

# $\alpha$ -Zincated phosphorus ylides

Matthias Steiner,<sup>a</sup> Hansjörg Grützmacher,<sup>\*a</sup> Hans Prtitzkow<sup>b</sup> and Laszlo Zsolnai<sup>b</sup>

<sup>a</sup> ETH-Zürich, Laboratorium für Anorganische Chemie, Universitätsstrasse 6, CH-8092 Zürich, Switzerland

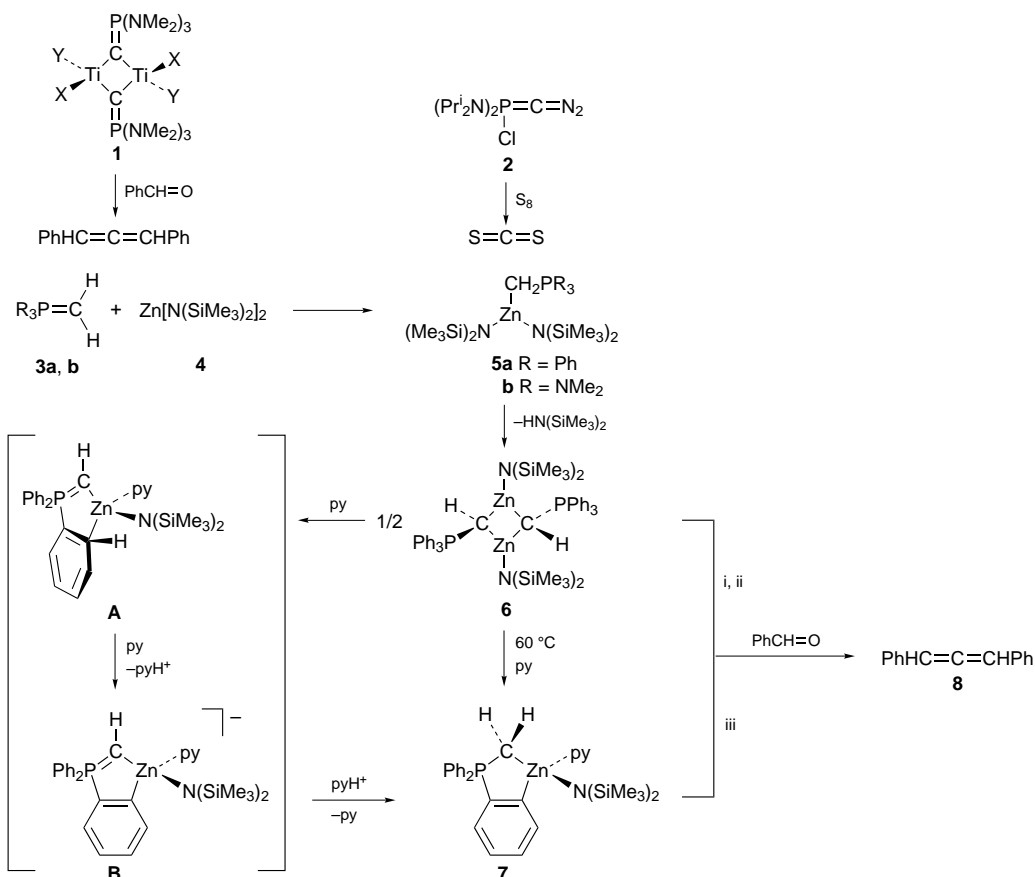
<sup>b</sup> Anorganisch Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

**1,3-Dizincata-2,4-diphosphoniacyclobutane rearranges into a zincataphosphoniaindane which reacts with benzaldehyde to give 1,3-diphenylallene.**

By reacting phosphorus ylides ( $R = \text{aryl}$ ) with mercury bis(trimethylsilylamide) we found a simple synthesis of  $\alpha$ -mercurated phosphorus ylides,  $\text{Ph}_3\text{P}=\text{CR}[\text{HgN}(\text{SiMe}_3)_2]$ , which react in a Wittig type alkenation reaction with aldehydes to give vinylmercury compounds.<sup>1</sup> We explored the possibility of synthesising comparable organozinc compounds in a similar way. These reagents seemed promising to us since they contain two oxophilic sites (P and low coordinated Zn) for the attack of a carbonyl oxygen centre. Like titanacycles **1**<sup>2</sup> or allenic diazophosphorus ylides **2**<sup>3</sup> they may serve as synthons for carbon atoms (Scheme 1). In the course of the studies, we observed an unprecedented cyclometallation reaction<sup>4</sup> involving, presumably, a low coordinated zinc centre.

