α-Zincated phosphorus ylides

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

By reacting phosphorus ylides (R = aryl) with mercury bis(trimethylsilyamide) we found a simple synthesis of α-mercurated phosphorus ylides, Ph$_3$P=CR[HgN(SiMe$_3$)$_2$], which react in a Wittig type alkenation reaction with aldehydes to give vinylmercury compounds.[1] 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**[2] or allenic diazophosphorus ylides **2**[3] they may serve as synthons for carbon atoms (Scheme 1). In the course of the studies, we observed an unprecedented cyclometallation reaction[4] 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[1] **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.†

While **5a** is thermally unstable, **5b** could be recrystallised from *n*-hexane and its structure determined by an X-ray analysis.‡ 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.[5] The P(1)–C(1) distance [1.738(3) Å] is slightly longer than corresponding distances in a lithium phosphorus ylide complex[6] (P–C 1.702 Å) or uncomplexed ylides themselves (*i.e.* **3a**: 1.693 Å).[7] Keeping solutions of **5a** at room temp. or adding pyridine causes loss of 1 equiv. of HN(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**‡ reveals a four-membered planar centrosymmetric Zn$_2$C$_2$ heterocycle in which the Ph$_3$PCH units adopt bridging positions between the tricoordinated zinc centres. The Zn–N [1.931(3) Å] and Zn–C distances [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
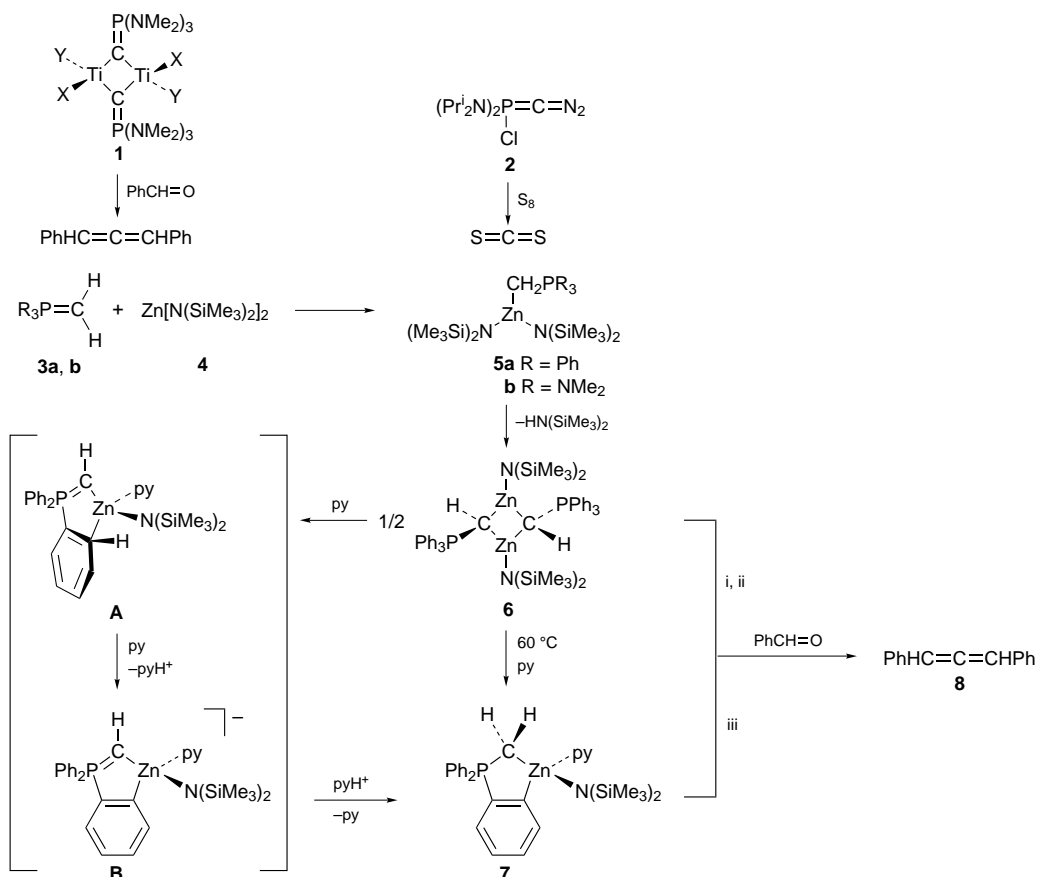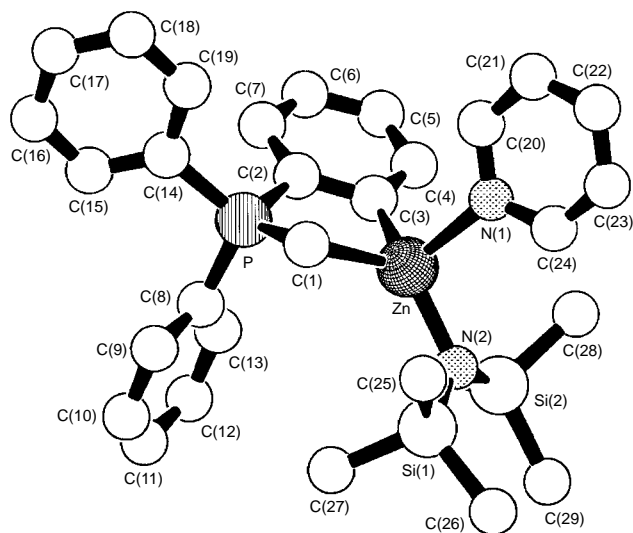

