

Reactivity differences between 2,4- and 2,5-disubstituted zirconacyclopentadienes: a highly selective and general approach to 2,4-disubstituted phospholes.

Guillaume Bousrez, Florian Jaroschik, Agathe Martinez, Dominique Harakat, Emmanuel Nicolas, X. Le Goff, Jan Szymoniak

► To cite this version:

Guillaume Bousrez, Florian Jaroschik, Agathe Martinez, Dominique Harakat, Emmanuel Nicolas, et al.. Reactivity differences between 2,4- and 2,5-disubstituted zirconacyclopentadienes: a highly selective and general approach to 2,4-disubstituted phospholes.. Dalton Transactions, Royal Society of Chemistry, 2013, epub ahead of print. 10.1039/c3dt51158h . hal-00839784

HAL Id: hal-00839784

<https://hal-polytechnique.archives-ouvertes.fr/hal-00839784>

Submitted on 1 Jul 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Reactivity differences between 2,4- and 2,5-disubstituted zirconacyclopentadienes: a highly selective and general approach to 2,4-disubstituted phospholes.

Guillaume Bousrez,^a Florian Jaroschik,^{*a} Agathe Martinez,^a Dominique Harakat,^a Emmanuel Nicolas,^b
Xavier F. Le Goff,^b Jan Szymoniak^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Mixtures of 2,4- and 2,5-disubstituted zirconacyclopentadienes were obtained by the reductive coupling of terminal alkynes using the Cp₂ZrCl₂/lanthanum system. Reactions of dihalophosphines with these mixtures afforded selectively the corresponding 2,4-disubstituted phospholes and 1,4-disubstituted butadienes. The new series of phospholes was characterized by multi-nuclear NMR spectroscopy and X-ray analysis. A possible explanation for the observed selectivity was obtained from X-ray studies and DFT analysis of the intermediate zirconacyclopentadienes.

Introduction

Zirconacyclopentadienes are important intermediates in organic synthesis, including transition-metal catalysis and macrocyclisation reactions. Since the first synthesis of tetraphenylzirconacyclopentadiene in 1961, several synthetic pathways have been explored. Especially, the emergence of low-valent zirconocene precursors, such as the Negishi, Takahashi or Rosenthal reagents, has contributed considerably to their development. These complexes reductively couple internal alkynes with a large variety of substituents. The regioselectivity can be influenced by trimethylsilyl (alpha-position), pentafluorophenyl or mesityl groups (beta-position). The hydrozirconation/methylation pathway developed by Buchwald is an interesting alternative as it gives readily access to trisubstituted complexes whereas the former reagents are especially suitable for tetrasubstituted compounds. However, most reagents cannot be employed in the coupling of two terminal alkynes and disubstituted zirconacyclopentadienes have been rarely described. In most cases, mixtures of products were obtained which could not be further exploited. Only the very bulky tris(trimethylsilyl)silyl group afforded the 2,5-disubstituted zirconacyclopentadiene as sole product. A switch to the bis(indenyl)zirconocene allows the 2,5-selective coupling of terminal alkynes. In 2006, the reductive dimerisation of terminal alkynes using a Mischmetall generated zirconocene(II) equivalent was described. These reactions yielded clean mixtures of 2,4- and 2,5-disubstituted zirconacyclopentadienes as shown by hydrolysis experiments. To date no further reaction involving 2,4-disubstituted zirconacyclopentadienes has been reported.

Among the numerous transformations of zirconacyclopentadienes, the synthesis of 5-membered heterocycles has attracted much interest. The so-called Fagan-

Nugent route involves the reaction of electrophilic main group halides based on boron, phosphorus, tin and others with zirconacyclopentadienes. We focused our interest on the synthesis of new phospholes, as they have recently become important building blocks in the fields of catalysis, coordination chemistry, material sciences and medicinal chemistry.¹⁻⁵ In addition, phospholide anions are interesting alternatives to cyclopentadienide ligands in organometallic chemistry.⁶ In view of these numerous applications, it seemed surprising that not all substitution patterns of phospholes have been investigated: the majority of phospholes is tetrasubstituted, with 2,5- and 3,4-disubstituted phospholes being also readily accessible.⁷ In contrast, very few examples of 2,4-disubstituted phospholes are known and no general synthetic route to such compounds has been reported.⁸ Such compounds may offer different steric and electronic properties, which could be exploited in ligand design for catalytic and organometallic purposes.

We report here a highly selective and general synthesis of 2,4-disubstituted phospholes using the Fagan-Nugent route in combination with the reductive coupling of terminal alkynes by the lanthanum generated zirconocene(II). An X-ray study and DFT calculations on the intermediate zirconacyclopentadienes offer some insights with respect to the observed selectivity.

