Electronic supporting information

Radical-initiated P,P-metathesis reactions of diphosphanes: evidence from experimental and computational studies

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Contents

1.1 – General considerations

All manipulations were performed under an atmosphere of dry nitrogen or argon using standard glovebox and Schlenk techniques. All glassware was flame-dried prior to use. Anhydrous THF, DCM, Et_2O and toluene were collected from a Grubbs-type solvent purification system, degassed via freeze-pump-thaw cycles and stored over 4 Å molecular sieves. CD_2Cl_2, $CDCl_3$ and C_6D_6 were also degassed with freeze-pump-thaw cycles and dried over 4 Å molecular sieves. 1,4-dioxane was purchased from Alfa Aesar dried over 4 Å molecular sieves and sparged prior to use.

Diisopropylamine and triethylamine were purchased from Alfa Aesar and dried over 4 Å molecular sieves. Magnesium, Iodine, TEMPO, TTBP, NCS and each of the five chlorophosphines were purchased either from Sigma-Aldrich (Merck Chemicals) or Alfa Aesar and used as received.

Sonication experiments were performed using a Sonics Vibracell sonicator with a 13 mm probe and a custom (in-house prepared) Suslick cell with a Young's tap for Schlenk line attachment. All experiments were performed under a dry nitrogen atmosphere.

NMR experiments were conducted with conventional NMR tubes (wrapped with parafilm around the cap to delay oxidation onset) or amberised 500 MHz tubes (where stated) and performed on either a Jeol ECS 300, Jeol ECS 400 or a Bruker Nano 400 spectrometer, with ^{31}P spectra referenced to 85% H_3PO_4. Low temperature and kinetics experiments were performed on a Jeol ECS 300 spectrometer, with inverse-gated decoupling in the case of kinetics experiments.

UV-Vis experiments were performed with an Agilent Technologies Cary 300 UV-Vis in double beam mode (absorption). 20 μM solutions of diphosphane in CH_2Cl_2 were prepared under a dry nitrogen atmosphere and baselined with respect to a CH_2Cl_2 blank.

Photolysis experiments were performed with a NightSearcher handheld LED UV lamp (5 W, λ_{max} = 365 nm). Product specifications indicate irradiance values of 1.65 W m^{-2} in the near UV (UVA) and 0.00211 W m^{-2} in the UBC-UVC region.

1.2 – General synthetic procedure

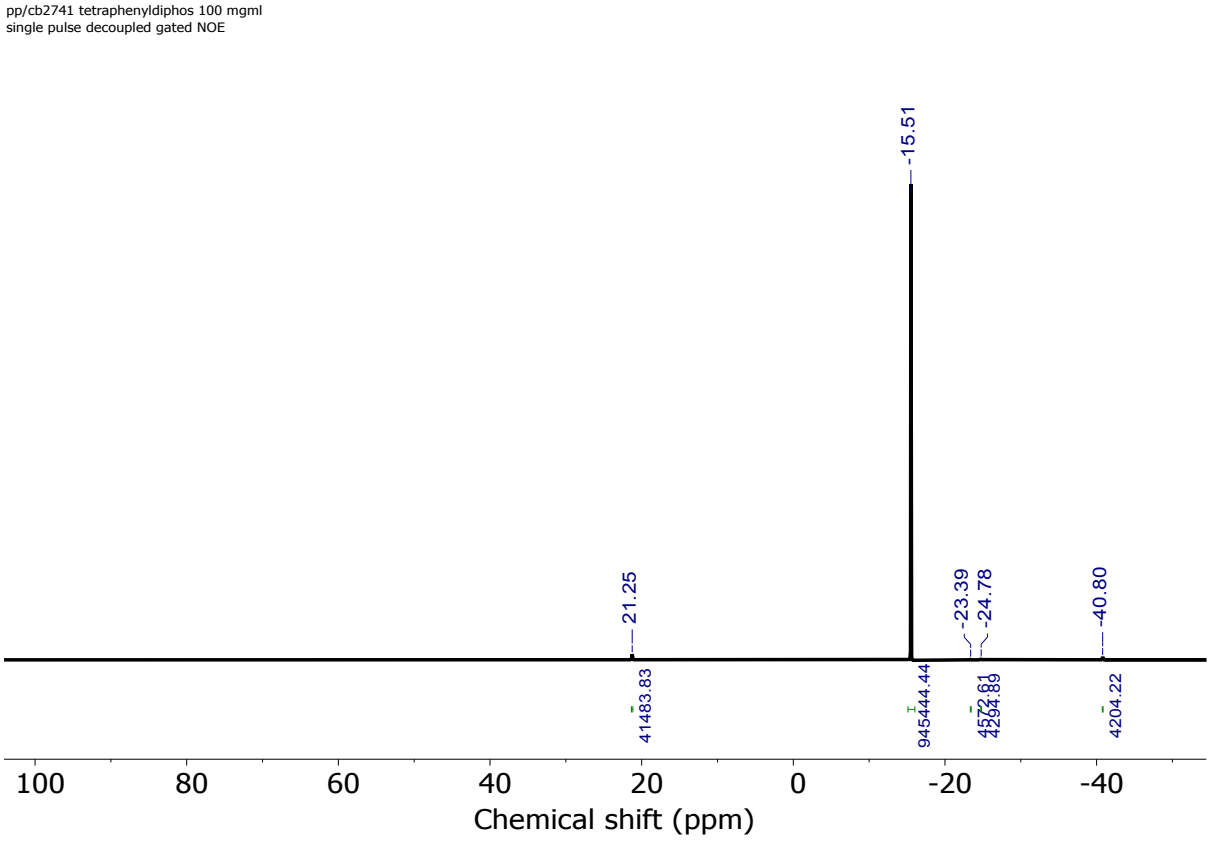
The synthesis of diphosphanes **A_2–C_2** and **E_2** was performed as exemplified by the synthesis of tetraphenyldiphosphane, **A_2**:

To a Schlenk flask equipped with a stirrer bar, of magnesium (440 mg, 18.1 mmol) and 2 crystals of iodine were added prior to flame-drying *in vacuo*. THF (30 ml) was added and the mixture was then stirred vigorously at room temperature for 30 min. Chlorodiphenylphosphine (1.63 ml, 2.00 g, 9.05 mmol) was added dropwise and left to stir overnight. The solution was then filtered from the excess magnesium via cannula, and the THF removed *in vacuo*. Toluene (30 ml) was then added and to the resultant solution followed by 1,4-dioxane (1.54 ml, 18.1 mmol) and the mixture stirred vigorously for 5 min and then left to stand for 5 h. The solution was then cannula filtered again, and the toluene removed under reduced pressure yielding the product **A_2** as a white powder (1.255 g, 75%).

