Tetrahedron Letters 50 (2009) 4321–4323

Contents lists available at ScienceDirect

Tetrahedron Letters

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

An alternative approach to 3-(diphenylphosphino)hexahelicene

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ARTICLE INFO

Article history:
Received 4 February 2009
Revised 21 April 2009
Accepted 28 April 2009
Available online 3 May 2009

Keywords:
Helicenes
Phosphines
Heck reaction
Photodehydrocyclisation
Helical complexes

ABSTRACT

3-(Diphenylphosphino)hexahelicene is synthesised in good yield and purity, via a three-step sequence involving a palladium-catalysed Mizoroki–Heck coupling reaction and classical oxidative photocyclisation. Mononuclear ruthenium and palladium complexes of 3-(diphenylphosphino)hexahelicene are prepared and characterised.

Significant interest has been directed towards the construction of polycyclic aromatic structures that exhibit distortions from planarity, such as the helicenes.[1] These helically shaped molecules have found applications as potentially useful components in chiral discotic liquid crystalline materials,[2] as building blocks for helical conjugated polymers[3] and as rotors.[4] Furthermore, functionalised helicenes have proved successful as catalysts[5] and ligands[6] in asymmetric synthesis due to their rigid framework and high optical stability.

Typically, most of the strategies adopted for the synthesis of these compounds suffer from a lack of general applicability and low yields. However, only a few approaches have been employed for the synthesis of racemic or optically active phosphorus-containing helicenes. In 1997, Terfort et al. reported the synthesis of the first helical-chiral phosphane ligands in racemic form: bis(diphenylphosphino)[5]- and [6]-helicenes.[7]

In an independent study, Reetz et al. reported the synthesis of optically active 2,15-bis(diphenylphosphino)hexahelicene and described its use in both enantioselective hydrogenations[8] and palladium-promoted allylic substitutions.[9] More recently, Katz has synthesised optically active bidentate phosphines containing hexa- and hepta-helicene skeletons.[10] Teplý et al. prepared 3-(diphenylphosphino)hexahelicene **1** using a multistep procedure based on a key intramolecular [2+2+2] cycloisomerisation of a substituted triyne.[11] The authors did not report the resolution of this helical phosphine or its use in catalysis. Moreover, in this sequence, the phosphine was obtained using harsh reaction conditions in a low overall yield. A shorter access to phosphine **1** than that mentioned above and/or by another higher yielding procedure would be desirable for examination of this compound as a ligand or for broader exploitation. To our knowledge, no transition metal complex of 3-(diphenylphosphino)hexahelicene has been described previously.

In recent years, we have utilised the palladium-catalysed Mizoroki–Heck coupling reaction and classical oxidative photocyclisation for the synthesis of various functionalised helically chiral aromatic structures.[12,13] In this Letter we report the use of the same strategy for the synthesis of helically chiral hexacyclic phosphine **1** by taking advantage of an appropriate functional group to introduce a phosphorus to a preformed helical derivative. Our synthetic approach makes use of a benzo[*c*]phenanthrene as the starting material for the synthesis of the helicene precursor which is then easily converted into the corresponding helically chiral hexacyclic system by oxidative photocyclisation.

Scheme 1 shows our general synthetic strategy to construct the helical hexacyclic phosphine **1** which is based on a three-step reaction sequence utilising Mizoroki–Heck couplings, photocyclisation and lithiation–phosphinylation.

The Mizoroki–Heck coupling[14] of the benzo[*c*]phenanthrene **2** with an excess of 3-bromostyrene in the presence of sodium acetate and Herrmann's palladacycle [*trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium] as the catalyst, in *N*,*N*-dimethylacetamide (DMA), provided the helicene precursor **3** in 78% yield after heating for 48 h at 140 °C (Scheme 1). The starting material, 2-bromobenzo[*c*]phenanthrene **2**, is available in two steps and good yield, by photocyclisation of 2-(4-bromostyryl)naphthalene, which is conveniently prepared via a palladium-promoted Mizoroki–Heck reaction.[12b]

