Polyhedron 87 (2015) 349–353

Contents lists available at ScienceDirect

Polyhedron

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

From phosphonium salts to binuclear ortho-palladated phosphorus ylides

Ali Naghipour [a,*], Khadijeh Badpa [a], Behrouz Notash [b]

[a] Department of Chemistry, Faculty of Science University, Ilam 69315, Iran
[b] Department of Chemistry, Shahid Beheshti University, G.C., Evin, Tehran 1983963113, Iran

ARTICLE INFO

Article history:
Received 14 October 2014
Accepted 23 November 2014
Available online 4 December 2014

Keywords:
Synthesis
Phosphonium
Ylide
Binuclear
Palladium

ABSTRACT

This current piece of research presents an easy and direct way for the synthesis of binuclear ortho-palladated phosphorus ylide derivatives of acetone and chloroacetone in high yield and high purity by the reaction of the phosphonium salts $[CH_3COCH_2PPh_3]Cl$ (**1**) and $[ClCH_2COCH_2R]Cl$ (R = PPh_3 (**2**), R = $P(PhMe)_3$ (**3**)) with palladium(II) acetate in methanol under mild conditions to afford the dimeric orthopalladated complexes, $[Pd(CH_3COCHPPh_3)(\mu\text{-}Cl)]_2$ (**4**), $[Pd(ClCH_2COCHPPh_3)(\mu\text{-}Cl)]_2$ (**5**) and $[Pd(ClCH_2COCHP(PhMe)_3)(\mu\text{-}Cl)]_2$ (**6**).

1. Introduction

Phosphorus compounds, such as phosphonium salts, phosphorus ylides and their transition metal complexes, notably palladium(II) metallacycle complexes, have been known for three decades. However, recently they have attracted much more attention as exciting catalyst precursors for different types of cross coupling reactions [1–3]. Phosphonium salts have a range of advantages, including the existence of a wide variety of organic derivatives, functionalized types of branches and their use as catalysts in several organic reactions, including oxidation. More important than these factors is their new usage as an agent for imaging and diagnosing tumors [4–8], anticancer treatment [9] and as a transport vector for targeting mitochondria [10–15].

Phosphorus ylides were considered as an outstanding achievement in the chemistry of the twentieth century and were found to be useful in a wide variety of interesting reactions to synthetic chemists, especially in the synthesis of natural product compounds with biological and pharmacological activities [16–18]. Keto-stabilized phosphorus ylides are interesting topics for investigation because they have different ylide to metal coordination modes [9–15], such as C-coordinated through the Cα atom, O-bonded through carbonyl O, P-bonded or a special position in which a combination of these bonds are present. Stabilized yilides, especially keto ylides, have been studied as important ligands in organometallic and coordination chemistry [19–21].

The most common method of synthesizing transition metal phosphorus ylide complexes is summarized in three stages: first is the synthesis of the phosphonium salt; second is the preparation of the phosphorus ylide by treating the phosphonium salt with a base, and third is the reaction of this phosphorus ylide with the appropriate transition metal salts, such as metal halides. As the synthesis of phosphorus ylides is quite difficult, needing controlled conditions such as pH, temperature, dry solvent and working under an inert gas, herein the authors report the preparation of chloroacetone phosphonium salts and the synthesis of di-μ-chloro bis[five-membered Pd(II) chloroacetone triphenylphosphane phosphorus ylide] complexes directly from the reaction of the phosphonium salt with palladium(II) acetate, giving the palladium(II) phosphorus ylide under mild conditions without synthesizing the phosphorus ylide separately. The crystal structure of the unsymmetric dimer of palladium(II), with two five-membered rings containing the chloroacetone phosphorus ylide, shows that orthometallation is also achieved under these simple conditions.

2. Experimental

2.1. Materials

All reactions were carried out at room temperature using standard techniques. Reactants and reagents were obtained from

* Corresponding author. Tel./fax: +98 841 2227022.
E-mail address: naghipour2002@yahoo.com (A. Naghipour).

http://dx.doi.org/10.1016/j.poly.2014.11.029
0277-5387/

Merck Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [22].

2.2. Physical measurements

Melting points were measured on a Stuart SMP_3 apparatus. IR spectra in the range 4000–400 cm^{-1} were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (^1H, ^{31}P and ^{13}C NMR) recorded on a 400 MHz Bruker spectrometer in $CDCl_3$ or DMSO-d_6 as the solvent at room temperature. Chemical shifts (δ) are reported based on internal TMS (^1H and ^{13}C) and external 85% phosphoric acid (^{31}P). Elemental microanalyses were carried out with a CHNS-O costech ECS 4010 analyzer.

