Electronic Supplementary Information for Dalton Transactions

Reactivity of cyclooligophosphanes: Synthesis and structural characterisation of *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ and *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$

Electronic Supplementary Information.

The electronic supplementary information contains:

a) graphical representations of the experimental and simulated $^{31}P\{^1H,^{11}B\}$ NMR spectra of **3,**

b) graphical representation of the ^{31}P MAS spectrum of **3**,

c) graphical representation of the low-temperature NMR experiment on **3**,

d) graphical representation of the $^{31}P\{^1H\}$ $^{31}P\{^1H\}$ COSY NMR spectrum of **4**,

e) graphical representations of the optimised (B3LYP) structures of the symmetrical diastereomers of *cyclo*-$(P_4Ph_4CH_2)$ (**2**) and *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**)

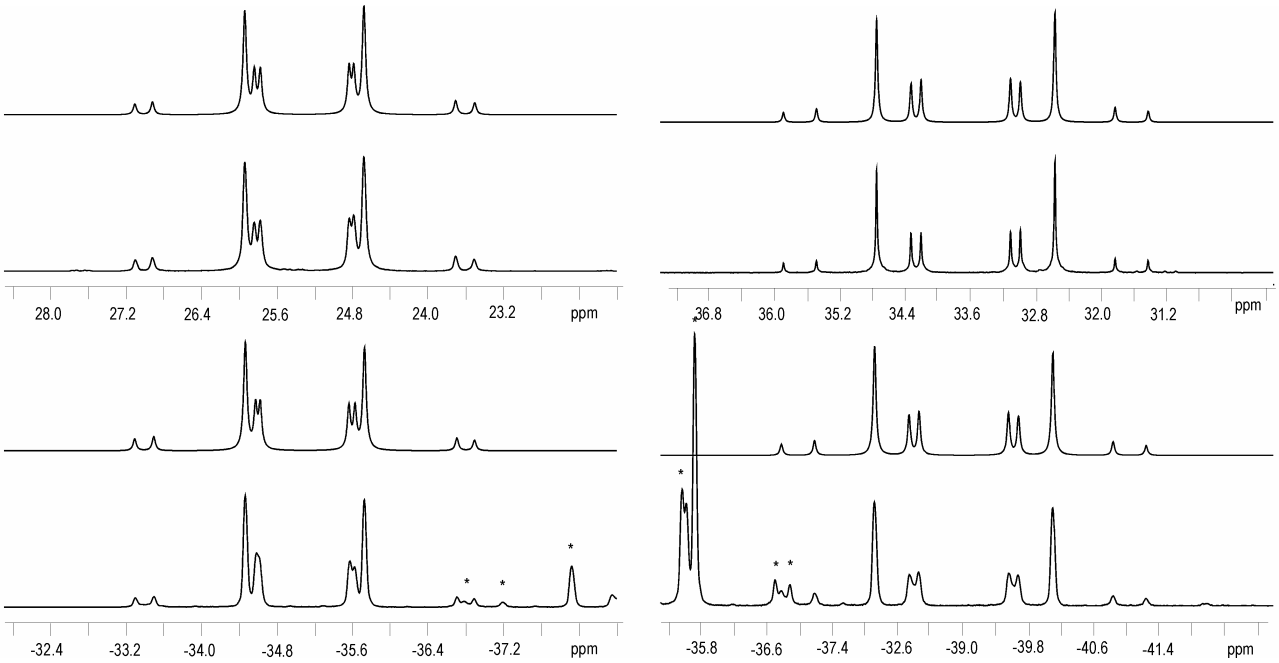
a) Experimental and simulated $^{31}P\{^1H,^{11}B\}$ NMR spectra of 3

- A negative sign was used for the coupling constants $^1J_{PP}$ and the remaining signs and coupling constants were calculated with the program SPINWORKS (K. Marat, SPINWORKS, version 2000 05 10, University of Manitoba).

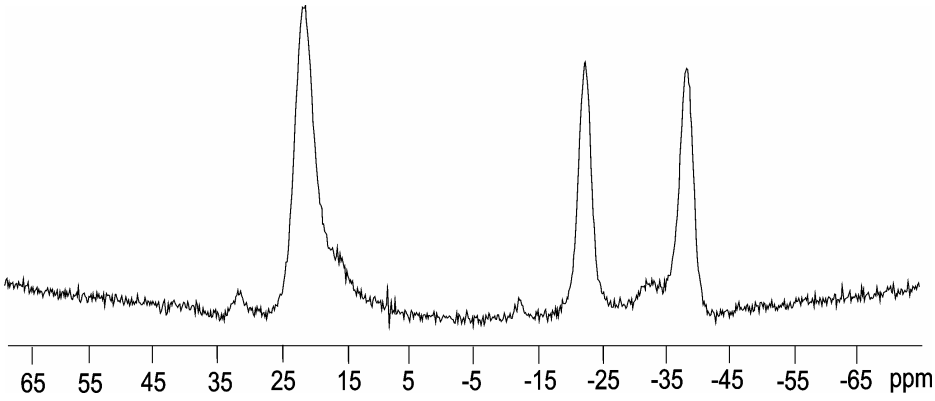
Table S.1 Simulated ^{31}P NMR parameters of **3**.