Each of these diphosphanes was produced in approximately 75% yield as white powders with the exception of **C_2** which was a pale-yellow powder.

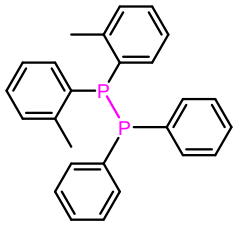
Diphosphane **D_2** was prepared in an analogous fashion in refluxing Et_2O over the course of 5 days. The crude product was isolated as above and then filtered through an alumina plug to remove residual chlorophosphine and secondary phosphine oxide. The final product was isolated as a white powder (214 mg, 23%) containing ~10% secondary phosphine side product.

To determine the level of residual chlorophosphine contamination in the synthesised diphosphanes, a concentrated sample was made and the ^{31}P NMR spectrum measured. For example a solution of **A_2** (100 mg ml^{-1}) was analysed by ^{31}P NMR (400 MHz, THF). From ESI 1.1 there is no evidence of chlorophosphine. The signal:noise ratio of this spectrum indicates that 0.05% contamination would be readily detected. It was concluded that there is a maximum of 0.05% chlorophosphine content.



ESI 1.1. Tetraphenyldiphosphane (**A_2**) in THF at concentrations of 100 mg ml^{-1}.

1.3 – Synthesis of the unsymmetrical diphosphane **AE**



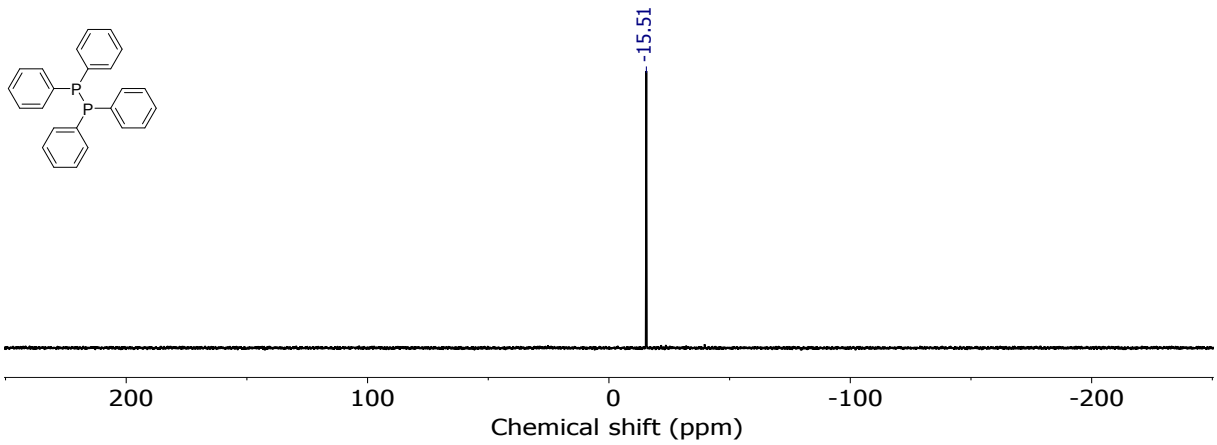
AE

Di(*ortho*-tolyl)phosphine (258 mg, 1.20 mmol) was added to a Schlenk flask and dissolved in CH_2Cl_2 (5 ml). This solution was then cooled to 0 °C prior to the slow addition of borane-dimethylsulfide complex (1.23 ml, 100 mg, 1.32 mmol). After 1.5 h the solvent was removed *in vacuo*. The residue was then triturated with hexane (5 ml), that was removed *in vacuo* prior to the addition of tetrahydrofuran (5 ml). The resultant borane-protected phosphine solution was cooled to -78 °C prior to the dropwise addition of *n*-butyllithium (0.83 ml, 1.32 mmol, 1.6 M), which resulted in the formation of a deep orange solution. After 35 min, chlorodiphenylphosphine (0.216 ml, 266 mg, 1.20 mmol) was added dropwise and the reaction was left to stir at -78 °C for 5 h. The rection mixture was then allowed to warm to room temperature and diethylamine (0.5 ml, 354 mg, 4.83 mmol) added. After 1 h, volatiles were removed *in vacuo* affording a white powder. The crude product was then filtered by cannula to a second Schlenk flask in toluene (3 x 10 ml), yielding the unsymmetrical diphosphane **AE** in 80 % purity. This product was then recrystallized from hot methanol (30 ml) affording the pure product **AE** as a colourless crystalline solid (65 mg, 14 % yield). ^{1}H NMR (400 MHz, C_6D_6): 7.88 (m, 2H, Ar*H*), 7.49 (m, 4H, Ar*H*), 6.96 (m, 10H, Ar*H*), 6.84 (m, 2H, Ar*H*), 2.07 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): -35.1 (d, J_{PP} 150.4 Hz, *P*(Ph)); -16.3 (d, J_{PP} 150.4 Hz, *P*(*o*-Tol). MS (APCI+) m/z: [M+H$^+$] 399.1412 (theor. 399.1426).