Experimental part

All reactions were conducted under an argon atmosphere using standard Schlenk techniques and an argon-filled Jacomex BS531-type dry box. Tetrahydrofuran and diethylether were collected under argon from a PURSOLV MD-3 (Innovative Technologie Inc.) solvent purification unit. Zirconocene dichloride was purchased from Strem Chemicals. Alkynes were purchased from Aldrich and Alfa Aesar or synthesized from the corresponding aldehydes according to reported literature procedures.¹

Lanthanum ingot was purchased from Aldrich and Strem Chemicals and freshly filed in the drybox prior to use. ^1H , ^{13}C , ^{19}F , ^{29}Si and ^{31}P NMR spectra were recorded in CDCl_3 , unless specified, on a 250MHz Bruker Avance I spectrometer equipped with a QNP probe and a 500MHz Bruker Avance III spectrometer equipped with a BBFO+ probe. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm). One and two dimensional experiments, including NOESY and HOESY (^1H - ^{31}P) experiments were performed for the NMR assignments of phospholes. High resolution ESI-MS spectra were recorded on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. High resolution EI-MS spectra were obtained on a GCT-TOF mass spectrometer (Micromass, Manchester, UK) with EI source.

Synthesis of 1,4-diiodo-1,3- and 1,4-diphenylbutadienes 2a and 2b. A Schlenk tube was loaded with zirconocene dichloride (Cp_2ZrCl_2) (292 mg, 1.0 mmol), lanthanum (93 mg, 0.66 mmol) and THF (5 mL). The resulting mixture was stirred vigorously at room temperature until a deep red color appeared. At this stage, phenylacetylene (0.21 ml, 2 mmol) was added to the reaction mixture. After 3 h, iodine (570 mg, 2.25 mmol) was added portion-wise at room temperature and the reaction was stirred for 24 h. The resulting brown solution with a yellow precipitate was quenched with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (1 M, 5 mL) and water (25 mL) at room temperature. The aqueous layer was extracted with Et_2O (3×25 mL), and the organic phases were combined, washed with brine, dried over MgSO_4 , and concentrated under vacuum. The red residue was purified by flash column chromatography on silica gel using petroleum ether as eluent, yielding **2a** and **2b** in 25% (113 mg, 0.25 mmol) and 18% (82 mg, 0.18 mmol), respectively. NMR data of **2a** and **2b** are in accordance with the literature data.⁵

Optimised procedure for 1,2,4-triphenylphosphole. A Schlenk tube was loaded with Cp_2ZrCl_2 (584 mg, 2.0 mmol), lanthanum (186 mg, 1.3 mmol) and THF (10 mL). The resulting mixture was stirred vigorously at room temperature until a deep red color appeared. At this stage, the phenylacetylene (0.42 mL, 4.0 mmol) was added to the reaction mixture and the stirring was continued until complete disappearance of the alkyne as shown by TLC. Then the optimized amount of dichlorophenylphosphine (0.14 mL, 1.0 mmol) was added at -78°C . After slow warming to room temperature, the reaction mixture was stirred for 18 h. After that time, petroleum ether (20 mL) was added to the brown solution and the solution was filtered over a short column of basic aluminum oxide using petroleum ether/ethyl acetate 8:2 as eluent. The solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel using petroleum ether to yield phosphole **3a** in 70% yield (218 mg, 70 mmol). Crystals suitable for X-ray analysis were obtained by recrystallisation from diethyl ether. ^1H NMR (500 MHz, CDCl_3): 7.08 (dd, $J_{\text{P-H}} = 40.0$ Hz, $J_{\text{H-H}} = 1.5$ Hz, 1H, H1), 7.22-7.29 (m, 3H, H12, H15), 7.31 (d, $J_{\text{H-H}} = 8.0$ Hz, 2H, H11), 7.34-7.38 (m, 3H, H8, H16), 7.43 (d, $J_{\text{H-H}} = 7.0$ Hz, 2H, H7), 7.46 (d, $J_{\text{P-H}} = 7.5$ Hz, 2H, H14), 7.61 (d, $J_{\text{H-H}} = 8.0$ Hz, 2H, H10), 7.66 (dd, $J_{\text{P-H}} = 12.5$ Hz, $J_{\text{H-H}} = 1.5$ Hz, 1H, H3), 7.73 (d, $J_{\text{H-H}} = 7.0$ Hz, 2H, H6). ^{13}C NMR (125 MHz, CDCl_3): 126.6 (d, $J_{\text{P-C}} = 1.3$ Hz, CH, C6), 126.8 (d, $J_{\text{P-C}} = 9.5$ Hz, CH, C10), 127.5 (CH, C12), 128.0 (CH,

C1), 128.2 (CH, C8), 128.8 (CH, C7), 128.8 (d, $J_{\text{P-C}} = 6.6$ Hz, CH, C15), 128.9 (CH, C11), 129.7 (d, $J_{\text{P-C}} = 1.5$ Hz, CH, C16), 130.8 (d, $J_{\text{P-C}} = 9.9$ Hz, C, C13), 131.9 (d, $J_{\text{P-C}} = 10.3$ Hz, CH, C3), 134.0 (d, $J_{\text{P-C}} = 19.5$ Hz, CH, C14), 136.5 (d, $J_{\text{P-C}} = 15.9$ Hz, C, C9), 137.0 (d, $J_{\text{P-C}} = 3.0$ Hz, C, C5), 150.4 (d, $J_{\text{P-C}} = 7.8$ Hz, C, C2), 153.8 (d, $J_{\text{P-C}} = 2.0$ Hz, C, C4). ^{31}P NMR (200 MHz, CDCl_3): 11.3. HRMS (EI) for $\text{C}_{22}\text{H}_{17}\text{P}$: calc. (m/z) 312.1068; found (m/z) 312.1068.