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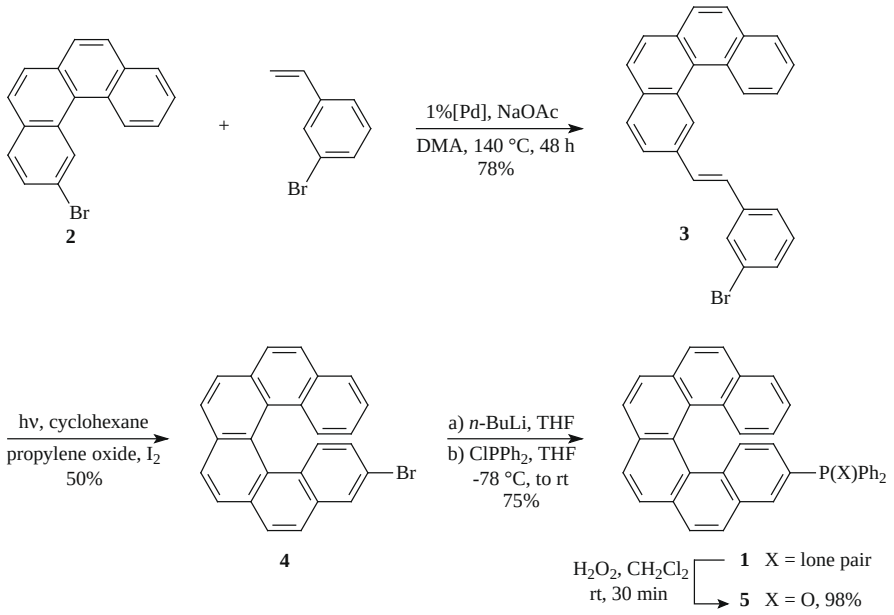
0040-4039/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2009.04.116

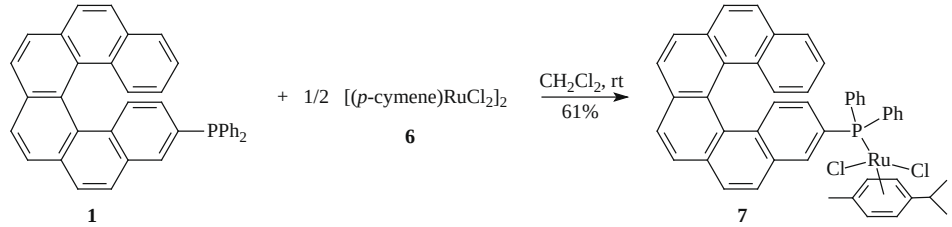


Scheme 1. Synthetic strategy for the synthesis of the helical phosphine **1**.

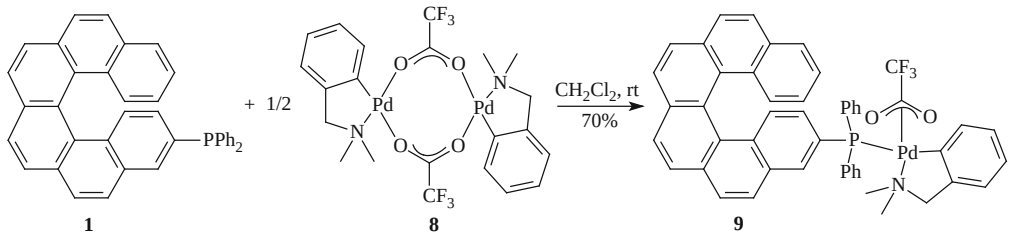
Alkene **3** underwent photocyclisation in the presence of a stoichiometric amount of iodine and an excess of propylene oxide.[15] Photolysis of **3** was performed on a 200 mg scale per run in a one litre reactor for about 120 min to afford the expected 3-bromohexahelicene **4** in 50% yield, after purification by column chromatography.[16] No other isomer was isolated from the reaction mixture, indicating that ring closure of **3** had occurred from the opposite side of the tetracyclic system.

For the photoconversion of larger amounts of alkene **3** it was preferable to carry out irradiation using portions of 0.55 mmol or less. The total irradiation time required for complete conversion of a large amount of **3** was not affected significantly by dividing the reactant into small batches, and the irradiated batches were combined for work-up. Also, this photochemical method has the advantage that tedious and difficult purification of the product is avoided.

The last step of the synthetic sequence is the formation of the phosphine which can be achieved through lithiation/phosphinylation of **4**. Thus, metallation of 3-bromohexahelicene **4** proceeded well via metal-halogen exchange using *n*-butyllithium at −78 °C. Subsequent treatment of the resulting lithiated species with chlorodiphenylphosphine yielded the desired 3-(diphenylphosphino)hexahelicene **1** in 75% yield and in 29% overall yield over three steps, starting from the readily available benzo[*c*]phenanthrene **2** (Scheme 1). Oxidation of helical phosphine **1**, using 35% hydrogen peroxide solution, provided the corresponding phosphine oxide **5** in excellent yield. Compound **5** is more stable than phosphine **4** and could be resolved, by HPLC, using a column



Scheme 2. Synthesis of the helically chiral ruthenium complex **7**.