Scheme 1 *Reagents and conditions*: i, 60 °C, 24 h, no py, 7%; ii, 60 °C, 16 h, py, 12%; iii, 60 °C, 16 h, 31%

HN(SiMe$_3$)$_2$ we warmed **6** to 60 °C in presence of pyridine. A clean reaction was evidenced by one new ^{31}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 zincataphosphoniaindane **7**, we assume that pyridine cleaves the four-membered Zn$_2$C$_2$ heterocycle **6** to give intermediate **A** which corresponds to an η^1-arene complex to an electrophilic metal centre. Precedence for such a Zn–arene interaction is found in ZnPh$_2$ 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).[8] 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$_3$)$_2$. Earlier work showed that **1a** may be lithiated by Bu^{n}Li either at the CH$_2$ group or at the *ortho*-position of one of the phenyl groups attached to the phosphorus centre.[9] 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$_2$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 zincataindane **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[10] 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$_3$)$_2$ bond [1.982(3) Å] is 0.1 Å shorter than the Zn–N$_{py}$ 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^5,σ^4-phosphorus centre, the P–C(1) (sp^3) bond [1.732(4) Å] is significantly shorter than the P–C(2) (sp^2) bond [1.803(3) Å].

Footnotes and References

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† *Selected* ^{1}H (200 MHz), ^{13}C (50.232 MHz), ^{29}Si (17.75 MHz) and ^{31}P (36.19 MHz) *NMR data for* **5a,b** (C$_6$D$_6$), **6** ([^{2}H$_8$]THF) *and* **7** (C$_6$D$_6$): **5a**: Mp 187–189 °C. ^{1}H NMR: δ 0.37 (s, 36 H, SiMe$_3$), 1.30 (d, 2 H, $^2J_{HP}$ 16.8 Hz, CH$_2$), 6.95–7.16 (m, 9 H, *m*, *p*-H, PPh$_3$), 7.54–7.80 (m, 6 H, *o*-H, PPH$_3$). ^{13}C δ 3.7 (d, $^1J_{CP}$ 29.1 Hz, CH$_2$). ^{29}Si NMR: δ 6.6. ^{31}P NMR: δ 30.1. **5b**: 75 °C (decomp.). ^{1}H NMR: δ 0.48 (s, 36 H, SiMe$_3$), 1.53 (d, 2 H, $^2J_{HP}$ 17.0 Hz, CH$_2$), 2.08 (d, 18 H, $^3J_{HP}$ 9.3 Hz, NMe$_2$). ^{13}C: δ 2.8 (d, $^1J_{CP}$ 91.7 Hz, CH$_2$). ^{29}Si NMR: δ −7.0. ^{31}P NMR: δ 74.0. **6**: Mp 94–96 °C. ^{1}H NMR: δ −0.22 (s, 18 H, SiMe$_3$), 0.01 [A part of AA'XX', 1 H, (J_{HP} + J_{HP}) 17.7 Hz, CH], 7.35–7.53 (m, 9 H, *m*-, *p*-H, PPh$_3$), 7.62–7.74 (m, 6 H, *o*-H, PPh$_3$). ^{13}C NMR: δ 6.1 (d, $^1J_{CP}$ 27.7 Hz, C$_{ring}$). ^{29}Si NMR: δ −7.3. ^{31}P NMR: δ 28.1. **7**: Mp 79 °C. ^{1}H NMR: δ 0.47 (s, SiMe$_3$, $^2J_{HSi}$ 6.2 Hz), 0.76 (d, $^2J_{CP}$ 9.5 Hz, CH$_2$), 6.55–6.64 (m, arom H), 6.80–740 (m, arom H). ^{13}C NMR (75.469 MHz, C$_6$D$_6$): δ 1.3 (d. $^1J_{CP}$ 47.5 Hz, CH$_2$), 126.4 (d, $^2J_{CP}$ 13 Hz, 6'-C, C$_6$H$_4$), 130.9 (d, $^4J_{CP}$ 4.0 Hz, 4'-C, C$_6$H$_4$), 131.5 (d, $^3J_{CP}$ 18.1 Hz, 5'-C, C$_6$H$_4$), 136.1 (d, $^1J_{CP}$ 105.7 Hz, 1'-C, C$_6$H$_4$), 139.4 (d, $^3J_{CP}$ 21 Hz, 3'-C, C$_6$H$_4$), 176.0 (d, $^2J_{CP}$ 45 Hz, 2'-C, C$_6$H$_4$). ^{29}Si NMR: δ −6.0 ^{31}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_o^2 values (SHELXL-93). **5b**: monoclinic, $P2_1/n$, a = 16.065(12), b = 12.239(7), c = 17.191(11) Å, β = 109.81(5)°, U = 3180(4) Å^3, Z = 4, 3.0 < 2θ < 50.0°, 4568 reflections, 281 parameters, R_1 = 0.0357 (only observed reflections), wR_2 = 0.0604. **6**: monoclinic, $P2_1/n$, a = 12.352(14), b = 15.94(16), c = 14.999(16) Å, β = 114.37(8)°, U = 2690(5) Å^3, Z = 2, 3.62 < 2θ < 50.00°, 4290 reflections, 342 parameters, R_1 = 0.041 (only observed reflections), wR_2 = 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^3, Z = 4, 4.1 < 2θ < 47.00°, 10037 reflections, 719 parameters, R_1 = 0.039 (only observed reflections) wR_2 = 0.0961. CCDC 182/677.

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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).