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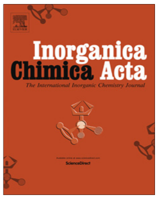

Research paper

Synthesis and crystal structure of an acetylenic ferrocenyl substituted phosphaalkene

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(*E*)-(5,5-Dimethyl-1,4-diferrocenylhex-2-yn-1-ylidene)(2,4,6-tri-*tert*-butylphenyl) phosphine (**3**) was obtained in the reaction of 2,4,6-tri-*tert*-butylphenyl phosphine (**1**) with 1,4-diferrocenyl butadiyne (**2**) in minor yields. Compound **3** was structurally characterized by single crystal X-ray diffraction. The molecular structure of **3** consists of a linear butyne C_4 backbone, which is in conjugation with a phosphene moiety resulting in the phosphapent-2-yn-4-ene motif with one ferrocenyl substituent bonded to a C_{sp3} and the other one to the C_{sp2} carbon atom. Both sandwich moieties are located at the same site of the C_4 axis opposing the *tert*-butyl groups. This results in an alternated stacking within the crystal packing along [0 1 0] with weak *T*-shaped π interactions within the ferrocenyl containing layer. Electrochemical measurements revealed two reversible redox events for the two ferrocenyl groups at −20 mV and at 135 mV.

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1. Introduction

The synthesis of phosphaacetylene in 1961 raises the interest for the syntheses of compounds with *P,C* double and triple bonds, of which, however, $HC{\equiv}P$ and $H_2C{=}PH$ are highly unstable at room temperature [1–4]. One possibility to stabilize molecules with *P,C* double or triple bonds is the kinetic stabilization by sterically demanding substituents, *i.e.* the 2,4,6-tri-*tert*-butylphenyl group [5–18]. Due to the steric hindrance, this substituent is well-suited for the stabilization of $P{=}C$ double bonds [5,9,19–23]. In contrast, molecules containing a conjugated $P{=}C$ double bond and a $C{\equiv}C$ triple bond to form acetylenic phosphaalkene-ynes are rarely described [24,25]. The incorporation of a phosphorus atom in a π conjugated system results in easily modifiable optoelectronic properties [24–30]. Furthermore, phosphaalkenes and –alkines were used in the synthesis of triazaphospholes, which are promising luminescent materials [31].

Herein, we describe an example of an en-yne $P{=}C{-}C{\equiv}C$ compound which was obtained in the synthesis of 2,5-diferrocenyl-substituted phospholes [32]. Such molecules are of interest, for example, to study electron transfer processes in the corresponding mixed-valent species between the ferrocenyl/ferrocenium units [33–48]. Phospholes bearing sterically demanding substituents can be used for a flattening of the phosphorus' environment resulting in an increase of the delocalization [32,49–53]. For the synthesis of ferrocenyl phospholes, phosphines $ArPH_2$ (Ar = phenyl, ferrocenyl, mesityl, 2,4,6-triphenylphenyl, 2,4,6-tri-*tert*-butylphenyl) are reacted with 1,4-diferrocenyl butadiyne [32]. Solely, in the case of Ar = 2,4,6-tri-*tert*-butylphenyl, next to the desired phosphole, the formation of (*E*)-(5,5-dimethyl-1,4-diferrocenylhex-2-yn-1-ylidene)(2,4,6-tri-*tert*-butylphenyl) phosphine was observed. Herein, the properties, structural and electrochemical behavior of this molecule are described.

2. Materials and methods

2.1. General data

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl, toluene was obtained from a MBRAUN (MB-SPS 800) solvent drying and purification system (double column solvent filtration, working pressure 0.5 bar). For electrochemistry HPLC grade dichloromethane was purified by distillation from calcium hydride. For column chromatography silica with a particle size of 40–60 mm (230–400 mesh (ASTM), Fa. Macherey-Nagel) was used.

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2.2. Instruments

FT IR spectra were recorded with a Nicolet IR 200 spectrometer (Thermo Company). NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 125.7 MHz for ^{13}C{^{1}H} and 202.5 MHz for ^{31}P{^{1}H} spectra). Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR: $CDCl_3$, $\delta = 7.26$; ^{13}C{^{1}H} NMR: $CDCl_3$, $\delta = 77.16$; ^{31}P{^{1}H} NMR: standard external rel. 85% H_3PO_4, $\delta = 0.0$; $P(OMe)_3$, $\delta = 139.0$). The melting point was determined using a Gallenkamp MFB 595 010 M melting point apparatus. The high-resolution mass spectrum was recorded with a Bruker Daltonik micrOTOF-QII spectrometer.