2.3. Synthesis of the monophosphonium salts

2.3.1. $[CH_3COCH_2PPh_3]^+Cl^-$ (**1**)

A solution consisting of triphenylphosphane (PPh_3) (0.655 g, 2.5 mmol) and dichloroacetone, $ClCH_2COCH_2Cl$ (2.5 mmol, 0.318 g) in benzene was stirred at room temperature for 6 h. The resulting suspension was filtered off, and the obtained precipitate washed with diethyl either and benzene, and then dried to give $[ClCH_2COCH_2PPh_3]Cl$ as a white powder. Yield: 0.84 g, 95%. M.p.: 240 °C. *Anal.* Calc. for $C_{21}H_{20}ClOP$ (354.81 g/mol): C, 71.1; H, 5.7. Found: C, 71.3; H, 5.8%. IR (KBr disk, ν cm^{-1}): 1702 (CO), 689–900 (C–H in Ph), 1587 (C=C in Ph), 1437 (P-CH_2), 2768 (CH_3). ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 4.50–4.55 (br, 2H, PCH_2); 2.54 (br, CH_3); 7.29–7.87 (m, 15H, PPh_3). ^{31}P NMR (162 MHz, DMSO-d_6, δ_P ppm): 19.77 (s, PPh_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ_C ppm): 24 (br, CH_3); 76.76, 77.11, 77.42 (br, $CDCl_3$); 40.03–40.67 (br, PCH_2); 118.38, 119.27, 121.36, 122.27, 129.74, 129.74, 130.05, 130.18, 133.13, 133.24, 133.86, 133.97, 134.63, 134.66 (Ph); 201.17, 201.23 (s, CO).

2.3.2. $[ClCH_2COCH_2PPh_3]^+Cl^-$ (**2**)

Compound **2** was obtained as a white solid, following a similar procedure to that for **1**, but using dichloroacetone ($ClCH_2COCH_2Cl$) and triphenylphosphane (PPh_3) as the starting materials. Yield: 0.95 g, 98%. M.p.: 230 °C. *Anal.* Calc. for $C_{21}H_{19}ClOP$ (353.80 g/mol): C, 71.3; H, 5.4. Found: C, 71.1; H, 5.5%. IR (KBr disk, ν cm^{-1}): 1727.26 (CO), 721–900 (C–H in Ph), 1485–1588 (C=C in Ph), 1439 (PCH_2), 685 (C–Cl in CH_2Cl). ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 5.25-5.29 (br, 2H, PCH_2); 3.75–3.77 (br, 2H, CH_2Cl); 6.86–7.89(m, 15H, PPh_3). ^{31}P NMR (162 MHz, DMSO-d_6, δ_P ppm): 20.35 (s, PPh_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ_C ppm): 37.48–38.09 (br, PCH_2); 50.19, 50.30 (CH_2Cl); 77.04, 77.25, 77.26 (br, $CDCl_3$); 129.90, 130.02, 130.16, 130.29, 133.20, 133.31, 133.91, 134.01, 134.28, 134.89 (Ph); 195.10 (s, CO).

2.3.3. $[ClCH_2COCH_2P(PhMe)_3]^+Cl^-$ (**3**)

Compound **3** was obtained as a white solid, following a similar procedure to that for **1**, but using dichloroacetone ($ClCH_2COCH_2Cl$) and tri(p-tolyl)phosphane ($P(PhMe)_3$) as the starting materials. Yield: 0.91 g, 85%. M.p.: 220 °C. *Anal.* Calc. for $C_{24}H_{25}Cl_2OP$ (431.33 g/mol): C, 66.8; H, 5.8. Found: C, 70.0; H, 5.9%. IR (KBr disk, ν cm^{-1}): 1729 (CO), 670–900 (C–H in Ph), 1600 (C=C in Ph), 1403 (PCH_2), 650 (C–Cl in CH_2Cl), 2795–2711 (CH_3). ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 6.33–6.36 (br, 2H, PCH_2); 4.89 (br, 2H, CH_2Cl); 2.43 (br, 3H, CH_3); 7.28–7.73 (m, 15H, PPh_3). ^{31}P NMR (162 MHz, DMSO-d_6, δ_P ppm): 19.71 (s, PPh_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ_C ppm): 37.63–38.22 (br, PCH_2); 50.51, 50.60 (CH_2Cl); 21.83 (br, CH_3); 77.08–77.40 (br, $CDCl_3$); 130.51, 130.65, 130.77, 130.91, 130.98, 133.20, 133.78, 133.90 (Ph); 195.20, 195.27 (s, CO).

