A Zirconocene–η^2-Phosphabenzyne Complex as an Intermediate *en route* to Functional Phosphinines

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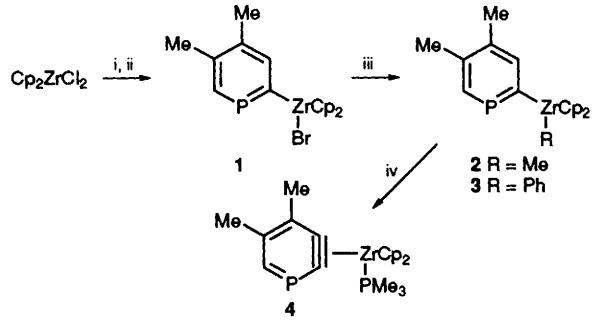
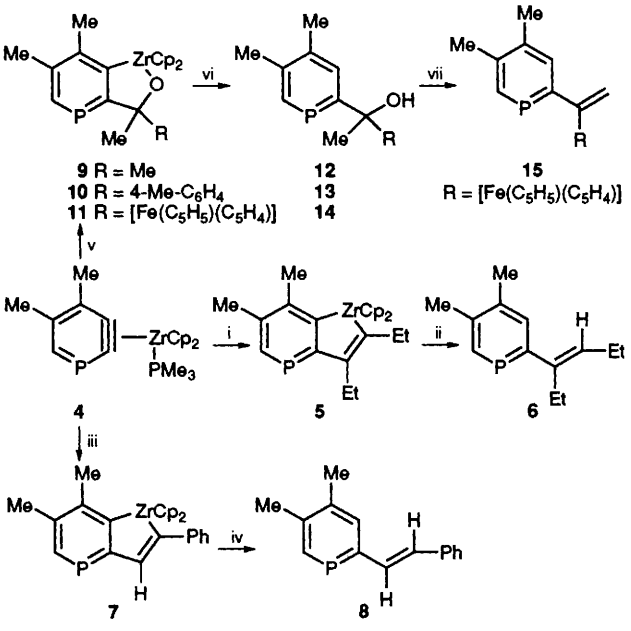
A (η^2-phosphabenzyne)dicyclopentadienylzirconium–trimethylphosphine adduct is obtained as a stable complex by thermal loss of RH from a $Cp_2Zr(R)$-2-substituted phosphinine (R = Me or Ph) in the presence of PMe_3; C≡C and C=O multiple bonds selectively insert into the Zr–C_2(ring) bond of this complex.

Zirconocene–η^2-benzyne complexes now constitute a well established tool in organic synthesis.[1] In a preceding work, we described the insertion of zirconocene into the C–Br bond of 2-bromophosphinines.[2] As a logical extension of the parallelism between arene and phosphaarene–transition metal chemistry, we describe now, from these insertion products, the synthesis of a new zirconocene–η^2-phosphabenzyne complex and some aspects of its reactivity. Our strategy (Scheme 1) is closely related to the work of Buchwald *et al.* on the trimethylphosphine adduct of the zirconocene–benzyne complex.[3]



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li (2 equiv.), thf, −80 °C, 1 h; ii, 1 equiv. 2-bromo-4,5-dimethylphosphinine, 20 °C, 1 h; iii, RLi (1 equiv.), thf, −80 to +20 °C, 15 min; iv, PMe_3 (2 equiv.), +70 °C, 2 h, (75% yield from 2-bromophosphinine)



Scheme 2 *Reagents and conditions*: i, 2 equiv. EtC≡CEt, toluene, 20 °C, 15 h; ii, 1 mol dm^{-3} HCl (excess) CH_2Cl_2, 20 °C, 10 min, 50%; iii, 2 equiv. PhC≡CH, toluene, 20 °C, 6 h; iv, 1 mol dm^{-3} HCl (excess) CH_2Cl_2, 20 °C, 1 h, 50%; v, 1.1 equiv. RC(O)Me, thf or toluene, 20 °C, 12 h; vi, H_2O (excess), CH_2Cl_2, 20 °C, 15 h, 60–70%; vii, 1 mol dm^{-3} HCl (excess) CH_2Cl_2, 20 °C, 5 h, 55% overall yield