Synthesis of 2,5-diphenylzirconacyclopentadiene 1b. A Schlenk tube was loaded with Cp_2ZrCl_2 (292 mg, 1.0 mmol), lanthanum (93 mg, 0.66 mmol) and THF (5 mL). The resulting mixture was stirred vigorously at room temperature until a deep red color appeared. At this stage, phenylacetylene (0.21 mL, 2.0 mmol) was added to the reaction mixture and stirring continued for 3 h. The solution was filtered to remove insoluble LaCl_3 salts. Then the solvent was reduced to 2 mL under vacuum and put in the fridge at 4°C . From this solution a crop of dark red crystals of **1b** suitable for X-ray diffraction was obtained. The ^{13}C NMR data is in agreement with the analogous complex $[(\text{C}_5\text{H}_4\text{Me})_2\text{Zr}(\text{PhC}(\text{CH}_2)\text{CPh})]$.⁴

^1H NMR (250 MHz, C_6D_6): 5.91 (s, 10H), 7.03-7.06 (m, 5H), 7.13-7.14 (m, 2H), 7.27-7.33 (m, 5H). ^{13}C NMR (62.5 MHz, C_6D_6): 112.5 (CH), 119.6 (CH), 128.7 (CH), 129.8 (CH), 130.1 (CH), 130.5 (CH), 130.7 (CH), 149.9 (C), 192.7 (C). HRMS (ESI) for $\text{C}_{26}\text{H}_{23}\text{Zr}$ [M+H]: calc. (m/z) 425.0847; found (m/z) 425.0853.

X-ray crystallography. Single crystals were coated in Paratone-N oil and mounted on a loop. Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo $\text{K}\alpha$ ($\lambda = 0.71070$ Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. The crystal structures were solved using SIR 97 and refined using Shelxl97.^{2,3}

DFT-analysis. Calculations were performed with the Gaussian03 and Gaussian 09 suite of programs.^{6,7} The B3LYP functional⁸ was used for computation of monomers and NBO calculations as implemented in Gaussian 03, and the B97D functional⁹ for computation of the tetramer, as implemented in Gaussian09. The land2z basis set and associated core potential¹⁰ were used for Zr atoms, and main group elements (C and H)¹¹ were described with the 6-31G basis set. All basis sets were used as implemented in the program. Stationary points were identified as having no imaginary frequency. NBO analyses were performed using NBO 5.9¹² as implemented in Gaussian 03.

Reductive dimerization of terminal alkynes

The reductive dimerisation of phenylacetylene using the lanthanum generated zirconocene(II), yielded a dark red solution of a mixture of diphenylzirconacyclopentadienes **1a-c**, as evidenced by ESI-MS, X-ray crystallography (see below) and quenching experiments (Scheme 1). Hydrolysis of this mixture **1a-c** showed that the ratio of the 1,3- and 1,4-disubstituted butadiene isomers was 1:1, whereas the 2,3-isomer was present in lower than 5% yield according to NMR analysis.† Trace amounts of benzene derivatives were also present.¹¹ The observed ratio for the butadienes is close to the one reported by Erker et al. obtained with a zirconocene-diene complex and phenylacetylene. However, in our case no side-products arising from the zirconocene precursor were observed. This result was further

confirmed by the reaction of **1a-c** with iodine. The 1,4-diiodobutadienes **2a** and **2b** were obtained in a 1:1 ratio according to the crude NMR spectrum. Full conversion was observed without the addition of copper catalyst.¹² Compounds **2a** and **2b** were isolated in low 25% and 18% yield, respectively, due to partial decomposition on silica gel. **2a** was obtained previously only in trace amounts by the titanium-catalysed coupling of phenylacetylene.¹³

terminal alkyne have a limited influence on these ratios. The only exception is the p-chlorophenyl substituent which clearly favors the formation of 2,4-disubstituted phosphole **3c**.¹⁴ In order to further investigate this behaviour, the reaction with other electrophilic phosphorus reagents was examined. PhPBr₂ has been described as being more reactive than PhPCl₂.^{9a} However, when this reagent was used in the reaction with **1a-c**, only compound **3a** was formed. Heating at 60°C for 15h did not influence the reaction outcome. Reaction of **1a-c** with dichlorocyclohexylphosphine afforded only the 2,4-diphenylphosphole **3k**.