When a toluene solution of ylides **3a,b** is added to zinc amide **4** at room temp. in toluene the expected adducts<sup>1</sup> **5a,b** are formed. They can be isolated as colourless precipitates after short reaction times (10 min) by concentrating the volume of the reaction mixture to 20% and adding *n*-hexane.<sup>†</sup>

While **5a** is thermally unstable, **5b** could be recrystallised from *n*-hexane and its structure determined by an X-ray analysis.<sup>‡</sup> All bonds [av. Zn–N 1.956(3) Å, Zn–C 2.077(4) Å] to the slightly pyramidalised zinc centre (0.138 Å above the N(1)N(2)C(1) plane] are *ca.* 0.1 Å longer than comparable Zn–N (av. 1.857 Å) and Zn–C (av. 1.952 Å) bonds in other tricoordinated zinc compounds.<sup>5</sup> The P(1)–C(1) distance [1.738(3) Å] is slightly longer than corresponding distances in a lithium phosphorus ylide complex<sup>6</sup> (P–C 1.702 Å) or uncomplexed ylides themselves (*i.e.* **3a**: 1.693 Å).<sup>7</sup> Keeping solutions of **5a** at room temp. or adding pyridine causes loss of 1 equiv. of  $\text{HN}(\text{SiMe}_3)_2$  and leads almost quantitatively to zincatacyclobutane **6** which precipitates as colourless crystals from the reaction mixture. Compound **6** can be recrystallised from THF–*n*-hexane (1 : 6 v/v). X-Ray analysis of **6**<sup>‡</sup> reveals a four-membered planar centrosymmetric  $\text{Zn}_2\text{C}_2$  heterocycle in which the  $\text{Ph}_3\text{PCH}$  units adopt bridging positions between the tricoordinated zinc centres. The Zn–N [1.931(3) Å] and Zn–C [2.068(4) Å] being again longer than in other low coordinated zinc compounds compare well with the ones in **5b**. The Zn–C–Zn angles [84.5(1)°] are smaller than the C–Zn–C angles [95.5(1)°]. In order to extrude 1 more equiv. of



**Scheme 1** Reagents and conditions: i, 60 °C, 24 h, no py, 7%; ii, 60 °C, 16 h, py, 12%; iii, 60 °C, 16 h, 31%

HN(SiMe<sub>3</sub>)<sub>2</sub> we warmed **6** to 60 °C in presence of pyridine. A clean reaction was evidenced by one new <sup>31</sup>P resonance at δ 34.8 (**6**: δ 25.9). The new product **7** was purified by recrystallization from toluene–*n*-hexane and completely characterised including an X-ray analysis. In order to explain the formation of zincataphosphoniindane **7**, we assume that pyridine cleaves the four-membered Zn<sub>2</sub>C<sub>2</sub> heterocycle **6** to give intermediate **A** which corresponds to an η<sup>1</sup>-arene complex to an electrophilic metal centre. Precedence for such a Zn–arene interaction is found in ZnPh<sub>2</sub> which forms a trapezoid dimer in the solid state with two *ipso*-carbon centres of the phenyl substituents adopting an unsymmetrical bridging binding mode (Zn–C 2.01, 2.40 Å).<sup>8</sup> Being an intramolecular organometallic σ-complex, **A** possesses a *ortho*-hydrogen centre which becomes sufficiently acidic to be abstracted by pyridine to give intermediate **B**. Reprotonation at the C(1) centre yields the thermodynamically more stable product **7**. Unfortunately, we could not isolate compound **B** by deprotonation of **7** with a strong base like NaN(SiMe<sub>3</sub>)<sub>2</sub>. Earlier work showed that **1a** may be lithiated by Bu<sup>n</sup>Li either at the CH<sub>2</sub> group or at the *ortho*-position of one of the phenyl groups attached to the phosphorus centre.<sup>9</sup> Our results confirm that the first product may be obtained under kinetic control while the second one is thermodynamically more stable.

When zincatacyclobutane **6** is reacted with 4 equiv. of benzaldehyde in toluene at 60 °C, a pale yellow oil is obtained after hydrolysis from which *ca.* 7% diphenylallene **8** were isolated by column chromatography (*n*-pentane–Et<sub>2</sub>O 7 : 1 v/v). Other products could not be identified. If the reaction is performed in presence of pyridine, the yield of allene **8** is augmented to 12%. Suspecting compound **7** may be involved in the formation of allene we reacted the zincatindane **7** with 2 equiv. of benzaldehyde. Indeed, the allene was formed in 31% yield. The mechanism of the seemingly simply Wittig alkenation is still not known with certainty<sup>10</sup> and our results show that reactions between metallated ylides and carbonyl compounds may be even more complex.