	(R_P*,S_P*,S_P*,R_P*)-(±)-**3**	(R_P*,R_P*,R_P*,R_P*)-(±)-**3**
δ_A	+25.13(1)	+33.65(1)
δ_B	–35.08(1)	–38.99(1)
$^1J_{AB}$ / Hz	–188.5(3)	–266.6(2)
$^1J_{BB'}$ / Hz	–146.5(2)	–172.6(2)
$^2J_{AB'}$ / Hz	+35.1(1)	+1.8(1)
$^2J_{AA'}$ / Hz	–15.3(2)	–32.0(2)
rms	0.37	0.32

Fig. S.1 Experimental (lower) and simulated (upper) $^{31}P\{^1H,^{11}B\}$ NMR spectra of **3** (121.50 MHz, C_6D_6, overlapping resonances of the respective other stereoisomer are marked with an asterisk).



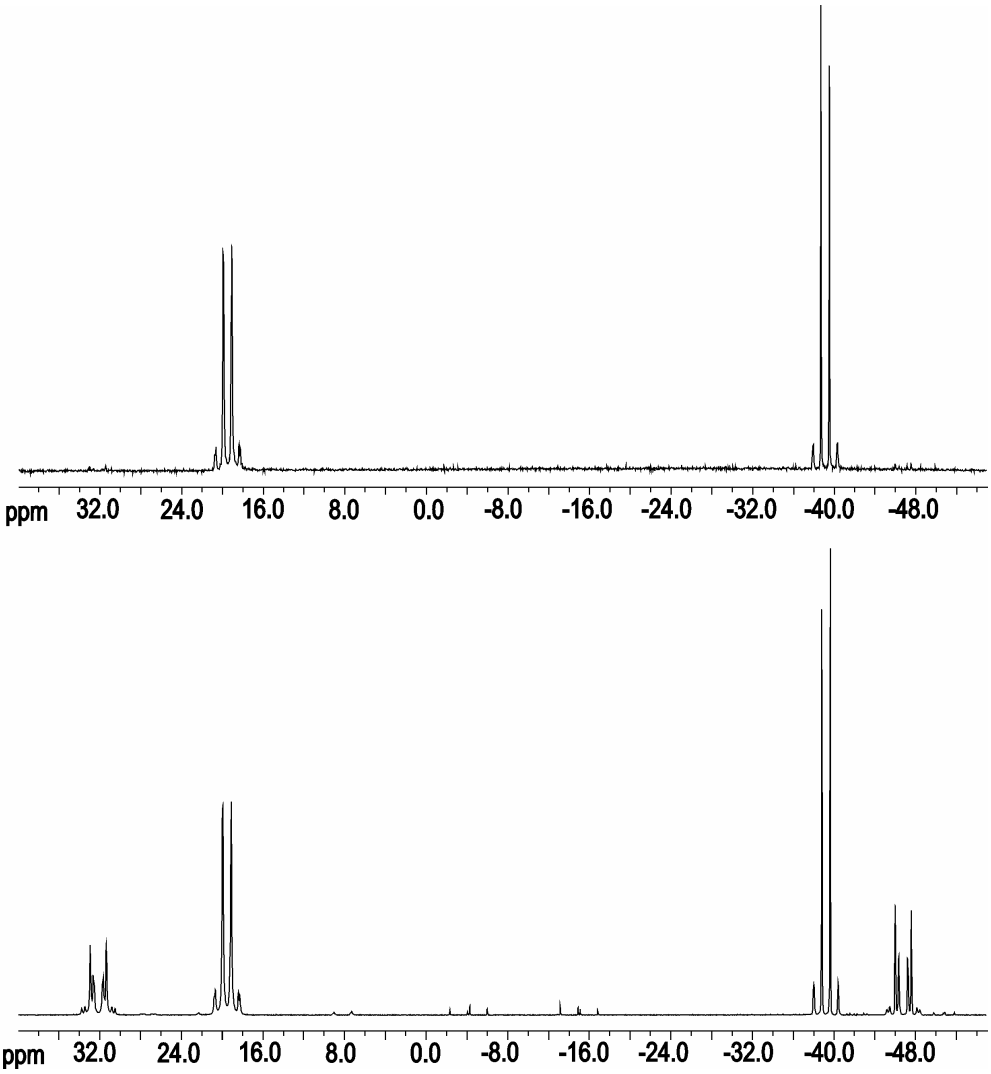
b) ^{31}P MAS spectrum of 3 (202.45 MHz)