(2)

Scheme 1 Hydrolysis and iodolysis of disubstituted zirconacyclopentadienes

Selective synthesis of 2,4-disubstituted phospholes

Further transformation of diiodide **2a** via iodine/lithium exchange followed by addition of dichlorophenylphosphine yielded the first 2,4-diphenylsubstituted phosphole **3a** in 65% yield (eq. 1).^{7a}

(1)

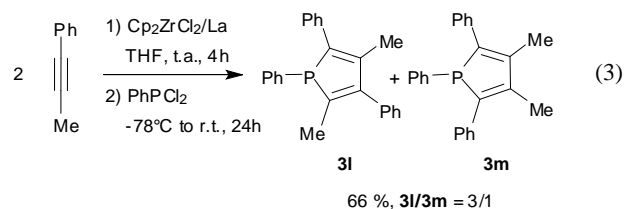
In order to simplify the procedure and circumvent the diiodide compounds, the addition of one equivalent of PhPCl₂ to diphenylzirconacyclopentadienes **1a-c** was investigated. Surprisingly, this did not lead to a mixture of the expected 1,2,4- and 1,2,5-triphenylphospholes, but after workup 1,2,4-triphenylphosphole **3a** and 1,4-diphenyl-1,3-butadiene **4a** were obtained in a 1:1 ratio (eq. 2, table 1). The products could be separated by column chromatography and identified by multinuclear NMR spectroscopy. Further improvement was achieved when only 0.55 equivalents of dichlorophenylphosphine was added as the formation of by-products due to unreacted phosphorus reagent could be avoided. Phosphole **3a** was isolated as a pale-yellow, relatively air-stable solid in 70% yield based on phosphorus reagent. This methodology was then extended to a large variety of phospholes carrying aryl **3b-f**, heteroaryl **3g**, alkyl **3h-i** and trimethylsilyl **3j** groups. An initial reaction was carried out with 1.0 equivalent of PhPCl₂ to determine the ratio between phosphole **3** and butadiene **4**. Based on this result, in a second reaction the optimised amount of dichlorophosphine was added to prepare the phospholes **3**. The isolated yields vary between 72 and 24% (Table 1) and in all cases, only the 2,4-disubstituted phospholes were obtained. The substituents R on the

Table 1 Synthesis and ³¹P NMR data of 2,4-disubstituted phospholes

Entry	R	R'	Ratio ^a 3/4	Yield ^b 3	³¹ P NMR ^c
a	Ph	Ph	1/1	70 (35)	11.3
b	p-CH ₃ -(C ₆ H ₅)	Ph	1/1	61 (30)	10.8
c	p-Cl-(C ₆ H ₅)	Ph	4/1	46 (39)	12.3
d	p-F-(C ₆ H ₅)	Ph	2/1	48 (34)	11.9
e	p-OMe-(C ₆ H ₅)	Ph	2/1	36 (26)	10.6
f	2-naphthyl	Ph	2/1	24 (17)	11.7
g	2-thienyl	Ph	1/1	57 (29)	13.4
h	n-pentyl	Ph	1/1	63 (32)	8.1
i	t-butyl	Ph	2/1	47 (33)	1.4
j	Me ₃ Si	Ph	1/1	72 (36)	31.9
k	Ph	c-C ₆ H ₁₁	1/1	40 (20)	26.0

^a determined by ¹H NMR from the crude reaction mixture; ^b isolated yield under optimised conditions with respect to phosphorous reagent and in parentheses with respect to zirconium reagent; ^c in CDCl₃.

In order to ensure that the observed reactivity did not originate from the employed zirconocene source Cp₂ZrCl₂/La, an experiment was conducted using phenylpropyne. As expected, in this case both phospholes **3l** and **3m** were formed in a 3:1 ratio in an overall 66% yield (eq. 3).



Finally, a competing experiment between di- and tetrasubstituted zirconacyclopentadienes coming from phenylacetylene **1a-c** and from phenylpropyne **1d-e** was performed. Addition of 0.5 equivalents of PhPCl₂ to this mixture

led to the exclusive formation of phosphole **3a**. Further addition of 0.5 equivalents of PhPCl₂ afforded a mixture of **3l** and **3m**, which further increased with more phosphorous reagent. The 2,5-disubstituted phosphole was not observed.

