DALTON COMMUNICATION

Ferrocenium salt induced ring expansion of a 2*H*-azaphosphirene complex: Synthesis of the first Δ^3-1,4,2-oxazaphospholene complexes †

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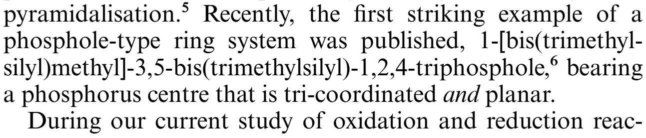
Received 15th June 2000, Accepted 19th June 2000
Published on the Web 4th July 2000

Regioselective ring expansion of the 2*H*-azaphosphirene tungsten complex 1 in CH_2Cl_2 is performed using sub-stoichiometric amounts of ferrocenium hexafluorophosphate and benzalaldehyde or cyclohexanone, thus yielding Δ^3-1,4,2-oxazaphospholene complexes 2a,c; the molecular structure of complex 2c was established by a single crystal X-ray diffraction study.

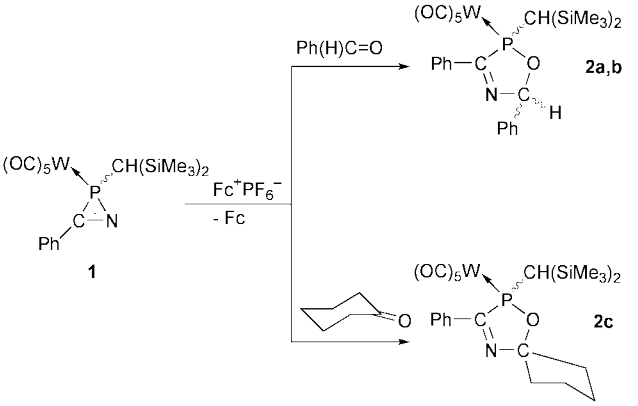
There is considerable current interest in the development of sophisticated ligands including either sp^2- and/or sp^3-hybridised phosphorus atoms in heterocyclic rings.[1] In the last few years, we have focussed our research on the synthesis of so-called biomimetic P-heterocycles of the diazole- and triazole-type, such as 2*H*-1,2-azaphospholes,[2] 2*H*-1,3,2-diazaphospholes[3] and 2*H*-1,4,2-diazaphospholes.[4] These were obtained as transition metal complexes using (i) selective P–C cleaving ring expansions of the 2*H*-azaphosphirene ring system as a new synthetic methodology (Scheme 1). Five-membered heterocycles of these or related types are especially interesting with regard to the intrinsic electronic ambiguity of a tri-coordinate phosphorus centre, which depends significantly on the degree of pyramidalisation.[5] Recently, the first striking example of a phosphole-type ring system was published, 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4-triphosphole,[6] bearing a phosphorus centre that is tri-coordinated *and* planar.



Scheme 1 Ring expansion reactions of 2*H*-azaphosphirene complexes (a=b denotes a π-system).

During our current study of oxidation and reduction reactions of 2*H*-azaphosphirene metal complexes, we have observed that such complexes undergo selective P–N cleaving ring expansion reactions (ii) at ambient temperature with various π-systems, when ferrocenium hexafluorophosphate ($Fc^+PF_6^-$) is present (Scheme 1). We now report the synthesis of the first Δ^3-1,4,2-oxazaphospholene complexes under very mild conditions using $Fc^+PF_6^-$, benzaldehyde and cyclohexanone and a 2*H*-azaphosphirene tungsten complex.

The reaction of 2*H*-azaphosphirene tungsten complex **1**[7] with 2 equivalents of either benzaldehyde or cyclohexanone and 0.2 equivalents of $Fc^+PF_6^-$[8] in dichloromethane at ambient temperature afforded regioselectively the Δ^3-1,4,2-oxazaphospholene complexes **2a** (together with **2b**, most probably a diastereoisomer) and **2c** (Scheme 2) in reasonable yields (45 and 44%, respectively); ferrocene was isolated in both reactions in *ca.* 10% yield. If one equivalent of the ferrocenium salt was added the reaction time decreased without affecting the selectivity of the reaction. In the case of benzaldehyde, ^{31}P NMR spectroscopic monitoring showed the formation of two reactive intermediates (<5–10% of all phosphorus-containing products) having resonances at δ 108 and 119. Because of the need for $Fc^+PF_6^-$ in these reactions or other oxidizing agents such as Cu(II) salts or elemental sulfur, in the absence of oxidizing agents no reactions occurred at ambient temperature, we propose that the ring expansion proceeds *via* electron transfer catalysis,[9] which, to the best of our knowledge, would be unprecedented in the chemistry of phosphorus-containing heterocycles.[10] At higher temperature the reactions yielded selectively 2*H*-1,3,2-oxazaphospholecomplexes *via* insertion of the C–O π-system into the P–C bond.[3b]



