H, COOH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 21 °C): δ 19.78 (d, $^2J_{PC}$ = 12.6 Hz, CH_2CO_2H), 31.31 ($^1J_{PC}$ = 18.6 Hz, CH_2P), 55.96 (s, OCH_3), 111.30 (s, Ar-*C*), 121.30 (s, Ar-*C*), 125.03 (d, $^1J_{PC}$ = 17.1 Hz, *ipso*-Ar-*C*), 130.66 (s, Ar-*C*), 132.42 (d, $^2J_{PC}$ = 5.2 Hz, Ar-*C*), 161.40 (d, $^2J_{PC}$ = 13.4 Hz, Ar-*C*), 174.57 (d, $^3J_{PC}$ = 13.9 Hz, CO_2H). $^{31}P\{^1H\}$ NMR (DMSO-d_6, 21 °C): δ −33.97 (s). IR (ν, cm^{-1}) 1695 (CO_2H). MS (FAB+) *m*/*z*: 318.11 (M^+).

2.3. Synthesis of trans-[PtCl(κ^2–P,O-**L**)(κ-P-**HL**)] (**1**)

In a Schlenk tube **HL** (100.0 mg, 0.314 mmol) was suspended in water (20 mL) and on addition of KOH (17.6 mg, 0.314 mmol), the suspension became a clear solution. To this latter solution a solution of $K_2PtCl_4\cdot4H_20$ (76.5 mg, 0.157 mmol) in water (20 mL) was added under stirring, which was continued at room temperature for 2 h. Afterwards, the solvent was completely removed obtaining the crude off-white product, which was suspended in a small amount of MeOH (2 mL), filtered off and then dried under vacuum. Yield 98.4 mg (72%). Mp 204 °C. *Anal.* Calc. for $C_{34}H_{37}ClO_8P_2Pt$ (866.11): C, 47.15; H, 4.31. Found: C, 47.01; H, 4.14%. ^1H NMR (DMF-d_7, 21 °C): δ 2.25 (m, 2H, CH_2), 2.53 (m, 2H, CH_2), 2.93 (m, 4H, CH_2), 3.85 (s, 6H, OCH_3), 3.92 (s, 6H, OCH_3), 6.99–7.91 (m, 16H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMF-d_7, 21 °C): δ 19.78 (s, CH_2CO_2), 22.64 (d, $^2J_{PC}$ = 28.3 Hz, CH_2P), 55.49 (s, OCH_3), 55.80 (s, OCH_3), 111.22–161.46 (Ar-*C*), 174.39 (s, CO_2H), 176.71 (s, CO_2^-). $^{31}P\{^1H\}$ NMR (DMF-d_7, 21 °C): δ 14.74 (d, $^2J_{PP}$ = 467.0 Hz, $^1J_{PtP}$ = 2793.0 Hz, $P(CO_2H)$), 16.86 (d, $^2J_{PP}$ = 467.0 Hz, $^1J_{PtP}$ = 2782.0 Hz, $P(CO_2^-)$). ^{195}Pt NMR (DMF-d_7, 21 °C): δ −3461.16 (t, $^1J_{PtP}$ = 2799.0 Hz). IR (ν, cm^{-1}) 1695 (CO_2H), 1671 (CO_2^-). MS (FAB+) *m*/*z*: 867.3 ($M+H^+$), 830.4 ($M-Cl^-$).