The structure of **7** is shown in Fig. 1. The five-membered heterocycle including a tetrahedrally distorted coordinated, chiral zinc centre (racemic mixture in the crystal) adopts an

envelope conformation [angle between P(1)C(1)Zn and the ZnC(3)C(2)P plane = 30°].

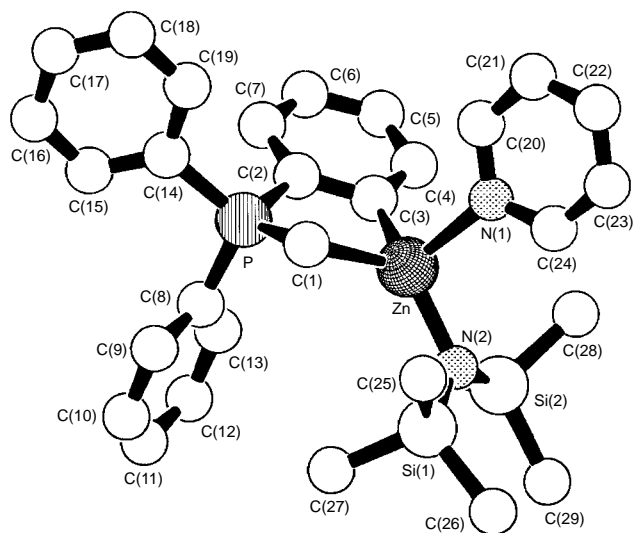
The Zn–C(3) (aryl) bond length [2.049(3) Å] is normal while the Zn–C(1) (alkyl) bond [2.138(4) Å] is long. The Zn–N(SiMe<sub>3</sub>)<sub>2</sub> bond [1.982(3) Å] is 0.1 Å shorter than the Zn–N<sub>py</sub> bond. Owing to electrostatic interactions between the negatively charged carbon center C(1) (being bonded to the electropositive Zn centre) and the highly positively charged λ<sup>5</sup>,σ<sup>4</sup>-phosphorus centre, the P–C(1) (sp<sup>3</sup>) bond [1.732(4) Å] is significantly shorter than the P–C(2) (sp<sup>2</sup>) bond [1.803(3) Å].