1.4 – Diphosphane characterisation ^{31}P{^{1}H} NMR spectra

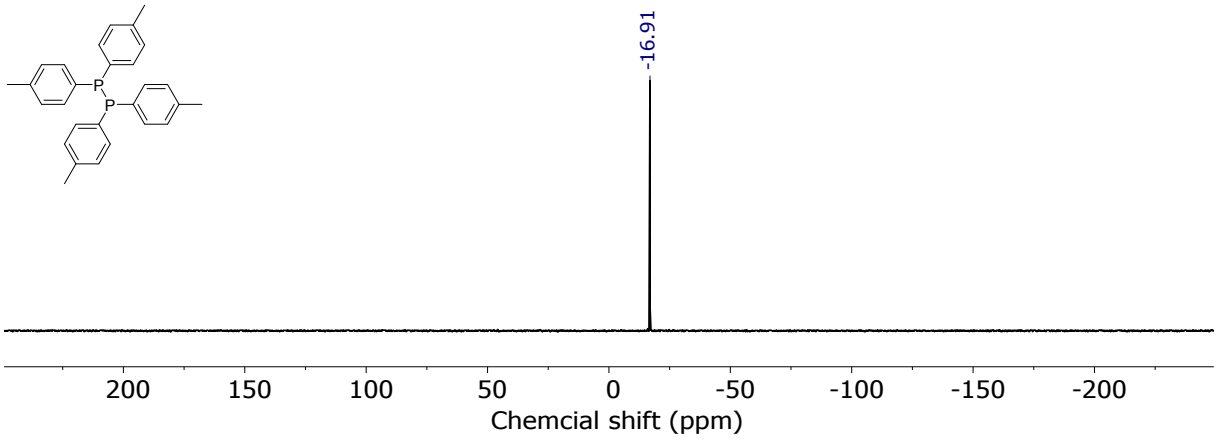
Tetraphenyldiphosphane **A_2**

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): -15.5 (s).



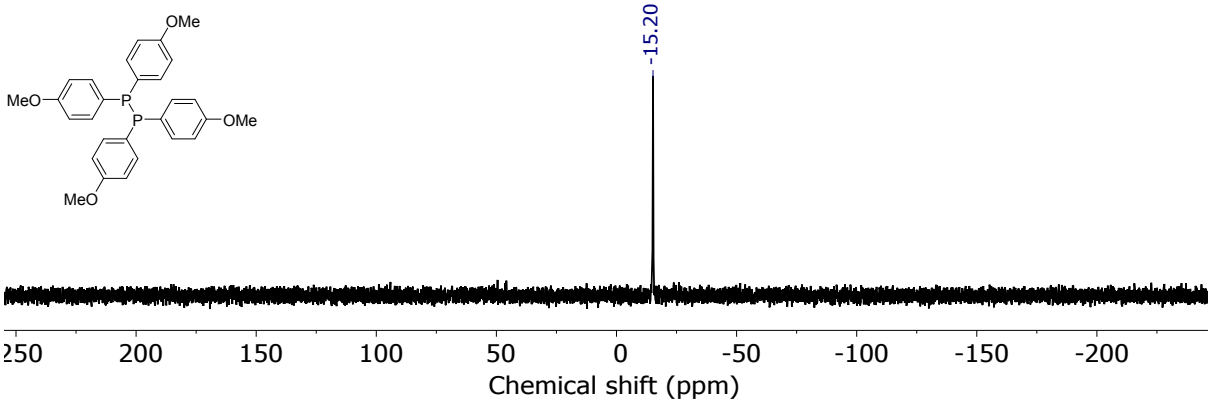
Tetra(*p*-tolyl)diphosphane **B_2**

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): -16.9 (s).



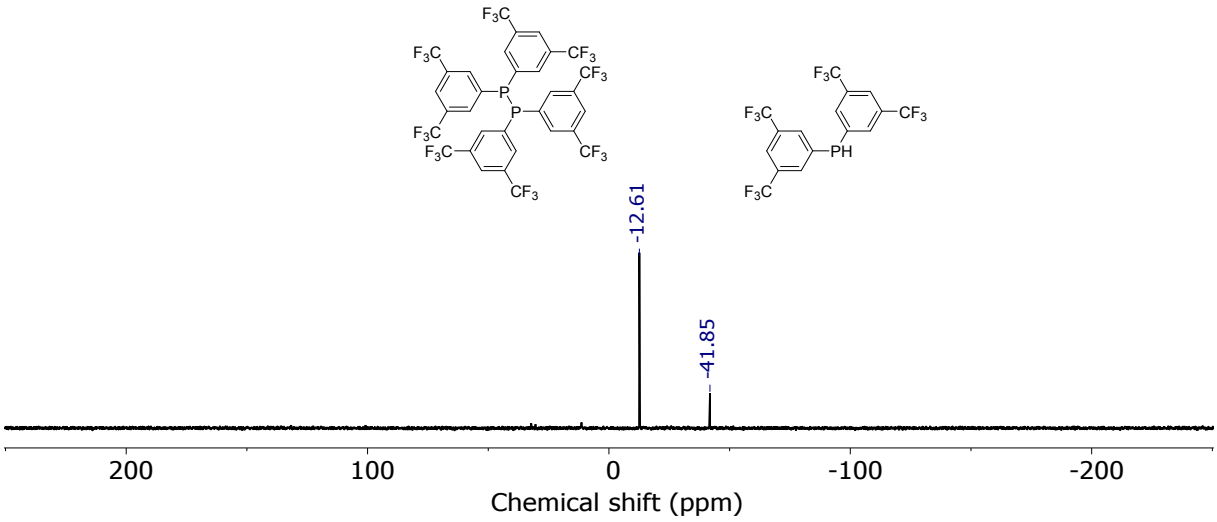
Tetra(*p*-anisyl)diphosphane **C_2**

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): -15.2 (bs).