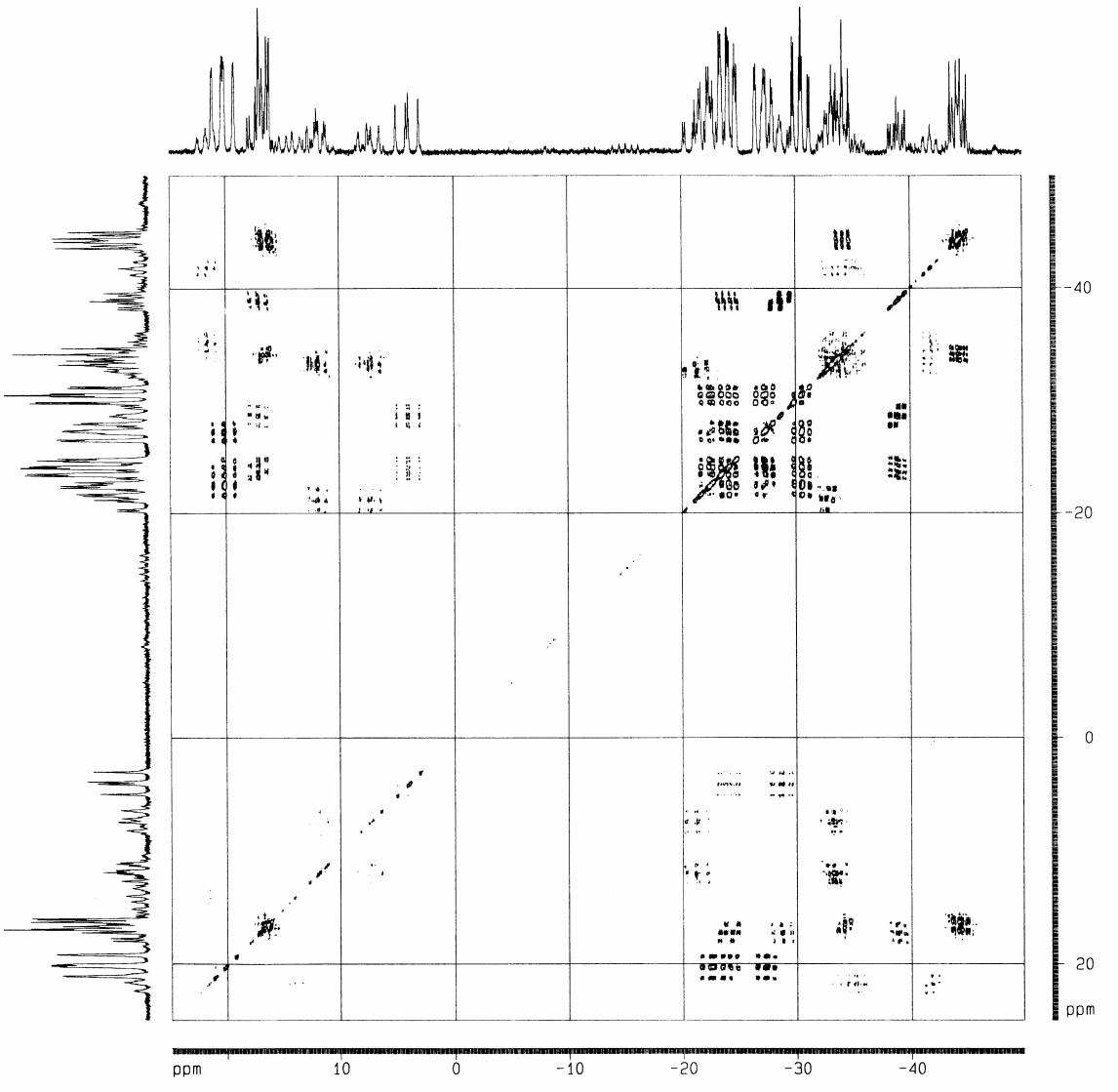
c) low-temperature NMR experiment on 3

– upper spectrum: $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz) recorded at –80 °C immediately after cooled C_7D_8 had been added to a sample of **3** in the NMR tube