## Footnotes and References

\* E-mail: gruetz@inorg.chem.ethz.ch

† Selected <sup>1</sup>H (200 MHz), <sup>13</sup>C (50.232 MHz), <sup>29</sup>Si (17.75 MHz) and <sup>31</sup>P (36.19 MHz) NMR data for **5a,b** (C<sub>6</sub>D<sub>6</sub>), **6** ([<sup>2</sup>H<sub>8</sub>]THF) and **7** (C<sub>6</sub>D<sub>6</sub>): **5a**: Mp 187–189 °C. <sup>1</sup>H NMR: δ 0.37 (s, 36 H, SiMe<sub>3</sub>), 1.30 (d, 2 H, <sup>2</sup>J<sub>HP</sub> 16.8 Hz, CH<sub>2</sub>), 6.95–7.16 (m, 9 H, *m*, *p*-H, PPh<sub>3</sub>), 7.54–7.80 (m, 6 H, *o*-H, PPh<sub>3</sub>). <sup>13</sup>C δ 3.7 (d, <sup>1</sup>J<sub>CP</sub> 29.1 Hz, CH<sub>2</sub>). <sup>29</sup>Si NMR: δ 6.6. <sup>31</sup>P NMR: δ 30.1. **5b**: 75 °C (decomp.). <sup>1</sup>H NMR: δ 0.48 (s, 36 H, SiMe<sub>3</sub>), 1.53 (d, 2 H, <sup>2</sup>J<sub>HP</sub> 17.0 Hz, CH<sub>2</sub>), 2.08 (d, 18 H, <sup>3</sup>J<sub>HP</sub> 9.3 Hz, NMe<sub>2</sub>). <sup>13</sup>C: δ 2.8 (d, <sup>1</sup>J<sub>CP</sub> 91.7 Hz, CH<sub>2</sub>). <sup>29</sup>Si NMR: δ –7.0. <sup>31</sup>P NMR: δ 74.0. **6**: Mp 94–96 °C. <sup>1</sup>H NMR: δ –0.22 (s, 18 H, SiMe<sub>3</sub>), 0.01 [A part of AA'XX', 1 H, (J<sub>HP</sub> + J<sub>HP</sub>) 17.7 Hz, CH], 7.35–7.53 (m, 9 H, *m*, *p*-H, PPh<sub>3</sub>), 7.62–7.74 (m, 6 H, *o*-H, PPh<sub>3</sub>). <sup>13</sup>C NMR: δ 6.1 (d, <sup>1</sup>J<sub>CP</sub> 27.7 Hz, C<sub>ring</sub>). <sup>29</sup>Si NMR: δ –7.3. <sup>31</sup>P NMR: δ 28.1. **7**: Mp 79 °C. <sup>1</sup>H NMR: δ 0.47 (s, SiMe<sub>3</sub>, <sup>2</sup>J<sub>HSi</sub> 6.2 Hz), 0.76 (d, <sup>2</sup>J<sub>CP</sub> 9.5 Hz, CH<sub>2</sub>), 6.55–6.64 (m, arom H), 6.80–7.40 (m, arom H). <sup>13</sup>C NMR (75.469 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.3 (d, <sup>1</sup>J<sub>CP</sub> 47.5 Hz, CH<sub>2</sub>), 126.4 (d, <sup>2</sup>J<sub>CP</sub> 13 Hz, 6'-C, C<sub>6</sub>H<sub>4</sub>), 130.9 (d, <sup>4</sup>J<sub>CP</sub> 4.0 Hz, 4'-C, C<sub>6</sub>H<sub>4</sub>), 131.5 (d, <sup>3</sup>J<sub>CP</sub> 18.1 Hz, 5'-C, C<sub>6</sub>H<sub>4</sub>), 136.1 (d, <sup>1</sup>J<sub>CP</sub> 105.7 Hz, 1'-C, C<sub>6</sub>H<sub>4</sub>), 139.4 (d, <sup>3</sup>J<sub>CP</sub> 21 Hz, 3'-C, C<sub>6</sub>H<sub>4</sub>), 176.0 (d, <sup>2</sup>J<sub>CP</sub> 45 Hz, 2'-C, C<sub>6</sub>H<sub>4</sub>). <sup>29</sup>Si NMR: δ –6.0. <sup>31</sup>P NMR: δ 34.2. All compounds gave satisfactorily elemental analyses.

‡ Crystallography: All data collected using Mo–Kα radiation, refinements by least-squares methods (full matrix) based on F<sub>o</sub><sup>2</sup> values (SHELXL-93). **5b**: monoclinic, P2<sub>1</sub>/n, *a* = 16.065(12), *b* = 12.239(7), *c* = 17.191(11) Å, *b* = 109.81(5)°, *U* = 3180(4) Å<sup>3</sup>, *Z* = 4, 3.0 < 2θ < 50.0°, 4568 reflections, 281 parameters, *R*<sub>1</sub> = 0.0357 (only observed reflections), *wR*<sub>2</sub> = 0.0604. **6**: monoclinic, P2<sub>1</sub>/n, *a* = 12.352(14), *b* = 15.94(16), *c* = 14.999(16) Å, β = 114.37(8)°, *U* = 2690(5) Å<sup>3</sup>, *Z* = 2, 3.62 < 2θ < 50.00°, 4290 reflections, 342 parameters, *R*<sub>1</sub> = 0.041 (only observed reflections), *wR*<sub>2</sub> = 0.1071. **7**: triclinic, P $\bar{1}$ , *a* = 10.139(6), *b* = 14.245(8), *c* = 24.464(13) Å, α = 95.67(4), β = 99.39(4), γ = 96.09(4)°, *U* = 3442(3) Å<sup>3</sup>, *Z* = 4, 4.1 < 2θ < 47.00°, 10037 reflections, 719 parameters, *R*<sub>1</sub> = 0.039 (only observed reflections) *wR*<sub>2</sub> = 0.0961. CCDC 182/677.



**Fig. 1** Molecular structure of **7**: hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn–N(1) 2.174(3), Zn–N(2) 1.982(3), Zn–C(1) 2.137(4), Zn–C(3) 2.050(3), P–C(1) 1.733(4), P–C(2) 1.803(3), C(2)–C(3) 1.409(4); N(1)–Zn–N(2) 103.4(1), N(1)–Zn–C(1) 101.5(1), N(1)–Zn–C(3) 102.2(1), N(2)–Zn–C(1) 122.4(1), N(2)–Zn–C(3) 130.1(1), C(1)–Zn–C(3) 92.9(1), Zn–C(3)–C(2) 113.3(2), C(3)–C(2)–P 114.9(2), C(1)–P–C(2) 108.3(2), P–C(1)–Zn 100.8(2).

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