Cyclisation of Bis(methylene)phosphoranes: a New Way to Five-membered Heterocycles

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The catalytic rearrangement of the metallo-bis(methylene)phosphorane **1** in the coordination sphere of an iron atom furnishes two isomeric five-membered heterocycles **2** and **3** resulting from the incorporation of the C_3H_5 ligand and one of the P–C double bonds; a similar reactivity could be obtained in the reaction of the chlorobis(methylene)phosphorane **4** with $AlBu^i_3$, which affords the 1*H*-λ^5-methylenephospholane **6**.

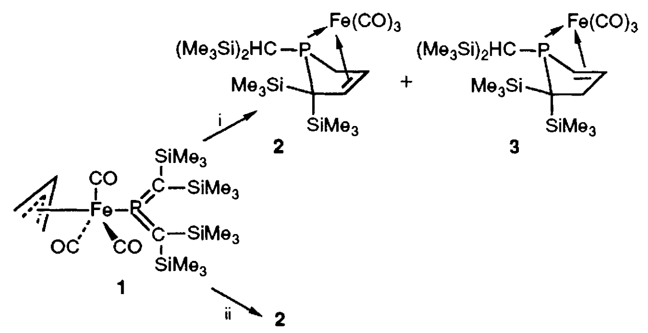
Bis(methylene)phosphoranes have developed into valuable ligands in transition metal complexes,[1] based mainly on the versatility of coordination of such ligands to metal centres. Among these, organometal-substituted derivatives of the type $L_nM{-}P[{=}C(SiMe_3)_2]_2$, with the $P[{=}C]_2$ moiety acting as a one-electron donor, have played a particularly important role in this development owing to their multi-faceted chemical behaviour.[1] In particular, the catalytic isomerization of a η-CpFe(CO)$_2$ derivative,[1a] yielding a phosphaferrocene, exemplified the high activity of these systems and their potential as building blocks in organoelement chemistry.

Thus, changing the metal atom or the kind of ligand should result in different reactivity. Here, we report the isomerisation reaction of the metallobis(methylene)phosphorane **1**,[1a] which proceeded *via* incorporation of the allylic ligand and afforded in the coordination sphere of an iron atom the five-membered heterocycles **2** and **3**.

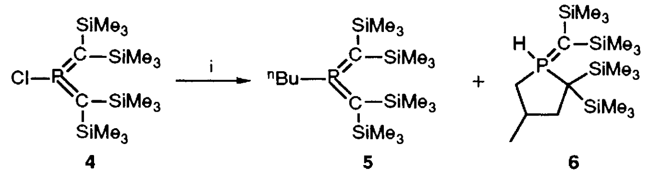
The formation of **2** and **3** can formally be regarded as a cycloaddition reaction of the allyl ligand in **1** with one of the P–C double bonds of the $\sigma^3\lambda^5$-phosphorane fragment. We propose that the reaction proceeds *via* an initial nucleophilic attack of the allylic ligand at the P^V-centre, which is followed by a metal-induced 1,3-hydrogen shift from the C_3 fragment to the second methylene carbon atom. A subsequent ring closure reaction leads to the phospholene complexes **2** and **3**. Compounds were purified by column chromatography (10 °C, 20 × 1 cm, Florisil, pentane). Interestingly, the major isomer **2** can alternatively be obtained in 82% yield within 3 to 8 h at ambient temperatures by adding a small amount of $P(Bu)_3$ to the metallomethylenephosphane **1**. The addition of tributylphosphane seems to catalyse the initial step of the abovementioned rearrangement.

Valuable information concerning the elucidation of the structure of **2** and **3** was provided by the presence of two deshielded ring carbon atoms (δ 130.9 and 120.5 **2**; δ 146.5 and 127.3 **3**) with a comparatively small magnitude of the phosphorus carbon coupling constants and by the significant highfield shift in the ^{31}P NMR spectra (δ 48.3 and 40.4),[3] as compared with **1** (δ 331.8). The presence of the $[Fe(CO)_3]$ fragment was readily deduced from the IR and high resolution mass spectra,† respectively.

A similar reactivity could be achieved in the reaction of the chlorobis(methylene)phosphorane **4** with triisobutylaluminium at elevated temperature, which furnished two isomeric products. As expected, the formation of the major product, the butylbis(methylene)phosphorane **5**, results from the substitution of the chlorine atom in **4**. Additionally the 1*H*-λ^5-(methylene)phospholane **6** could be obtained in 18% yield, the identity of which was indicated by characteristic signal patterns in the ^{31}P[δ 8.8 (dd, *J* 402.7 and 5.6 Hz)] and 1H NMR spectra [δ 6.53 (dt, 402.7 and 6.1 Hz, H–P)], respectively. Further support for the structure of **6** was inferred from the ^{13}C NMR and high resolution mass spectra.†[4]



Scheme 1 *Reagents and conditions*: i, 60 °C (30 d), toluene, yield 42% **2**, 8% **3**; ii, toluene + PBu_3, 30 °C (1 h),—$(Bu_3P)_2Fe(CO)_3$; yield 82% **2**



Scheme 2 *Reagents and conditions*: i, 30 °C (no solvent, vigorous stirring), + $AlBu^i_3$

Once again the reaction pathway is proposed to involve a metal-catalysed addition of a C_3 fragment at one of the P–C double bonds of the $\sigma^3\lambda^5$-phosphorane. However, the reported isomerization reactions were attributed to the highly polarized phosphorus–carbon (pp)-system[5] and underline the high reactivity and fascinating chemistry of bis(methylene)-phosphoranes, which is why further investigations are still in progress.