Scheme 3. Synthesis of the helically chiral palladium complex **9**.

packed with cellulose-tris(3,5-dimethylphenylcarbamate) and *n*-heptane/2-propanol (80:20) mixture as the mobile phase.[12a,d]

Having established a short procedure for the synthesis of the monophosphine **1**, we then further proceeded to explore its coordinating ability towards transition metals. To achieve this, phosphine **1** was first allowed to react with 0.5 equiv of $[(p\text{-cymene})RuCl_2]_2$ complex **6** in dichloromethane at room temperature to afford the mononuclear ruthenium complex **7** in 61% yield (Scheme 2). This compound was isolated as an orange-red, air stable solid and was characterised by NMR and mass spectrometry.[17]

Phosphine **1** was also reacted with the $[PhCH_2N(Me)_2Pd(\eta^3\text{–}OCOCF_3)]_2$ complex **8** at room temperature for 15 min to produce the mononuclear palladium complex **9** in 70% yield as an air stable, pale yellow compound (Scheme 3).[18]

In conclusion, we have developed a straightforward method for the preparation of helically chiral hexacyclic phosphine **1** starting from readily available and inexpensive materials. We completed the synthesis of the helical framework of **1** in three steps and in 29% overall yield. This class of compounds is known to possess interesting catalytic activities, and we feel that this method when combined with a simple resolution procedure will further facilitate the exploration of this helical phosphine.

Acknowledgement

The authors are grateful to DGRSRT (Direction Générale de la Recherche Scientifique et de la Rénovation Technologique) of the Tunisian Ministry of Higher Education, Scientific Research and Technology for the financial support.