2.3. Electrochemistry

Electrochemical measurements of **3** (1.0 mmol·L^{-1} $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte) in anhydrous dichloromethane were performed in a dried, argon purged electrochemical cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. For the measurements a three electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode and an Ag/Ag$^+$ (0.01 mmol·L^{-1} $[AgNO_3]$) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 μm and then with a ¼ micron diamond paste. The reference electrode was constructed from a silver wire inserted in a 0.01 mmol·L^{-1} $[AgNO_3]$ and a 0.1 mol·L^{-1} $[N^nBu_4][B(C_6F_5)_4]$ acetonitrile solution in a Luggin capillary with a Vycor® tip. This Luggin capillary was inserted in a second Luggin capillary containing a 0.1 mol·L^{-1} $[N^nBu_4][B(C_6F_5)_4]$ dichloromethane solution and a Vycor® tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within ±5 mV. Experimental potentials were referenced against an Ag/Ag$^+$ reference electrode but the presented results are referenced against ferrocene as an internal standard as required by IUPAC [54]. To achieve this, each experiment was repeated in the presence of 1 mmol·L^{-1} decamethylferrocene (Fc*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to 0.0 V. Under our conditions the Fc*/Fc*$^+$ redox couple was at −619 mV *vs* FcH/FcH$^+$, $\Delta E_p = 60$ mV, while the FcH/FcH$^+$ couple itself was at 220 mV *vs* Ag/Ag$^+$, $\Delta E_p = 61$ mV [55].

2.4. Single crystal X-ray diffraction analysis

Suitable single crystals of **3** for X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a dichloromethane solution containing **3** at ambient temperature. Data were collected with an Oxford Gemini S diffractometer at 109.85(10) K with Mo K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 [56,57]. All *non*-hydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions.

2.5. Reagents

All starting materials were obtained from commercial suppliers and were used without further purification. 2,4,6-Tri-*tert*-butylphenyl phosphine [58] and 1,4-diferrocenylbutadiyne [59] were prepared according to published procedures.