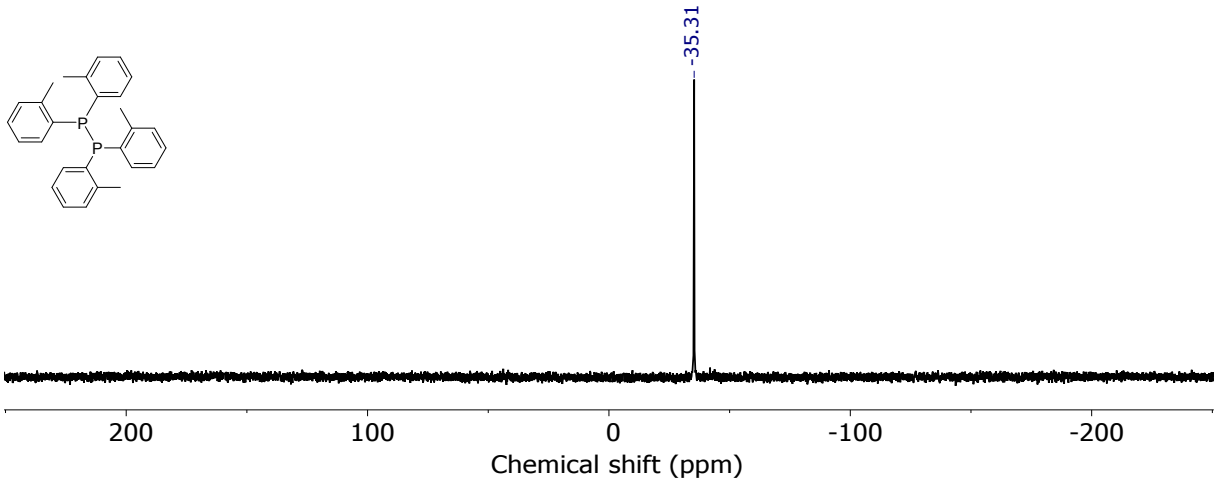
Tetra(3,5-bis(trifluoromethyl)phenyl)diphosphane **D_2**

$^{31}P\{^{1}H\}$ NMR (THF): -12.6 (s).



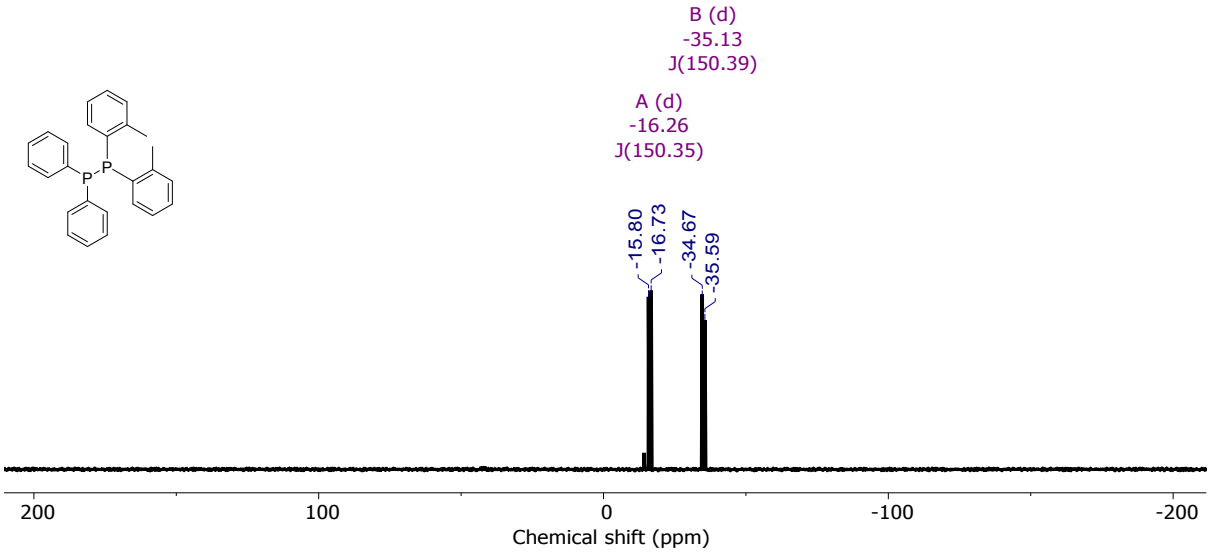
Tetra(*o*-tolyl)diphosphane **E_2**

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): -35.3 (s).

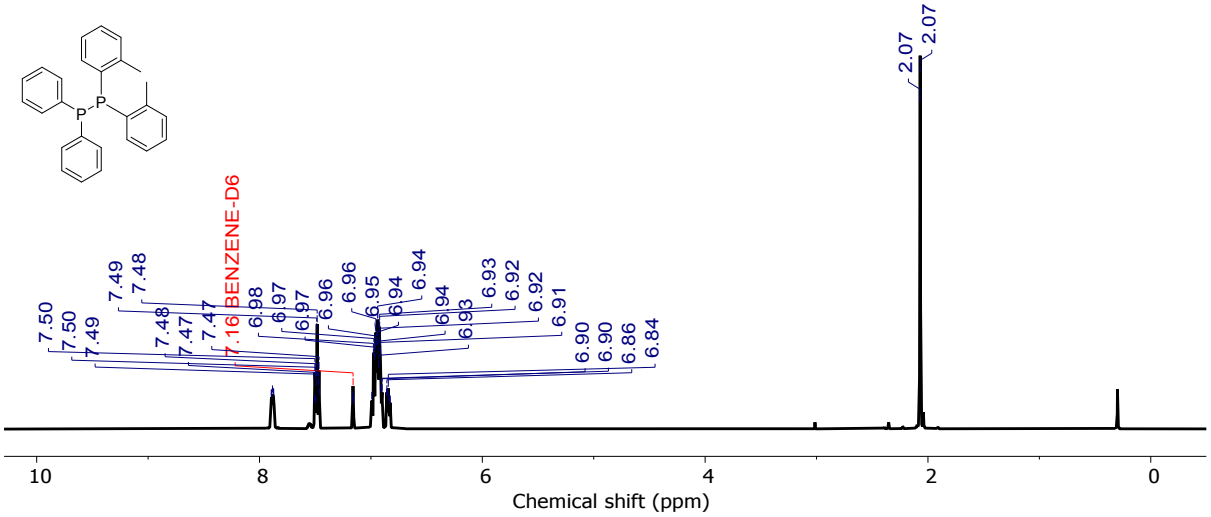


1,1-diphenyl-2,2-di-*o*-tolyldiphosphane **AE**

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): -16.3 (d), -35.1 (d).