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† ^{31}P NMR (32.203 MHz/C_6D_6): δ **2**: 48.3 (br), **3**: 40.4 (br), **6**: 8.8 (dd, *J* 402.7 and *J* 5.6 Hz). ^{13}C NMR (50 MHz/C_6D_6): δ **2**: 215.6 (s, CO), 214.7 (s, CO), 207.6 (d, *J* 9.9 Hz, CO), 130.9 (d, *J* 3.5 Hz, C=), 120.5 (d, *J* 14.4 Hz, C=), 38.2 (d, *J* 32.1 Hz, P-C), 22.5 (d, *J* 34.6 Hz, $PCSi_2$), 13.2 (d, *J* 1.5 Hz, PCH_2), 6.3 (d, *J* 9.9 Hz, SiMe), 3.3 (d, *J* 7.4 Hz, SiMe), 2.9 (d, *J* 1.9 Hz, SiMe), 2.8 (d, *J* 4.8 Hz, SiMe), **3**: 215.2 (s, CO), 213.6 (s, CO), 207.6 (d, *J* 16.2 Hz, CO), 146.5 (d, *J* 12.0 Hz, C=), 127.3 (d, *J* 10.4 Hz, C=), 38.2 (d, *J* 31.1 Hz, P–C), 18.9 (d, *J* 19.9 Hz, $PCSi_2$), 12.2 (d, *J* 23.0 Hz, CH_2), 5.3 (d, *J* 10.1 Hz, SiMe), 3.9 (s, SiMe), 2.7 (d, *J* 4.4 Hz, SiMe), 1.8 (d, *J* 3.9 Hz, SiMe), **6**: 41.4 [d, *J* 20.5 Hz, $PC(SiMe_3)_2$], 39.0 (d, *J* 26.7 Hz, PCH_2), 15.8 (d, *J* 37.4 Hz, $PCCH_2$), 14.1 (d, *J* 53.0 Hz, P=C), 11.4 (d, *J* 43.6 Hz, PCCH), 7.9 (d, *J* 4.1 Hz, Me), 4.9 (d, *J* 4.9 Hz, SiMe), 2.8 (d, *J* 7.7 Hz, SiMe), 2.6 (d, *J* 6.3 Hz, SiMe). ^1H NMR (200 MHz/C_6D_6): δ **2**: 5.19 (dd, *J* 11.2 Hz, 1H, CH=C), 3.11 (dt, *J* 11.2 Hz and 8.4 Hz, 1H, =CH–CH_2), 1.43 (d, *J* 8.4 Hz, 1H of CH_2), 1.41 (d, *J* 8.4 Hz, 1H of CH_2), 0.88 (s, 1H, P–CH), 0.28 (d, *J* 5.0 Hz, 18H, SiMe), 0.20 (s, 9H, SiMe), 0.19 (s, 9H, SiMe), **6**: 6.53 (dt, *J* 402.7 and *J* 6.1 Hz, 1H, PH), 2.52 (m, 1H, >CH-), 2.07 (m, 2H, $PCCH_2$), 1.80 (m, 2H, PCH_2), 0.76 (d, *J* 6.9 Hz, 3H, Me), 0.49 (s, 18H, SiMe), 0.27 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $SiMe_3$). IR (ν_{CO}/cm^{-1}, pentane): **2**: 1998s, 1963s, 1952vs, **3**: 2002s, 1965s, 1950vs. MS (60 eV/700 μA): *m/z* (%) = **2**: 528 (0.2) [M^+], 500 (2) [M^+ − CO], 472 (8) [M^+ − 2CO], 444 (100) [M^+ − 3CO], 73 (60)[$SiMe_3^+$], **3**: 528 (0.1)[M^+], 500 (2.5) (M^+ − CO], 472 (5) [M^+ − 2CO], 444 (100) [M^+ − 3CO], 73 (55) [$SiMe_3^+$], **6**: 404 (1) [M^+], 389 (2) [M^+ − Me], 331 (6) [M^+ − $SiMe_3$], 73 (100) [$SiMe_3^+$]. High Resolution Mass Spectra: Calc. for **2**: $C_{20}H_{41}FeO_3PSi_4$ 528.1220 Found 528.1204, **3**: $C_{20}H_{41}FeO_3PSi_4$ 528.1220 Found 528.1214, **6**: $C_{18}H_{45}PSi_4$ 404.2335 Found 404.2324. Yield: **2**: 42% (i) and 82% (ii), **3**: 8%, **6**: 18%.

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