2.4. Synthesis of the cyclopalladated complexes

2.4.1. Synthesis of $[Pd(CH_3COCHPPh_3)(\mu\text{-}Cl)]_2$ (**4**)

To a solution of the compound $[CH_3COCH_2PPh_3]Cl$, (0.355 g, 0.5 mmol) in methanol (15 mL), palladium(II) acetate (0.053 g, 0.25 mmol) was added, and the resulting solution was stirred at room temperature for 72 h. The suspension that formed was filtered off, washed with diethyl ether and dried. Yield: 0.184 g, 95%. M.p.: 210 °C. *Anal.* Calc. for $C_{42}H_{36}Cl_2O_2P_2Pd_2$ (918.43 g/mol): C, 54.9; H, 3.9. Found: C, 55.1; H, 4.0%. IR (KBr disk, ν cm^{-1}): 1713 (CO), 689–900 (C–H in Ph), 1438–1587 (C=C in Ph), 1438 (PCH_2) 2827 (CH_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 2.51 (br, 3H, CH_3); 4.59 (br, 2H, PCH_2); 5.90 (br, 2H, CH_2Cl_2); 7.03, 7.13, 7.16, 7.24, 7.29, 7.44, 7.49, 7.52, 7.55, 7.60, 7.67, 7.69, 7.71, 7.72, 7.81, 7.95, 7.98, 8.00, 8.05 (m, 19H, PPh_3). ^{31}P NMR (162 MHz, $CDCl_3$, δ_P ppm): 21.42 (s, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C ppm): 31.24 (br, CH_3); 39.04 (br, PCH_2); 124.62, 125.87, 128.69, 128.80, 129.10, 129.22, 129.34, 129.49, 129.61, 129.91, 130.02, 130.18, 130.32, 130.40, 132.41, 132.55, 132.85, 132.87, 134.00, 134.33, 134.43, 134.60, 136.52, 136.76, 136.91 (Ph); 201.38 (s, CO).

2.4.2. Synthesis of $[Pd(ClCH_2COCHPPh_3)(\mu\text{-}Cl)]_2$ (**5**)

To a solution of the compound $[ClCH_2COCH_2PPh_3][Cl]$ (0.194 g, 0.5 mmol) in methanol (15 mL), palladium(II) acetate (0.053 g, 0.25 mmol) was added, and the resulting solution was stirred at room temperature for 72 h. The suspension that formed was filtered off, washed with diethyl ether and dried to give **5** as a red brown powder. Yield: 0.205 g, 98%. M.p.: 220 °C. *Anal.* Calc. for $C_{42}H_{34}Cl_4O_2P_2Pd_2$ (987.32 g/mol): C, 51.1; H, 3.5. Found: C, 51.3; H, 3.6%. IR (KBr disk, ν cm^{-1}): 1734 (CO), 721–900 (C–H in Ph), 1485–1587 (C=C in Ph), 1439 (PCH_2), 688 (C–Cl in CH_2Cl). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 2.55 (br, 2H CH_2Cl); 4.90 (br, PCH); 5.72 (br, 2H, CH_2Cl_2); 7.78-7.90 (m, 15H, PPh_3). ^{31}P NMR (162 MHz, $CDCl_3$, δ_P ppm): 21.25 (s, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C ppm): 48.12 (br, 2H, CH_2Cl_2); 39.37 (br, PCH); 129.99, 129.10, 129.54, 129.63, 129.66, 130.53, 130.68, 133.14, 133.30, 133.73, 133.83, 133.84 (Ph); 193.72 (s, CO).

2.4.3. Synthesis $[Pd(ClCH_2COCH(PhMe)_3)(\mu\text{-}Cl)]_2$ (**6**)

Compound **6** was obtained as a red brown solid, following a similar procedure to that for **4**, but using $[ClCH_2COCH_2P(PhMe)_3]^+Cl^-$. Yield: 0.139 g, 96%. M.p.: 220 °C. *Anal.* Calc. for $C_{48}H_{46}Cl_4O_2P_2Pd_2$ (1071.48 g/mol): C, 53.8; H, 4.3. Found: C, 54.1; H, 4.4%. IR (KBr disk, ν cm^{-1}): 1733 (CO), 652–900 (C–H in Ph), 1599 (C=C in Ph), 1401 (PCH_2), 634 (C–Cl in CH_2Cl), 2918 (CH_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 2.24 (br, 3H CH_3 on Ph); 2.69 (br, PCH_2); 4.69 (br, 2H CH_2Cl); 7.02, 7.04, 7.11, 7.15, 7.17, 7.42, 7.50, 7.56, 7.58, 7.59, 7.60, 7.70, 7.71 (m, 19H, Ph). ^{31}P NMR (162 MHz, $CDCl_3$, δ_P ppm): 22.52 (s, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C ppm): 21.14 (br, CH_3 on Ph); 38.93 (br, PCH_2); 40.11 (br, 2H CH_2Cl); 129.51, 130.18, 130.32, 130.40, 132.41, 132.55, 132.80, 134.00, 134.33, 134.43, 134.60, 136.52, 136.76, 140.45 (Ph); 177.01 (s, CO).

2.5. X-ray crystallography

The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer at 120(2) K, using graphite monochromated Mo Kα radiation (0.71073 Å). Crystals of **3** and **5** were chosen using a polarizing microscope, mounted on a glass fiber and used for data collection. Cell constants and orientation matrices for the data collection were obtained by least-squares refinement of diffraction data from 6300 and 5089 unique reflections for **3** and **5**, respectively. Data were collected to a maximum 2θ value of 58.38° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [23] software package. The data were corrected for Lorentz and