^{1}H NMR (C_6D_6)


2.07
2.07
BENZENE-D6
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.16
6.98
6.97
6.97
6.96
6.96
6.95
6.94
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.90
6.90
6.86
6.84
10
8
6
4
2
0
Chemical shift (ppm)

2 – Equilibrium studies

General procedure for equilibrium studies.

To an oven-dried NMR tube, 0.025 mmol (~10 mg) of each diphosphane, $\mathbf{X_2}$ and $\mathbf{Y_2}$ were added under an Ar atmosphere. The NMR tube was then sealed, removed from the glovebox and cycled onto the Schlenk line. Thereafter 0.5 ml of dry solvent ($CDCl_3$, CD_2Cl_2, C_6D_6, PhMe, PhCl, PhF or THF) was added creating an $\mathbf{X_2}$ + $\mathbf{Y_2}$ solution. The NMR tube was then sealed and the cap lined with parafilm to slow the ingress of air. An initial $^{31}P\{^1H\}$ NMR experiment was then performed (64 scans, JEOL ECS300) within 20 min of solvent addition. The solution was then re-tested at irregular intervals until no further change in the ratio of diphosphane resonances was observed. Some spectra were recorded on a JEOL ECS400 or Bruker Advance 400 spectrometer for improved resolution.

Each spectrum is labelled by its reaction number in Table 1, and the two parent diphosphanes.

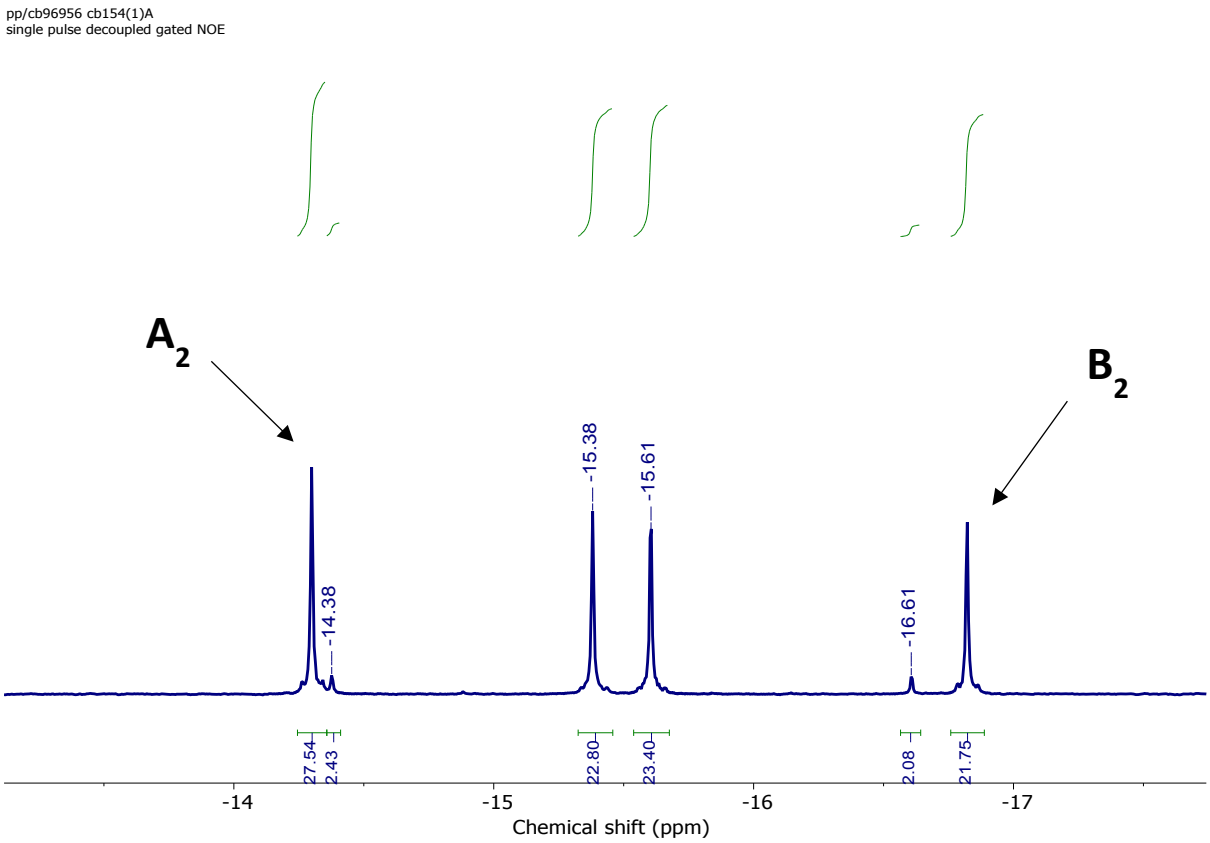
Due to the degeneracy of these metathesis reactions, forming 2 molecules of the **XY** species, the equilibrium equation becomes:

$$K = \frac{[XY]^2}{[X_2][Y_2]} \qquad \text{Eq. 1}$$

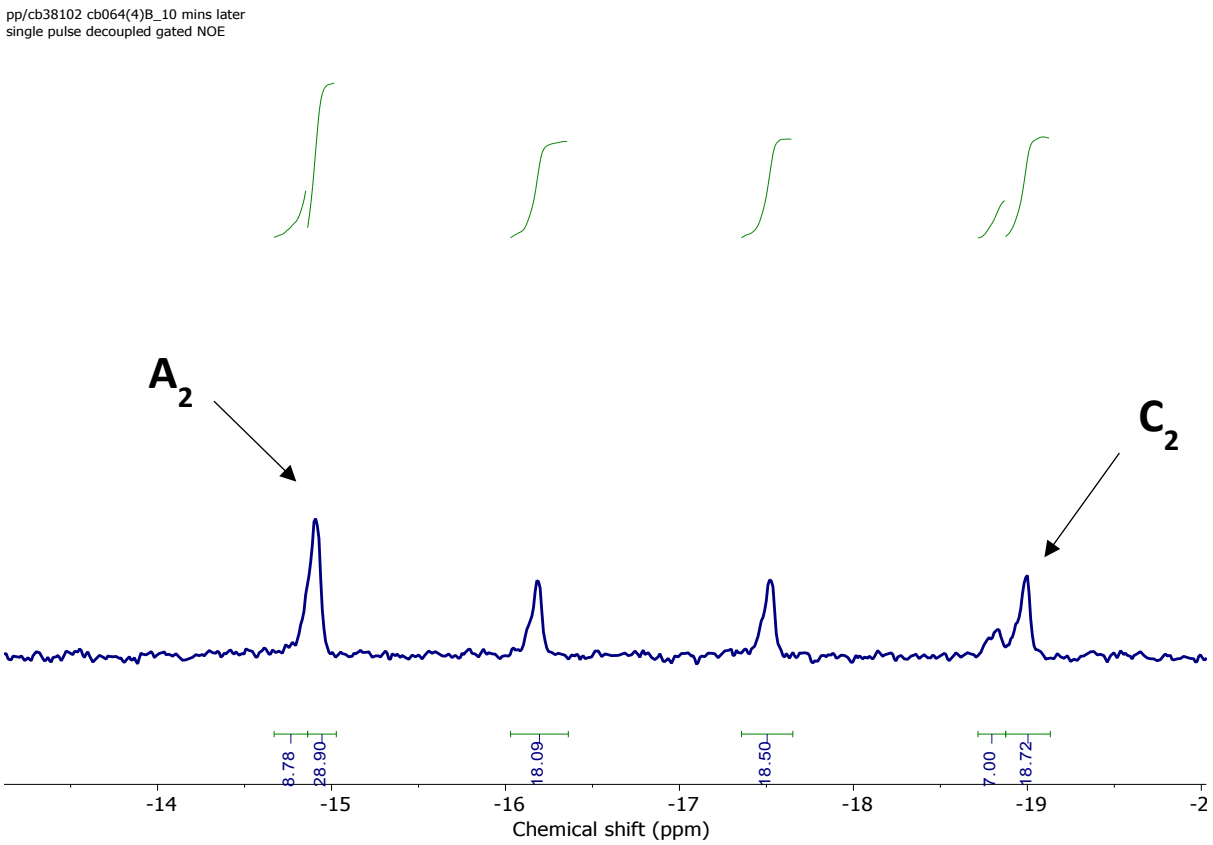
Meaning that for a statistical mixture, i.e. 1 mol $\mathbf{X_2}$, 1 mol $\mathbf{Y_2}$ and 2 mol **XY**, the *K* is 4.

In the case of reaction 3, the equilibrium constant is estimated because no residual $\mathbf{D_2}$ resonance is observed. For the sake of calculation it is assumed to be approximately 1% of the total spectrum (integral).