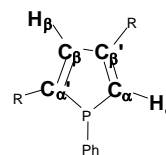
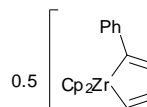


Table 2 Selected NMR data of some 2,4-disubstituted phospholes

R	¹ H (H _α , H _β) ^{a,b}	¹³ C (C _α , C _{α'} , C _β , C _{β'}) ^{a,c}
Ph (3a)	7.08 (40.0), 7.66 (12.5)	128.0 (0), 153.8 (2.0), 131.9 (10.3), 150.4 (7.8)
p-OMe-(C ₆ H ₅) (3e)	6.91 (38.0), 7.56 (12.5)	124.5 (0), 153.3 (1.8), 130.2 (10.0), 150.0 (7.6)
2-thienyl (3g)	6.88 (38.5), 7.43 (11.5)	124.9 (0), 147.0 (4.4), 130.5 (9.1), 143.8 (7.8)
t-butyl (3i)	6.24 (41.0), 6.75 (15.0)	122.7 (1.3), 161.8 (7.1), 130.9 (10.8), 165.8 (9.1)
Me ₃ Si (3j)	7.43 (40.5), 7.29 (18.5)	149.4 (10.8), 150.3 (26.1), 147.4 (10.1), 154.8 (5.5)

^a in CDCl₃; ^b in parentheses ²J_{PH} and ³J_{PH} coupling constants; ^c in parentheses ¹J_{PC} and ²J_{PC} coupling constants



Scheme 2 Competition experiment between di- and tetrasubstituted zirconacyclopentadienes

Characterisation of 2,4-disubstituted phospholes

Multinuclear NMR spectroscopy

The ³¹P NMR shifts of phospholes **3a-g** are only slightly influenced by the aryl substituents going from 10.6 ppm for the methoxy group to 13.4 ppm for the thienyl group. Compared to the corresponding 1,2,5-triphenylphosphole **5a**,¹⁵ compound **3a** displays a downfield shift of 10 ppm. In the ¹H NMR spectra the main feature of phospholes **3** is the large ²J_{P-H} coupling (40 Hz) between phosphorus and the hydrogen on the alpha ring carbon atom. In the ¹³C NMR spectra, the ¹J_{C-P} coupling depends on the substitution, ranging from 0 to 4 Hz for hydrogen and aromatic substituents to 26 Hz for the trimethylsilyl group. Further differences in the NMR shifts between differently substituted phospholes are summarized in Table 2.

X-ray analysis

Single crystals of **3a** suitable for X-ray analysis were obtained by crystallisation from diethyl ether at 4°C (Fig. 1). Compound **3a** displays many similar features compared to the 2,5-diphenyl analogue **5a** (table 3).^{16,17} The pyramidal phosphorus atom lies 0.065(1) Å below a least-square fitted phosphole plane, compared to 0.048(1) Å for **5a**. The P-C bonds are in the range of single bonds, with a slight difference between the unsubstituted (1.787(2) Å) and the phenyl-substituted (1.815(2) Å) ring carbons. The double bonds in the phosphole ring (1.360(2) Å and 1.355(2) Å) are localised. The phenyl rings are slightly twisted with respect to the phosphole plane (xx° and xx°) compared to 4.63(8)° and 7.99(7)° for **5a**.

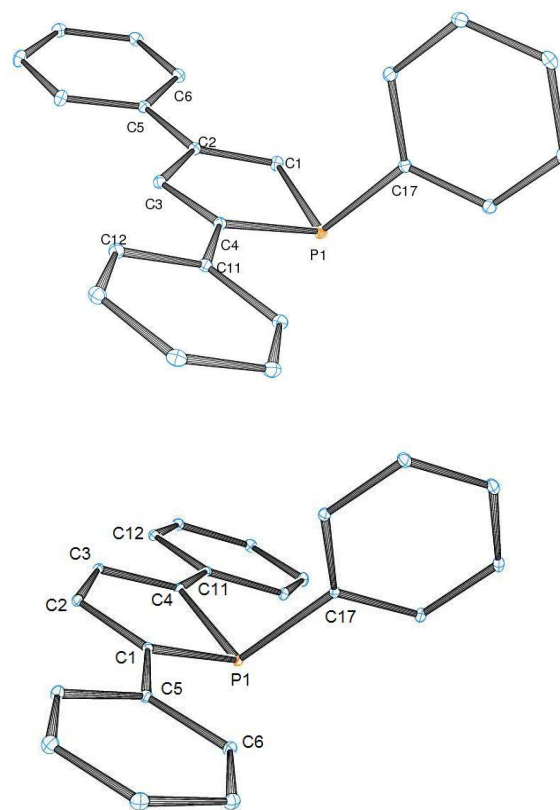


Fig. 1 Molecular structures of **3a** and **5a** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) of **3a** and **5a**

	3a	5a
P1-C1	1.787(2)	1.823(2)
P1-C4	1.815(2)	1.824(2)
P1-C17	1.828(2)	1.836(2)
C1-C2	1.360(2)	1.357(2)
C2-C3	1.466(2)	1.439(2)
C3-C4	1.355(2)	1.359(2)
C1-P1-C4	90.72(7)	91.34(8)
C1-P1-C17	105.91(7)	104.33(7)
C4-P1-C17	104.16(6)	105.49(7)
C1-C2-C3-C4	0.15(25)	0.37(25)

Disubstituted vs. tetrasubstituted zirconacyclopentadienes

It was previously observed that bulky alkyl ligands in the alpha position of zirconacyclopentadienes can hinder the formation of phospholes.¹⁸ However, the inertness of 2,5-diarylzirconacyclopentadienes towards PhPCl₂ was very intriguing as tetrasubstituted zirconacyclopentadienes carrying aryl groups in the 2 and 5 positions react readily with PhPX₂ as previously reported and shown above.^{9a,c} In order to gain more insight into this selective transformation, we focused next on the intermediate zirconacyclopentadienes.