Scheme 2 Reaction of complex **1** with $Fc^+PF_6^-$, benzaldehyde and cyclohexanone. *Reagents and conditions*: to a solution of 1 mmol of complex **1**, 2 mmol of benzaldehyde or cyclohexanone in 3 ml of dichloromethane was added 0.2 mmol $Fc^+PF_6^-$ and stirred at ambient temperature until **1** was consumed (^{31}P NMR control); work-up by column chromatography (SiO_2) at low temperature and crystallization from *n*-pentane yielded complexes **2a**,**c** as pale yellow solids (**2a**: 45%, mp 92 °C, decomp.; **2c**: 44%, mp 140 °C, decomp.).

The complexes **2a**,**c** were isolated by low-temperature chromatography and crystallisation; the constitutions of the complexes **2a**,**c** are unambigously established by their NMR spectroscopic data ‡ (^{13}C, ^{31}P) in solution and their MS data.‡ Furthermore, the ring constitution of complex **2c** was confirmed by X-ray structure analysis (Fig. 1).§

Complexes **2a**,**c** show resonances for the imino carbon atoms at δ 173.6 and 169.7 with coupling constant magnitudes $|J(^{31}P,^{13}C)|$ of *ca.* 13–16 Hz, and for the sp^3-hybridized carbon atoms at δ 108.1 and 113.1 with coupling constant magnitudes $|J(^{31}P,^{13}C)|$ of *ca.* 4–7 Hz. ^{31}P resonances are observed in a small range [δ 135.3 (**2a**), 141.5 (**2b**) and 136.4 (**2c**)] with characteristic coupling constants $|J(^{183}W,^{31}P)|$ of *ca.* 270–280 Hz. The molecular structure of complex **2c** (Fig. 1) confirms the constitution of the heterocyclic ring system, which is almost planar (mean

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† Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday.

DOI: 10.1039/b004795n

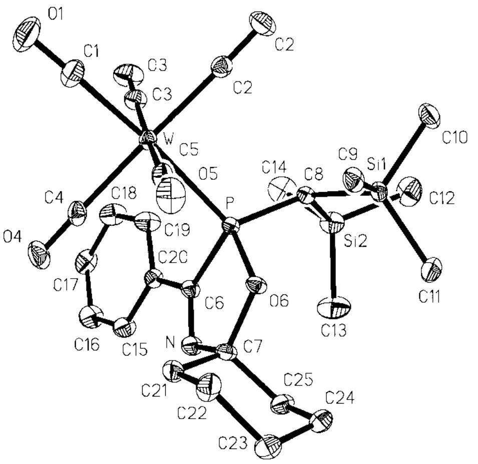

Fig. 1 Molecular structure of complex **2c** (ellipsoids represent 30% probability levels; solvent and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W–C1 2.011(3), W–P 2.5209(6), P–C8 1.821(2), P–O6 1.6309(17), P–C6 1.877(2), N–C6 1.273(3), N–C7 1.454(3), C7–O6 1.465(3); C8–P–W 117.45(8), O6–P–C6 88.92(9), P–C6–N 111.51(17), C6–N–C7 115.21(9), N–C7–O6 108.02(18).

deviation 0.042 Å) and shows, in comparison to {[2-bis(trimethylsilyl)methyl-5-phenylbenz[*c*]-1,2-oxaphospholane]pentacarbonyltungsten(0)}[11] **3** and 1,1-diphenyl-3,3,5,5,8,8-hexakis(trifluoromethyl)-2,4,9-trioxa-7-aza-1λ^5-phosphabicyclo[4.3.0]non-6-ene[12] **4**, C–O and P–O bond distances [C7–O6 1.465(3) and P–O6 1.6309(17) Å], which are very similar to those in **3** [C–O 1.463(4) and P–O 1.641(2)[11] Å], but differ significantly from those in **4** [C–O 1.374(3) and P–O 1.732(2)[12] Å]; the C–N double bond distances of **2c** and **4** are also slightly different [**2c**: N–C6 1.273(3) and **4**: N–C 1.291(4)[12] Å].