Compound **4** was obtained as an orange oxygen-sensitive oil. We were also unable to obtain crystalline products by using substituted Cp rings (Me or $SiMe_3$). Thus, the identification of **4** relies on its ^1H, ^{13}C and ^{31}P NMR spectra.† In line with the proposed structure, no β-H resonance is observed in the ^1H NMR spectrum and both C_2 and C_3 display a sizeable coupling with the PMe_3 phosphorus nucleus (25.90 and 24.45 Hz respectively). It is interesting that the transformation of the C–Zr σ bond of **2** into the π bond of **4** is accompanied by a strong upfield shift of the C_2 resonance while the $^1J_{C-P}$ coupling constant remains quite high: **2** δ(C_2) 217.65, $^1J_{C-P}$ 100.71 Hz; **4** δ(C_2) 178.39, $^1J_{C-P}$ 114.56 Hz. Like its counterpart the reactivity of **4** is quite interesting (Scheme 2).

The insertion of alkynes and ketones takes place selectively into the C_2–Zr bond of **4** as shown by the ^1H NMR spectra of **6**, **8** and **12–14** which display one α- and one β-H resonance for the phosphinine ring. The ^1H NMR spectrum of **8** also exhibits an ABX system corresponding to the vinylic hydrogens. One of these is coupled to phosphorus ($^3J_{H-P}$ 12.3 Hz), thus establishing the regiochemistry of the insertion. We are currently investigating several applications of this chemistry.

A. K. thanks the Alexander von Humboldt Foundation (Germany) for financial support.

Received, 28th June 1994; Com. 4/03925D

Footnote

† *Spectroscopic data*: **2**: ^{31}P NMR (81.01 MHz) (C_6D_6) δ 217.10; ^1H NMR (200.13 MHz) (C_6D_6) δ 0.45 (d, 3H, $^4J_{H-P}$ 9.75 Hz, Me–Zr), 2.11 (s, 3H, Me), 2.14 (d, 3H, J_{H-P} 3.39 Hz, Me), 5.85 (s, 10H, C_5H_5), 7.64 (d, 1H, $^3J_{H-P}$ 16.03 Hz, 3-H), 8.58 (d, 1H, $^2J_{H-P}$ 34.35 Hz, 6-H); ^{13}C NMR (50.32 MHz) (C_6D_6) δ 22.94 (d, $^3J_{C-P}$ 33.98 Hz, Me–Zr), 30.21 (s, Me), 36.27 (d, J_{C-P} 6.42 Hz, Me), 112.06 (s, C_5H_5), 134.77 (d, J_{C-P} 28.39 Hz, C4 or C5), 139.91 (d, J_{C-P} 15.19 Hz, C5 or C4), 140.73 (d, $^2J_{C-P}$ 12.59 Hz, C3), 155.72 (d, $^1J_{C-P}$ 68.66 Hz, C6), 217.65 (d, $^1J_{C-P}$ 100.72 Hz, C2).

4: ^{31}P NMR (C_6D_6) δ 222.71 (d, $^3J_{P-P}$ 24.68 Hz, P of phosphabenzyne), −4.32, (d, PMe_3); ^1H NMR (C_6D_6) δ 1.31 (d, 9H, $^2J_{H-P}$ 6.24 Hz, PMe_3), 2.54 (s, 3H, Me), 2.79 (d, 3H, J_{H-P} 3.63 Hz, Me), 5.30 (dd, 10H, $^3J_{H-P}$ 1.72 Hz, $^4J_{H-P}$ 0.49 Hz, C_5H_5), 8.97 (d, 1H, $^2J_{H-P}$ 34.30 Hz, 6-H); ^{13}C NMR (C_6D_6) δ 18.1 (dd, $^1J_{C-P}$ 18.19 Hz, $^4J_{C-P}$ 4.76 Hz, Me–P), 22.59, 22.70 (s, Me), 102.88 (s, C_5H_5), 137.70 (dd, $^3J_{C-P}$ 27.39 Hz, $^3J_{C-P}$ 2.46 Hz, C4), 139.55 (d, $^2J_{C-P}$ 15.71 Hz, C5), 159.70 (d, $^1J_{C-P}$ 65.0 Hz, C6), 178.39 (dd, $^1J_{C-P}$ 114.56 Hz, $^2J_{C-P}$ 25.90 Hz, C2), 183.09 (dd, $^2J_{C-P}$ 24.45 Hz, $^2J_{C-P}$ 9.66 Hz, C3).