X-ray study

X-ray quality crystals of **1b** were obtained from a THF solution of a mixture of **1a-c** at 4°C (Fig. 2). Compound **1b** contains two zirconacyclopentadiene complexes and one THF molecule in the unit cell. Bond lengths and angles involving zirconium are similar to other zirconacyclopentadienes, as for example in Cp₂Zr(C₄H₂(TTMS)₂) and Cp₂Zr(C₄Ph₄).^{9a,14b} The most important feature of **1b** is the nearly planar phenyl-zirconacyclopentadiene-phenyl system with twist angles ranging from 5.33° to 16.91°. This is in stark contrast to tetrasubstituted zirconacyclopentadienes where the phenyl rings in the 2 and 5 positions are bent at 40-60° due to steric crowding, for example in Cp₂Zr(C₄Ph₄) the twist angles are 48.69° and 54.34°.^{14b,c}

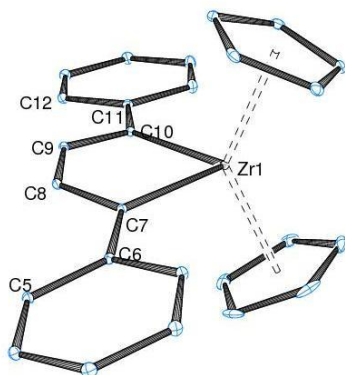


Fig. 2. Molecular structure of 2,5-diphenylzirconacyclopentadiene **1b** (50% probability ellipsoids), only one of the two complexes is shown. A THF molecule and hydrogen atoms are omitted for clarity. Selected bond

distances (Å) and angles (°): Zr(1)-C(7) 2.244(2), Zr(1)-C(10) 2.248(2), Zr(1)-C(21) 2.465(3), Zr(1)-C(24) 2.523(2), C(7)-C(8) 1.359(3), C(8)-C(9) 1.474(3), C(9)-C(10) 1.360(3), C(7)-Zr(1)-C(10) 86.74(7)

When the isolated complex **1b** was reacted with PhPCl₂ in THF-d⁸ no reaction was observed.

DFT-analysis

Based on the X-ray structure of **1b**, DFT calculations using the Gaussian03 suite of programs were carried out. Initially, the B3LYP functional was used, in conjunction with the 6-31G basis set for all main-group elements, and the lan12dz basis set for Zr. It was shown that the structure of **1b** could not be correctly calculated. A deviation in the dihedral angles of 10-20° was observed. Variation of basis sets and functionals did not improve the results. A closer look at the crystal structure revealed that intermolecular interactions (π-stacking) lead to a tetrameric structure, i.e. four zirconacyclopentadienes form an independent tetramer. This structure could be correctly reproduced using the B97D functional, which takes into account dispersion effects for short distance interactions (Table 4).

Table 4 Comparison of X-ray data and DFT calculations on **1b**

Dihedral angle ^a	X-ray data ^a	Monomer ^b	Tetramer ^c
C5-C8/C35-C38 [°]	16.91/5.33	25.75	13.33/5.56
C7-C10/C33-C36 [°]	0.86/0.11	1.15	1.34/0.21
C9-C12/C31-C34 [°]	12.89/13.3	25.77	13.33/7.91

^aTwo distinct complexes in unit cell; ^bB3LYP//6-31G (H, C) and lan12dz (Zr); ^cB97D//6-31++G (H), 6-31G (C) and lan12dz (Zr)

In solution, it seems however more likely that the monomeric structure is prevalent. The 2,4-diphenylzirconacyclopentadiene **1a** was therefore also calculated with the B3LYP functional and an NBO analysis of **1a** and **1b** was performed. For comparison reasons the tetrasubstituted complexes **1d** and **1e** arising from phenylpropyne were also calculated (Table 5, Fig. 3 and 4).