2.4. Synthesis of ($HNEt_3$) [PdClMe(κ^2-P,O-**L**)] (**2**)

In a Schlenk tube **HL** (50.0 mg, 0.157 mmol) was dissolved in deaerated CH_2Cl_2 (10 mL). Afterwards, NEt_3 (5.0 mL) was added to the solution and allowed to stir for 1 h. Then [PdClMe(η^4-COD)] (30.1 mg, 0.157 mmol) was added to the latter solution, which turned slightly yellow. After a reaction time of half an hour the solvent was removed completely and the resulting brownish solid was washed with *n*-hexane and dried under vacuum. Yield 45.8 mg (51%). Mp 109 °C (decomposition). *Anal.* Calc. for $C_{24}H_{37}ClNO_4Pd$ (576.40): C, 52.88; H, 6.79. Found: C, 52.73; H, 6.59%. ^1H NMR (CD_2Cl_2, 21 °C): δ 0.08 (d, $^3J_{PH}$ = 2.8 Hz, 3H, $PdCH_3$), 1.25 (t, $^3J_{HH}$ = 7.2 Hz, 9H, CH_3CH_2), 2.42 (dm, $^2J_{PC}$ = 29.6 Hz, 2H, CH_2CO_2), 2.70 (m, 2H, CH_2P), 3.21 (q, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3CH_2), 3.86 (s, 6H, OCH_3), 7.00–7.73 (m, 8H, Ar-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ −6.43 (s, $PdCH_3$), 8.44 (s, CH_3CH_2), 22.27 (d, $^1J_{PC}$ = 32.14 Hz, CH_2P), 33.27 (s, CH_2CO_2), 45.07 (s, CH_3CH_2), 55.51 (s, OCH_3), 111.05 (d, $^3J_{PC}$ = 4.1 Hz, Ar-*C*), 118.10 (d, $^1J_{PC}$ = 17.2 Hz, *ipso*-Ar-*C*), 120.34 (d, $^2J_{PC}$ = 11.9 Hz, Ar-*C*), 132.61 (s, Ar-*C*), 160.38 (s, Ar-*C*), 179.26 (s, CO_2^-). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ 37.66 (s). IR (ν, cm^{-1}) 1585 (CO_2^-). MS (FAB+) *m*/*z*: 439.0 (M^+-HNEt_3-Cl).

2.5. X-ray crystal structure determinations

Single crystals of **HL**, suitable for an X-ray structure analysis, were obtained by slow evaporation of a 1:1 (v/v) water–EtOH solution of **HL** on air, while single crystals of **1** were obtained from a corresponding water-acetic acid-acetone solution. Single crystals

Table 1
Crystallographic data and structure refinement details for compounds **HL**, **1** and **3**$\cdot CH_2Cl_2$.[a]

	HL	**1**	**3**$\cdot CH_2Cl_2$
Empirical formula	$C_{17}H_{19}O_4P$	$C_{34}H_{37}ClO_8P_2Pt$	$C_{37}H_{44}Cl_4O_8P_2Pd_2$
Formula weight	318.29	866.11	1033.26
a (Å)	12.9634(4)	12.4658(2)	19.1988(3)
b (Å)	8.1575(6)	16.1336(2)	13.9774(2)
c (Å)	15.3186(8)	17.3074(3)	17.2253(2)
α (°)			
β (°)	98.790(3)	94.6333(8)	93.7793(7)
γ (°)			
V ($Å^3$)	1600.90(15)	3469.46(9)	4612.35(11)
Z	4	4	4
D_{calc} (Mg/m^3)	1.321	1.658	1.488
Absorption coefficient (mm^{-1})	0.187	4.263	1.124
F(0 0 0)	672	1720	2080
Θ Range for data collection (°)	1.59–27.50	1.64–27.47	1.80–27.48
Limiting indices	$-16 \leqslant h \leqslant 16$	$-15 \leqslant h \leqslant 16$	$-24 \leqslant h \leqslant 24$
	$-10 \leqslant k \leqslant 10$	$-20 \leqslant k \leqslant 20$	$-18 \leqslant k \leqslant 18$
	$-19 \leqslant l \leqslant 19$	$-22 \leqslant l \leqslant 22$	$-22 \leqslant l \leqslant 22$
Reflections collected	9060	30 073	39 158
Independent reflections (R_{int})	3672 (0.0376)	7954 (0.0230)	10 569 (0.0380)
Data/restraints/parameters	3638/0/203	7912/0/420	10 459/17/499
Goodness-of-fit on F^2	1.033	1.030	1.026
Final *R* indices [$I > 2\sigma(I)$] R_1, wR_2	0.0372, 0.0950	0.0253, 0.0609	0.0371, 0.0881
R indices (all data) R_1, wR_2	0.0460, 0.1130	0.0321, 0.0718	0.0465, 0.1052
Largest difference in peak and hole (e $Å^{-3}$)	0.200 and −0.210	1.260 and −0.910	0.974 and −0.570

[a] Temperature, 243(2) K; crystal shape, prism; crystal size, 0.25 × 0.15 × 0.10 (**HL**, **1**), 0.45 × 0.20 × 0.03 (**3**$\cdot CH_2Cl_2$); crystal colour, colourless; crystal system, monoclinic; space group, $P2_1/c$; absorption corrections, multi-scan; refinement method, full-matrix least-squares on F^2.