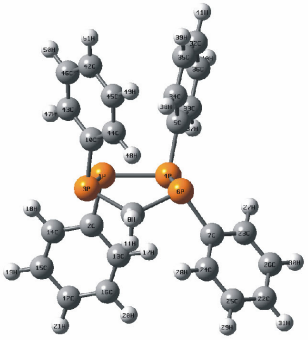
– lower spectrum: $^{31}P\{^{1}H\}$ NMR spectrum of the same sample measured again at –80 °C, but after the sample had been briefly brought to room temperature



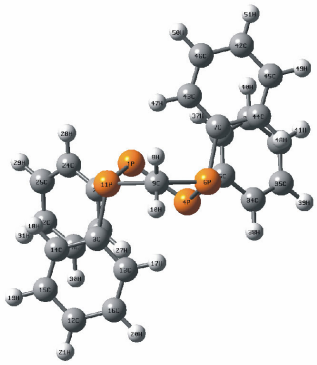
d) $^{31}P\{^{1}H\}$ $^{31}P\{^{1}H\}$ COSY NMR spectrum of 4 (283.43 MHz, $CDCl_3$)



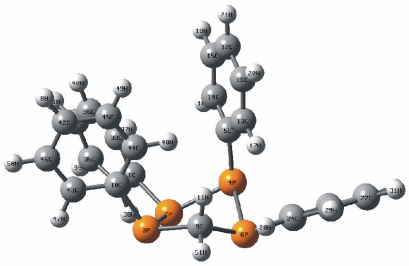
e) graphical representations of the optimised (B3LYP) structures of the symmetrical diastereomers of *cyclo*-($P_4Ph_4CH_2$) (2) and *cyclo*-1,4-$(BH_3)_2$($P_4Ph_4CH_2$) (3)



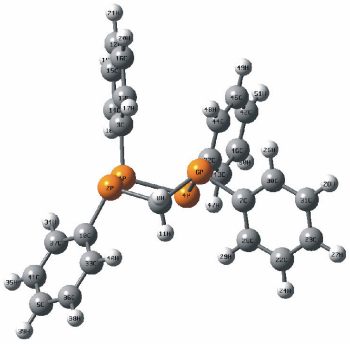
(R_P,S_P,S_P,R_P)-*cyclo*-($P_4Ph_4CH_2$)



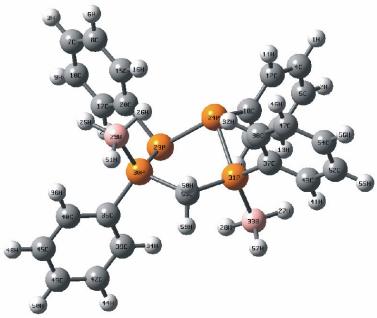
(S_P,S_P,S_P,S_P)-*cyclo*-($P_4Ph_4CH_2$)



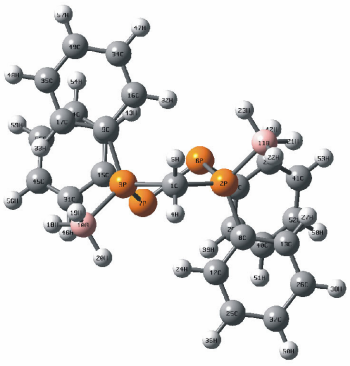
(R_P,R_P,S_P,S_P)-*cyclo*-($P_4Ph_4CH_2$)



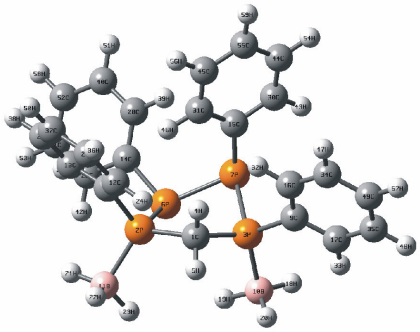
(S_P,R_P,S_P,R_P)-*cyclo*-($P_4Ph_4CH_2$)



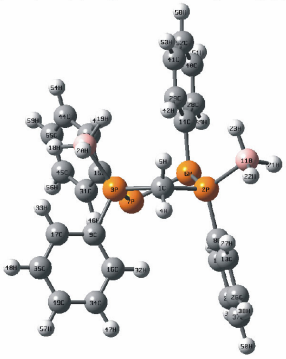
(S_P,R_P,R_P,S_P)-*cyclo*-1,4-$(BH_3)_2$($P_4Ph_4CH_2$)



(R_P,R_P,R_P,R_P)-*cyclo*-1,4-$(BH_3)_2$($P_4Ph_4CH_2$)



(R_P,R_P,S_P,S_P)-*cyclo*-1,4-$(BH_3)_2$($P_4Ph_4CH_2$)



(S_P,R_P,S_P,R_P)-*cyclo*-1,4-$(BH_3)_2$($P_4Ph_4CH_2$)