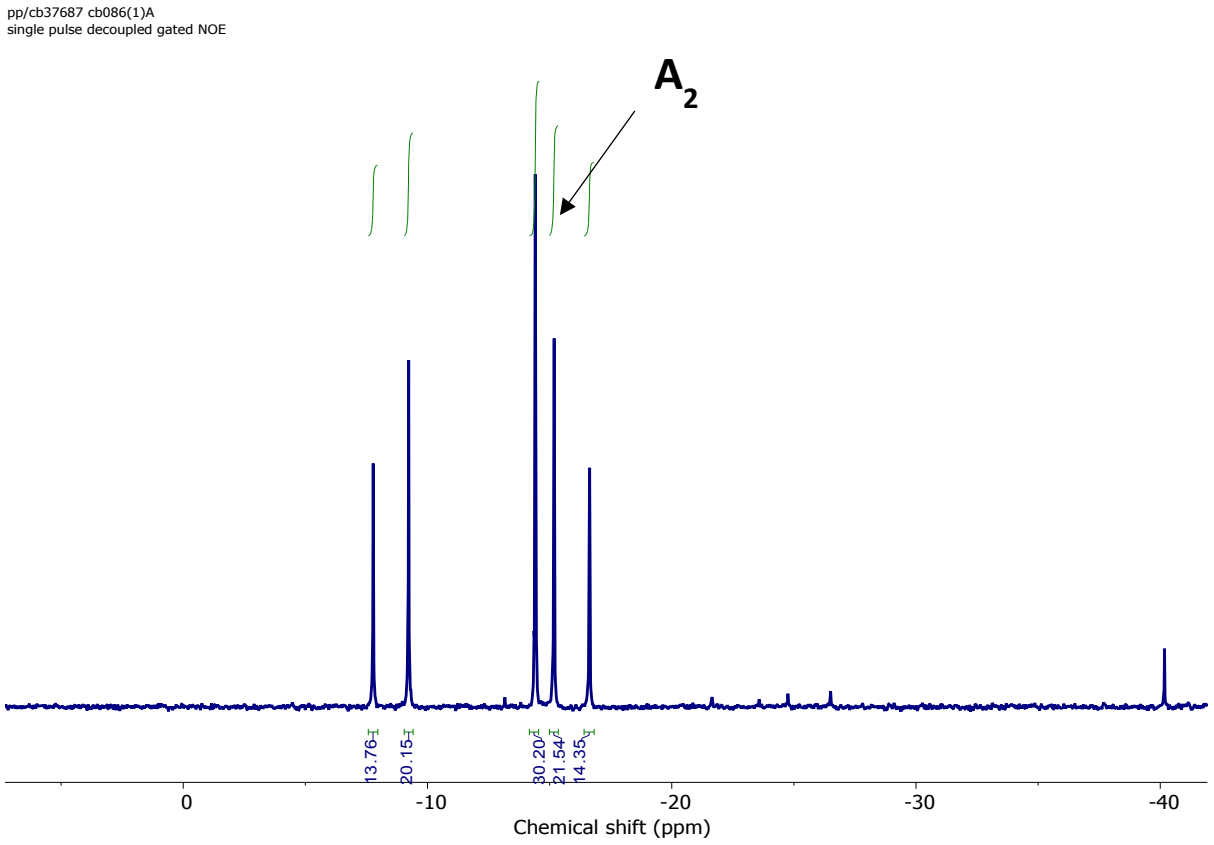
1^a	$\mathbf{A_2}$	$\mathbf{B_2}$



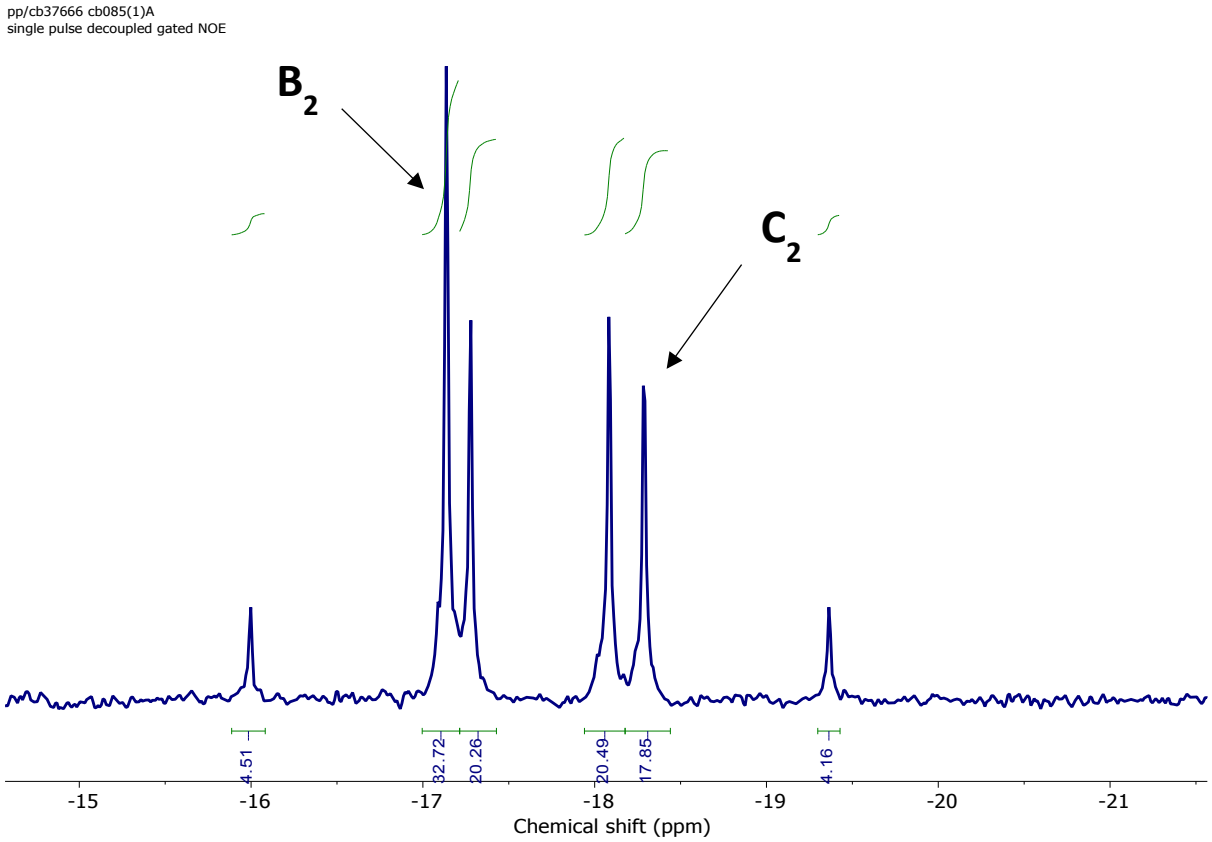
2^b **A_2** **C_2**

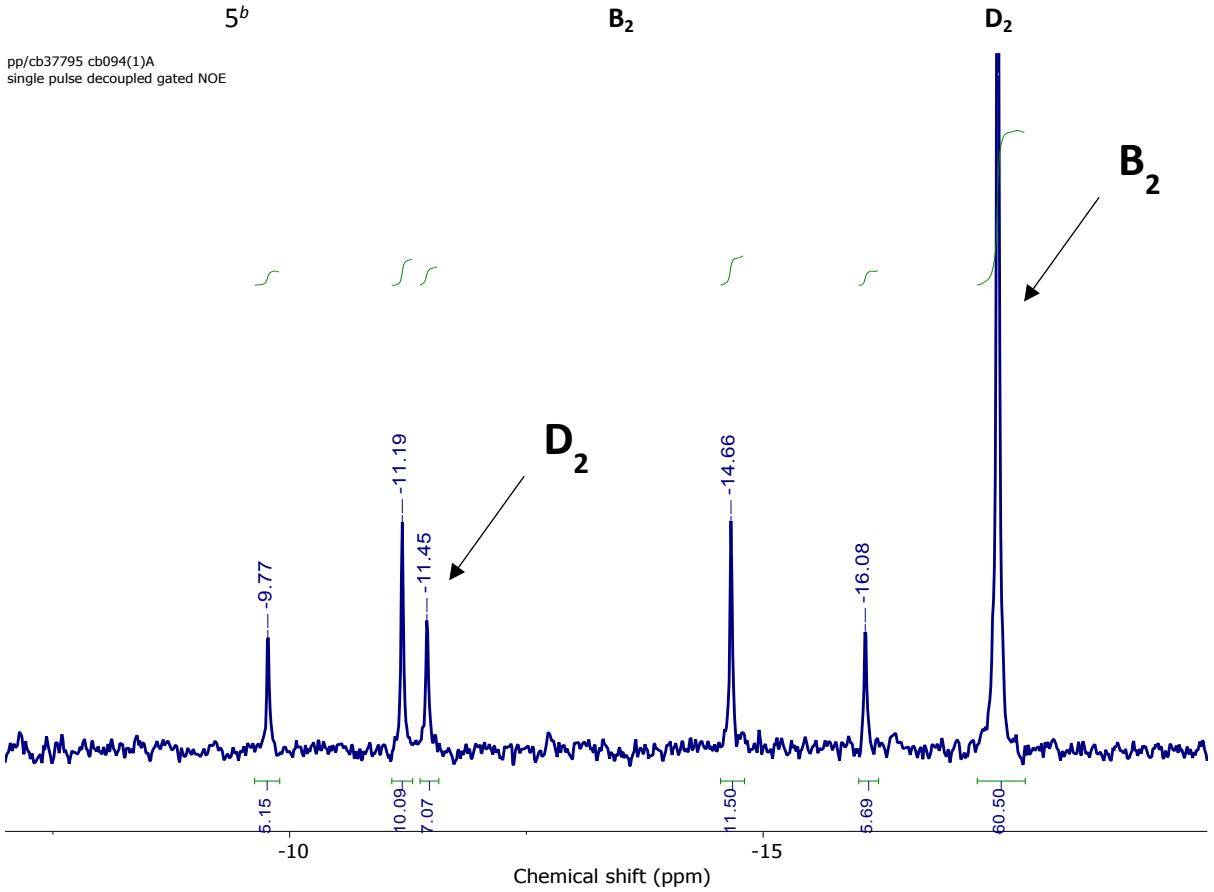

pp/cb38102 cb064(4)B_10 mins later