2.6. Synthesis of ***(E)-(5,5-dimethyl-1,4-diferrocenylhex-2-yn-1-ylidene)(2,4,6-tri-tert-butylphenyl) phosphine (3)***

To 0.25 g (0.9 mmol) of 2,4,6-tri-*tert*-butylphenyl phosphine (**1**) dissolved in a 1:1 mixture of tetrahydrofuran/toluene (40 mL, *v*/*v*) were added drop-wisely 0.4 mL (2.5 *M*, 0.9 mmol) of butyllithium at 0 °C. After stirring this solution for 30 min at 0 °C the solution was added drop-wisely to 0.43 g (1.0 mmol) of 1,4-diferrocenylbutadiyne (**2**) dissolved in 20 mL of tetrahydrofuran. The resulting reaction solution was stirred overnight at ambient temperature and afterwards, all volatiles were removed in vacuo. The remaining solid was purified by column chromatography (column size: 3 × 15 cm, silica) using a *n*-hexane/dichloromethane mixture (ratio 10:1; *v*/*v*) as the eluent. After evaporation of all volatiles, **3** was obtained as a red solid. Yield: 0.03 g (0.04 mmol, 5% based on **1**). 2,5-Diferrocenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1*H*-phosphole was obtained as main product (0.23 g, 0.3 mmol, 36%) [32]. IR data (KBr, v/cm^{-1}): 3100 (w, C—H), 2968 (s, C—H), 2873 (m, C—H), 2188 (w, C≡C). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): 0.64 (s, 9H, CH_3/CH^tBu), 1.33 (s, 9H, *p*-CH_3/C_6H_2), 1.58 (s, 9H, *o*-CH_3/C_6H_2), 1.63 (s, 9H, *o*-CH_3/C_6H_2), 3.18 (d, $^5J_{HP} = 3.2$ Hz, 1H, CH^tBu), 4.03 (m, 1H, C_5H_4), 4.04 (m, 1H, C_5H_4), 4.08 (m, 1H, C_5H_4), 4.12 (s, 5H, C_5H_5), 4.18 (m, 1H, C_5H_4), 4.28 (s, 5H, C_5H_5), 4.41 (m, 1H, C_5H_4), 4.45 (m, 1H, C_5H_4), 4.92 (m, 1H, C_5H_4), 5.00 (m, 1H, C_5H_4), 7.45 (m, 2H, C_6H_2). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 28.1 (s, $CH_3/CHC(CH_3)_3$), 31.6 (s, *p*-CH_3/C_6H_2-$C(CH_3)_3$), 33.5 (d, $^4J_{CP} = 6.2$ Hz, *o*-CH_3/C_6H_2-$C(CH_3)_3$), 33.7 (d, $^4J_{CP} = 6.6$ Hz, *o*-CH_3/C_6H_2-$C(CH_3)_3$), 35.2 (s, $^qC/C_6H_2$-*p*-$C(CH_3)_3$), 36.1 (d, $^5J_{CP} = 2.7$ Hz, $^qC/CHC(CH_3)_3$), 38.4 (s, $^qC/C_6H_2$-*o*-$C(CH_3)_3$), 38.5 (s, $^qC/C_6H_2$-*o*-$C(CH_3)_3$), 46.6 (d, $^4J_{CP} = 1.6$ Hz, CH^tBu), 66.2 (d, $J_{CP} = 17.4$ Hz, CH/C_5H_4), 67.0 (s, CH/C_5H_4), 67.1 (s, CH/C_5H_4), 69.1 (s, CH/C_5H_4), 69.2 (s, C_5H_5), 69.4 (s, CH/C_5H_4), 69.5 (s, CH/C_5H_4), 69.6 (s, C_5H_5), 69.9 (s, CH/C_5H_4), 84.2 (d, $J_{CP} = 24.7$ Hz, C≡C), 86.6 (s, C^i/C_5H_4), 90.6 (d, $^2J_{CP} = 34.5$ Hz, C^i/C_5H_4), 105.8 (d, $J_{CP} = 11.1$ Hz, C≡C), 122.1 (d, $^3J_{CP} = 13.0$ Hz, CH/C_6H_2), 136.5 (d, $^1J_{CP} = 54.8$ Hz, $C^i/C1$-C_6H_2), 149.7 (s, $^qC/C4$-C_6H_2), 153.8 (s, $^qC/C2/C6$-C_6H_2), 154.4 (s, $^qC/C2/C6$-C_6H_2), 163.2 (d, $^1J_{CP} = 40.8$ Hz, C=P). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): 261.9 (s). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{46}H_{57}Fe_2P$: 752.2893, found: 752.2931 $[M]^+$.

3. Results and discussion

(*E*)-(5,5-Dimethyl-1,4-diferrocenylhex-2-yn-1-ylidene)(2,4,6-tri-*tert*-butylphenyl) phosphine (**3**) was obtained by reacting 2,4,6-tri-*tert*-butylphenyl phosphine (**1**) and 1,4-diferrocenylbutadiyne (**2**) according to a reaction procedure described by Märkl and Potthast [60–62] in the presence of *n*-butyllithium (Scheme 1). The respective *Z*-isomer was not isolated.

As **3** was obtained in every reaction of **1** with **2** in minor yield by using *n*-butyllithium as lithiation reagent, one of the ^{t}Bu groups of the 2,4,6-tri-*tert*-butylphenyl phosphine has to be transferred to the C_4 chain of **2**. The migration of ^{t}Bu groups is widely known for supermesityl compounds in the presence of electrophiles, due to the good stabilization of the resulting carbocations [63–66]. However, an electrophilic mechanism is improbable. The formation of unexpected **3** is likely due to a nucleophilic attack of a vinyl anion at a phosphine ^{t}Bu group. After deprotonation of the phosphine with ^{n}Buli [67], the attack at the butadiyne C_1 carbon gives an allenic intermediate LiFcC=C=C=CFc(PHAr). In a consecutive step, this anion nucleophilically reacts with a ^{t}Bu group of a further ArPHLi molecule giving Fc(^{t}Bu)C=C=C=CFc(PHAr). Either by 1,5-sigmatropic rearrangement or by a deprotonation/protonation mechanism, the P-bonded proton is transferred to the C4 carbon atom resulting in butyne **3**.

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