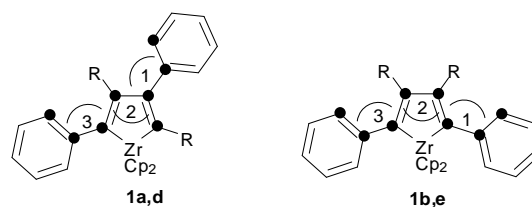
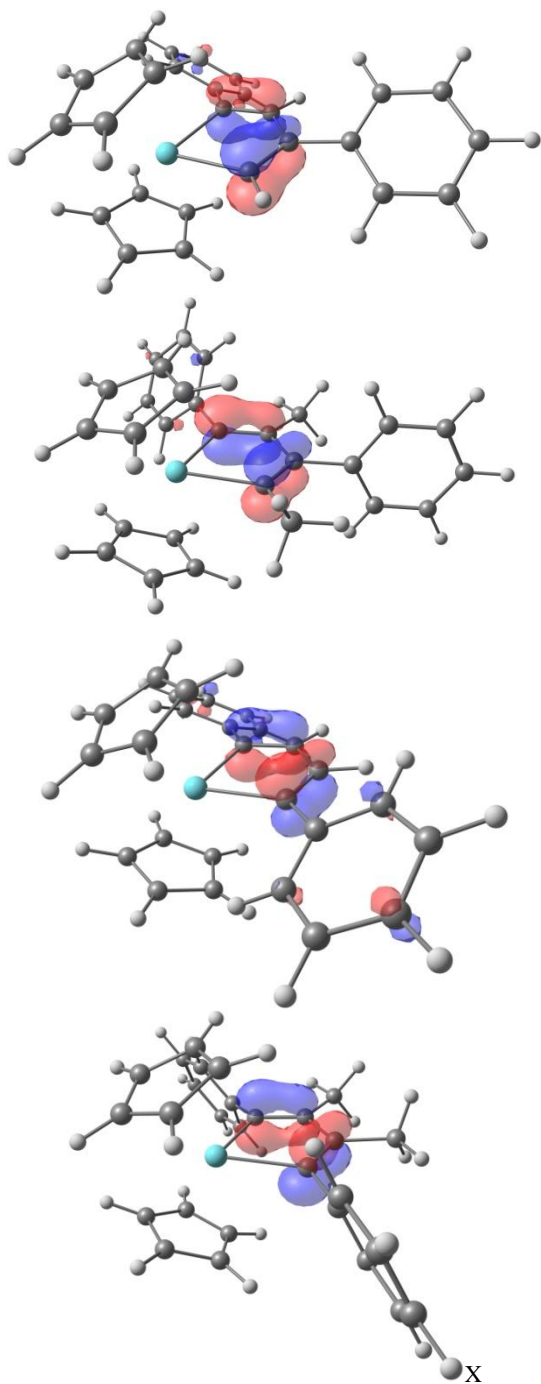


Table 5 Comparison of calculated^a dihedral angles (°) of **1a,b,d,e**

	Angle 1	Angle 2	Angle 3
2,4-Ph,3,5-H (1a)	+35.44	+2.90	+31.43
2,5-Ph,3,4-H (1b)	+25.75	+1.15	+25.76
2,4-Ph,3,5-Me (1d)	+89.95	-1.39	-56.62
2,5-Ph,3,4-Me (1e)	+54.91	+1.90	+54.91

^aB3LYP//6-31G (H, C) and lan12dz (Zr)



5 **Fig. 3** HOMOs and optimised geometries of zirconacyclopentadienes **1a, 1b, 1d** and **1e**

Fig.4 NBO analysis and HOMO energies of **1a, 1b, 1d** and **1e**

10

These calculations lead to the following observations: (i) the HOMOs of all complexes are on the zirconacyclopentadiene backbones, however the energy differences are too small to explain the observed selectivity; (ii) an important difference in the twist angles of the phenyl groups is observed between **1b** (25.75°) and **1e** (54.91°); (iii) the unsubstituted α -carbon in **1a** has a significantly more negative charge (-0.63) than the corresponding phenyl-substituted carbons in **1b** (-0.41) and **1e** (-0.42) and the methyl-substituted carbon in **1d** (-0.38). This difference in charge is in agreement with a more reactive intermediate **1a** compared to **1b, d, e**. However, the complete inertness of **1b** towards dihalophosphines seems to be mainly related to steric hindrance arising from the small tilt angle of the phenyl groups.

15

20

25 Conclusions

In conclusion a straightforward one-pot synthesis of a large series of 2,4-disubstituted phospholes has been described making use of the difference in reactivity between 2,4- and 2,5-disubstituted zirconacyclopentadienes towards electrophilic phosphorous reagents. An X-ray study and DFT analyses of the intermediate zirconacyclopentadienes point towards steric reasons and only slight electronic influences to explain this selectivity. Further studies to extend this methodology to other 5-membered heteroles as well as the investigation of the chemistry of the new phosphole building blocks are currently under way.

30

35

We thank the CNRS, the Université de Reims and the Region Champagne-Ardenne for financial support and the platform PIAnET for technical support. Assistance from Miss Carine Machado (mass spectrometry) is acknowledged.