Currently, electrochemical and ESR studies to elucidate the reaction mechanism are in progress, furthermore, we are exploiting this new synthetic methodology by employing nitriles instead of carbonyl derivatives.[13]

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Mr Andreas Weinkauf for the crystallographic measurement.

Notes and references

‡ Satisfactory elemental analyses were obtained for complexes **2a**,**c**. NMR data were recorded in $CDCl_3$ solutions at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P), using $SiMe_4$ and 85% H_3PO_4 as standard references; *J*/Hz. Selected spectroscopic data for **2a** (≅8 : 1 mixture of **2a**,**b**): ^{13}C NMR: δ 2.9 [d, $^3J_{PC}$ 1.9, $Si(CH_3)_3$], 3.3 [d, $^3J_{PC}$ 2.8, $Si(CH_3)_3$], 33.3 (d, $^1J_{PC}$ 16.7, CH), 108.1 (d, $^2J_{PC}$ 6.3 PO*C*), 126.5 (s, Ph), 128.6 (s, Ph), 130.6 (s, Ph), 130.7 (s, Ph), 132.7 (d, J_{PC} 25.2, Ph), 137.8 (d, J_{PC} 3.5, Ph) 173.6 (d, J_{PC} 13.3, P*C*N), 197.1 (d, $^3J_{PC}$ 7.4, *cis*-CO), 198.9 (d, $^3J_{PC}$ 28.2, *trans*-CO); ^{31}P NMR: δ 135.3 (s, $^1J_{PW}$ 280.2); *m*/*z* (EI) 723 (M^+, 28). **2c**: ^{13}C NMR: δ 1.9 [d, $^3J_{PC}$ 1.6, $Si(CH_3)_3$], 2.2 [d, $^3J_{PC}$ 2.6, $Si(CH_3)_3$], 21.8 (s, CH_2), 22.0 (s, CH_2), 23.9 (s, CH_2), 35.4 (d, $^1J_{PC}$ 13.3, CH), 36.1 (s, CH_2), 36.3 (s, CH_2), 113.1 (d, $^2J_{PC}$ 4.7 PO*C*), 127.5 (s, Ph), 129.3 (s, Ph), 130.2 (s, Ph), 132.7 (d, J_{PC} 25.2, Ph), 169.7 (d, J_{PC} 15.4, P*C*N), 198.2 (d, $^3J_{PC}$ 7.2, *cis*-CO), 199.4 (d, $^3J_{PC}$ 26.3, *trans*-CO); ^{31}P NMR: δ 136.4 (s, $^1J_{PW}$ 273.4); *m*/*z* (EI) 715 (M^+, 8).

§ Crystal structure analysis of **2c**·$0.5C_5H_{12}$: empirical formula $C_{27.5}H_{40}NO_6PSi_2W$, $M = 751.6$; monoclinic, space group *C*2/*c*; $a = 36.058(4)$, $b = 10.4819(12)$, $c = 19.602(2)$ Å, $\beta = 119.330(6)°$, $V = 6458.9(13)$ Å^3, $Z = 8$, $D_c = 1.546$ Mg m^{-3}; $\lambda = 0.71073$ Å, $T = 143(2)$ K. The crystal (0.27 × 0.24 × 0.17 mm) was mounted in inert oil. 38692 intensities were measured (ω and θ scans, 2θ 3–60°) using using Mo-Kα radiation on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiple scans) 9462 were unique ($R_{int} = 0.0454$) and used for all calculations (SHELXL-97[14]). All hydrogen atoms were refined with a riding model or as rigid methyl groups. Final $wR(F^2)$ was 0.0589, with conventional $R(F)$ 0.0247, for 186 parameters and 351 restraints; highest peak 1.479, hole −0.861 e Å^{-3}.

CCDC reference number 186/2042.

See http://www.rsc.org/suppdata/dt/b0/b004795n/ for crystallographic files in .cif format.

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