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16. *Spectral data for 3-bromohexahelicene* **4**: pale yellow solid, showing a violet fluorescence when dissolved; $R_f = 0.41$ (cyclohexane/ethyl acetate, 98:2); mp = 196–198 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 6.72–6.79 (m, 2H), 7.27 (t, $J = 6.9$ Hz, 1H, H-14 or H-15), 7.46 (d, $J = 9.3$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.7$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.93–8.03 (m, 8H); ^{13}C NMR: (75 MHz, $CDCl_3$): δ (ppm): 119.43 (C), 123.87 (C), 125.05 (CH), 125.90 (CH), 126.19 (CH), 126.78 (CH), 126.95 (CH), 127.22 (CH), 127.32 (CH), 127.54 (CH), 127.60 (2CH), 127.67 (CH), 127.72 (CH), 127.81 (C), 127.82 (C), 128.12 (CH), 128.63 (C), 129.33 (CH), 129.60 (CH), 129.61 (C), 131.21 (C), 131.43 (C), 131.85 (C), 133.15 (C), 133.32 (C); MS (EI): $m/z = 407$ [M^+]; Anal. Calcd for $C_{26}H_{15}Br$: C, 76.67; H, 3.71. Found: C, 76.57; H, 3.69.
17. *Spectral data for the Ru-complex* **7**: orange–red solid; mp = 195–197 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 0.99 (d, $J = 7.2$ Hz, 3H, Me), 1.03 (d, $J = 7.2$ Hz, 3H, Me), 1.74 (s, 3H, Me), 2.77 (m, 1H, C*H*Me$_2$), 4.68 (d, $J = 6$ Hz, 1H, CH*p*-cym), 4.80 (d, $J = 6$ Hz, 1H, CH*p*-cym), 5.00 (d, $J = 5.8$ Hz, 1H, CH*p*-cym), 5.12 (d, $J = 5.7$ Hz, 1H, CH*p*-cym), 6.68 (ddd, $J_1 = 8$ Hz, $J_2 = 7.2$ Hz, $J_3 = 1.2$ Hz, 1H), 6.93 (td, $J_1 = 9$ Hz, $J_2 = 1.8$ Hz, 1H, H-15), 7.10–7.35 (m, 8H), 7.49–7.63 (m, 5H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.82–7.94 (m, 7H), 7.97 (d, $J = 8.4$ Hz, 1H), 8.36 (dd, $J = 1.5$ Hz, $J_{H-P} = 11.7$ Hz, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 18.47 (Me), 22.26 (Me), 22.38 (Me), 30.71 (CH*p*-cym), 87.53 (CH*p*-cym), 87.59 (CH*p*-cym), 88.19 (CH*p*-cym), 89.06 (CH*p*-cym), 96.45 (C*p*-cym), 111.30 (C*p*-cym), 124.42 (C), 124.92 (CH), 125.90 (CH), 126.86 (CH), 127.42 (CH), 127.62 (CH), 127.63 (CH), 127.77 (d, $J_{C-P} = 8.67$ Hz, CH), 128.04 (CH), 128.08 (2CH), 128.19 (CH), 128.22 (CH), 128.25 (CH), 128.28 (CH), 128.31 (CH), 128.53 (CH), 128.56 (CH), 129.08 (d, $J_{C-P} = 8.17$ Hz, CH), 130.36 (CH), 130.49 (CH), 131.09 (C), 131.11 (C), 131.24 (C), 131.59 (C), 131.87 (C), 132.41 (C), 132.49 (C), 133.25 (C), 133.43 (C), 133.61 (C), 133.87 (C), 134.05 (C), 134.63 (CH), 134.72 (2CH), 134.88 (CH), 135.33 (d, $J_{C-P} = 11.70$ Hz, CH); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm): 25.07 (s); ESI-MS: $m/z = 818.1$ [M^+]; HRMS (MALDI-TOF) calcd for $C_{48}H_{39}Cl_2PRu$ [M^+]: 818.12099. Found: 818.12023.
18. *Spectral data for the Pd-complex* **9**: pale yellow solid; mp = 208–210 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 2.78 (m, 6H, $2CH_3$), 4.00 (d, $J = 13.5$ Hz, 1H), 4.14 (d, $J = 13.5$ Hz, 1H), 6.41 (m, 2H), 6.79 (t, $J = 7.5$ Hz, 1H), 6.88 (t, $J = 7$ Hz, 1H), 7.02 (d, $J = 8.5$ Hz, 1H), 7.06 (dd, $J = 8.5$ Hz, $J_{H-P} = 1.5$ Hz, 1H), 7.28–7.52 (m, 8H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.64–7.70 (m, 3H), 7.84 (d, $J = 9$ Hz, 1H), 7.87 (d, $J = 8$ Hz, 1H), 7.92–8.03 (m, 7H), 8.05 (d, $J = 8$ Hz, 1H), 8.59 (dd, $J = 1.5$ Hz, $J_{H-P} = 14$ Hz, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 49.86 (Me), 49.98 (Me), 71.57 (CH_2), 121.57 (CH), 122.63 (CH), 124.13 (C), 124.67 (CH), 125.19 (d, $J_{C-P} = 5.55$ Hz, CH), 125.33 (CH), 125.50 (C), 126.21 (CH), 126.92 (CH), 127.13 (d, $J_{C-P} = 4.72$ Hz, CH), 127.40 (C), 127.48 (CH), 127.62 (CH), 127.67 (C), 127.72 (d, $J_{C-P} = 3$ Hz, CH), 127.97 (CH), 128.11 (CH), 128.19 (d, $J_{C-P} = 3$ Hz, CH), 128.35 (CH), 129.59 (d, $J_{C-P} = 9$ Hz, CH), 129.80 (CH), 129.92 (CH), 130.18 (CH), 130.40 (d, $J_{C-P} = 2.32$ Hz, CH), 130.62 (d, $J_{C-P} = 2.30$ Hz, CH), 130.68 (C), 130.82 (d, $J_{C-P} = 1.87$ Hz, C), 130.99 (C), 131.32 (CH), 131.41 (C), 131.46 (C), 131.91 (C), 132.19 (C), 133.19 (C), 134.30 (CH), 134.46 (CH), 134.63 (CH), 134.79 (CH), 137.66 (CH), 137.88 (CH), 137.96 (CH), 138.11 (CH), 141.54 (C), 143.63 (d, $J_{C-P} = 3.37$ Hz, C), 148.36 (d, $J_{C-P} = 2.10$ Hz, C); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm): 41.12 (s); ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −74.75 (d, $J_{F-P} = 105.46$ Hz); ESI-MS: $m/z = 866.1$ [M+H]$^+$; Anal. Calcd for $C_{49}H_{37}NO_2F_3PPd$: C, 67.94; H, 4.31; N, 1.62. Found: C, 67.74; H, 4.29; N, 1.62.