40

Notes and references

^a Institut de Chimie Moléculaire de Reims, UMR CNRS 7312, Université de Reims, BP 1039, 51687 Reims, France. Fax: +33 326913166; Tel: +33 326913244; E-mail florian.jaroschik@univ-reims.fr and

^b jan.szymoniak@univ-reims.fr

^b Laboratoire "Hétéroéléments et Coordination", Ecole Polytechnique and CNRS, 91128 Palaiseau Cedex, France

† Electronic Supplementary Information (ESI) available: Experimental and DFT data. CCDC [] See DOI: 10.1039/b000000x/

- § The dehydrohalogenation of 1-halogenophospholium salts worked in the case of 1,3-dimethylbutadiene (ref 8a), however, 1,3-diarylbutadienes are difficult to access and readily undergo homo-Diels Alder reactions.
- ‡ The ratio **2a/2b** = 1/2.5 reported in 2006 (ref. 10) was based on GC analysis and did not take into account the facile homo-Diels Alder reaction of the butadienes.
- 1 F. Mathey, *Chem. Rev.*, 1988, **88**, 429.
 - 2 D. Carmichael, in *Phosphorus (III) Ligands in Homogeneous Catalysis: Design and Synthesis, Chapt. 7: Phospholes*, (Ed. P. Kamer and P. W. N. M. van Leeuwen), Wiley VCH, 2012.
 - 3 (a) Y. Matano and T. Imahori, *Acc. Chem. Res.*, 2009, **42**, 1193; (b) P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627.
 - 4 (a) Y. Ren and T. Baumgartner, *Dalton Trans.*, 2012, **41**, 7792; (b) Y. Matano and T. Imahori, *Org. Biomol. Chem.*, 2009, **7**, 1258; (c) T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681.
 - 5 S. Urig, K. Fritz-Wolf, R. Réau, C. Herold-Mende, K. Toth, E. Davioud-Charvet and K. Becker, *Angew. Chem. Int. Ed.*, 2006, **45**, 1881.
 - 6 (a) S. Labouille, F. Nief, X.-F. Le Goff, L. Maron, D. R. Kindra, H. L. Houghton, J. W. Ziller and W. J. Evans, *Organometallics*, 2012, **31**, 5196; (b) F. Jaroschik, F. Nief, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, **26**, 3552.
 - 7 (a) F. Nief, B. Tayart de Borms, L. Ricard and D. Carmichael, *Eur. J. Inorg. Chem.*, 2005, 637; (b) J. Hydrio, M. Gouygou, F. Dallemer, G. A. Balavoine and J.-C. Daran, *Eur. J. Org. Chem.*, 2002, **4**, 675; (c) M. Ogasawara, K. Yoshida and T. Hayashi, *Organometallics*, 2001, **20**, 1014;
 - 8 (a) W. P. Freeman, Y. J. Ahn, T. K. Hollis, J. A. Whitaker, V.C. Vargas, R. J. Rubio, K. D. Alingog, E. B. Bauer and F. S. Tham, *J. Organomet. Chem.*, 2008, **693**, 2415; (b) G. Keglevich, T. Chuluunbaatar, A. Dobó and L. Töke, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1495.
 - 9 (a) O. Fadhel, Z. Benkö, M. Gras, V. Deborde, D. Joly, C. Lescop, L. Nyulászai, M. Hissler and R. Réau, *Chem. Eur. J.*, 2010, **16**, 11340;
 - 35 (b) Y. Matano, M. Nakashima and H. Imahori, *Angew. Chem. Int. Ed.*, 2009, **48**, 4002; (c) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászai and R. Réau, *Chem. Eur. J.*, 2001, **7**, 4222. (d) P. J. Fagan, W. A. Nugent and J. C. Calabrese, *J. Am. Chem. Soc.* 1994, **116**, 1880.
 - 40 10 C. Denhez, S. Médégar, F. Héllion, J.-L. Namy, J.-L. Vasse and J. Szymoniak, *Org. Lett.*, 2006, **8**, 2945.
 - 11 A. Joosten, M. Soueidan, C. Denhez, D. Harakat, F. Héllion, J.-L. Namy, J.-L. Vasse and J. Szymoniak, *Organometallics*, 2008, **27**, 4152.
 - 45 12 C. Xi, S. Huo, T. H. Afifi, R. Hara and T. Takahashi, *Tetrahedron Lett.*, 1997, **38**, 4099.
 - 13 S. Yamaguchi, R.-Z. Jin, K. Tamao and F. Sato, *J. Org. Chem.*, 1998, **63**, 10060.
 - 14 (a) V. H. Gessner, J. F. Tannaci, A. D. Miller and T. Don Tilley, *Acc. Chem. Res.*, 2011, **44**, 435. (b) A. D. Miller, J. F. Tannaci, S. A. Johnson, H. Lee, J. L. McBee and T. Don Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 4917. (c) S. A. Johnson, F.-Q. Liu, M. C. Suh, S. Zürcher, M. Haufe, S. S. H. Mao and T. Don Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 4199.
 - 50 15 B. Lukas, R. M. G. Roberts, J. Silver and A. S. Wells, *J. Organomet. Chem.*, 1983, **256**, 103.
 - 16 W. P. Ozbirn, R. A. Jacobsen and J. C. Clardy, *J. Chem. Soc. D*, 1971, 1062.
 - 17 A low-temperature (150 K) crystal structure of **5a** was recorded.
 - 60 18 F. Nief, D. Turcitu and L. Ricard, *Chem. Commun.*, 2002, 1646.