5: ^{31}P NMR ($CDCl_3$) δ 175.48; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3H, $^3J_{H-H}$ = 7.47 Hz, Me), 1.02 (t, 3H, $^3J_{H-H}$ = 7.54 Hz, Me), 1.42 (d, 3H, J_{H-P} = 3.07 Hz, Me), 1.92 (q, 2H, $^3J_{H-H}$ = 7.54 Hz, CH_2), 2.13 (s, 3H, Me), 2.57 (qd, 2H, $^3J_{H-H}$ = 7.47 Hz, $^4J_{H-P}$ = 2.00 Hz, CH_2), 6.19 (s, 10H, 2 C_5H_5), 8.06 (d, 1H, $^2J_{H-P}$ = 38.78 Hz, 6-H).

6: ^{31}P NMR ($CDCl_3$) δ 182.03; ^1H NMR (C_6D_6) δ 1.05 (m, 6H, 2 Me), 1.98 (d, 3H, J_{H-P} 3.3 Hz, Me), 2.01 (s, 3H, Me), 2.09 (m, 2H, CH_2), 2.65 (q, 2H, $^3J_{H-H}$ 7.53 Hz, CH_2), 5.82 (td, 1H, $^3J_{H-H}$ 7.23 Hz, $^4J_{H-P}$ 2.54 Hz, CH), 7.64 (d, 1H, $^3J_{H-P}$ 5.79 Hz, 3-H), 8.31 (d, 1H, $^2J_{H-P}$ 38.3 Hz, 6-H).

7: ^{31}P NMR (THF) δ 204.96 (d, $^2J_{H-P}$ 36.49 Hz).

8: ^{31}P NMR ($CDCl_3$) δ 182.53 (d, $^2J_{H-P}$ 38.91 Hz); ^1H NMR ($CDCl_3$) δ 2.40 (d, 3H, J_{H-P} 3.67 Hz, Me), 2.44 (d, 3H, J_{H-P} 1.40 Hz, Me), 7.28 (dd, 1H, $^3J_{H-H}$ 17.19 Hz, $^3J_{H-P}$ 12.30 Hz, CH) 7.31 (d, 1H,

$^3J_{H-H}$ 17.19 Hz, CH), 7.36–7.45 (m, 5H, C_6H_5), 7.78 (d, 1H, $^3J_{H-P}$ 5.79 Hz, 3-H), 8.47 (d, 1H, $^2J_{H-P}$ 38.65 Hz, 6-H).

9: ^{31}P NMR ($CDCl_3$) δ 187.23; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 6H, 2 Me), 1.69 (d, 3H, J_{H-P} 3.60 Hz, Me), 2.13 (s, 3H, Me), 6.19 (s, 10H, 2 C_5H_5), 8.11 (d, 1H, $^2J_{H-P}$ 38.0 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ 24.58 (d, J_{C-P} 3.56 Hz, Me), 26.83 (s, Me), 35.56 (d, $^3J_{C-P}$ 9.80 Hz, 2 Me), 87.30 (d, $^2J_{C-P}$ 33.45 Hz, C–O), 114.0 (s, C_5H_5), 137.79 (d, J_{C-P} 15.39 Hz, C4 or C5), 144.37 (d, J_{C-P} 21.28 Hz, C5 or C4), 153.96 (d, $^1J_{C-P}$ 43.26 Hz, C6), 185.05 (d, $^2J_{C-P}$ 13.38 Hz, C3), 202.45 (d, $^1J_{C-P}$ 59.35 Hz, C2).

12: ^{31}P NMR ($CDCl_3$): δ 176.22; ^{1}H NMR ($CDCl_3$) δ 1.55 (d, 3H, J_{H-P} 2.76 Hz, Me), 1.55 (s, 3H, Me), 1.97 (s, 6H, 2 Me), 7.83 (d, 1H, $^3J_{H-P}$ 5.44 Hz, 3-H), 8.23 (d, 1H, $^2J_{H-P}$ 40.0 Hz, 6-H).

15: ^{31}P NMR ($CDCl_3$) δ 184.61.

References

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