single pulse decoupled gated NOE
A2
C2
8.78
28.90
18.09
18.50
7.00
18.72
-14
-15
-16
-17
-18
-19
-2
Chemical shift (ppm)

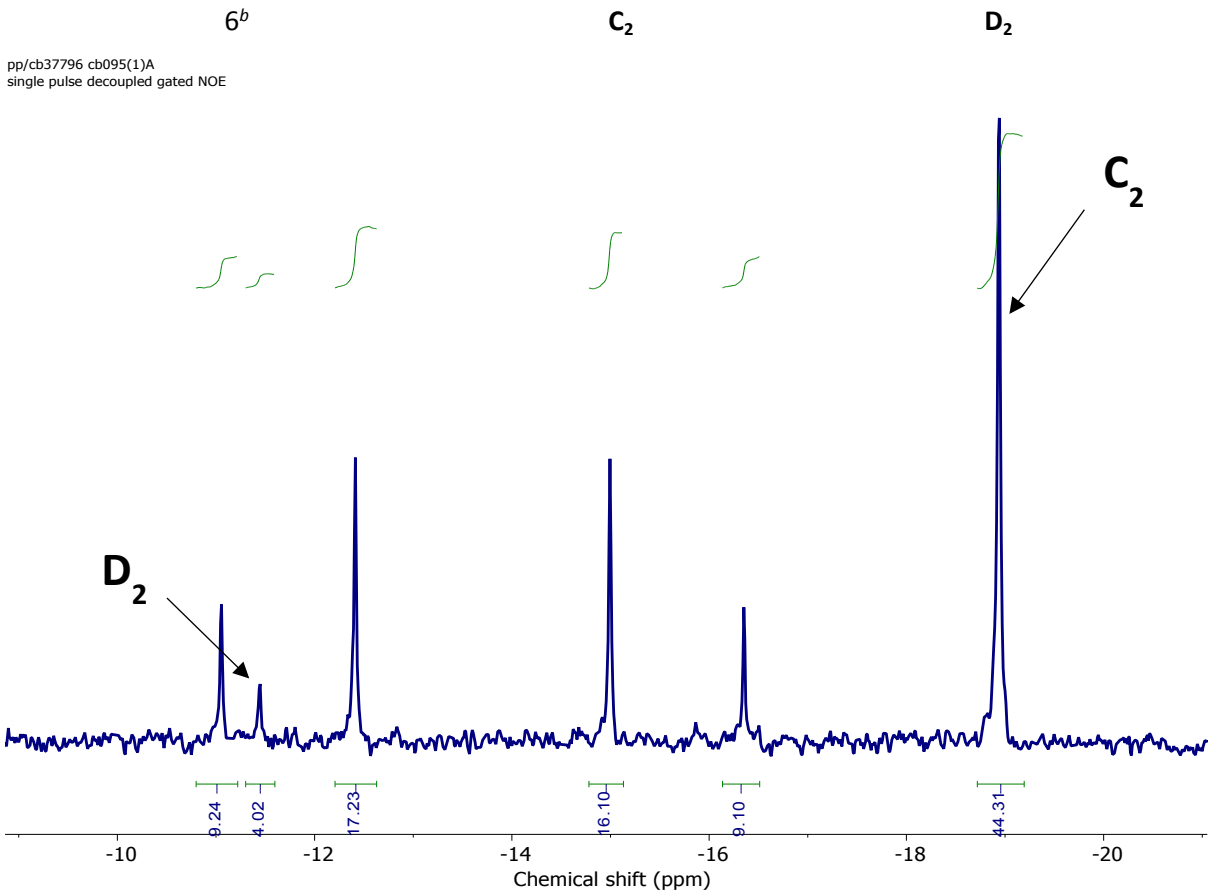
3^c **A_2** **D_2**

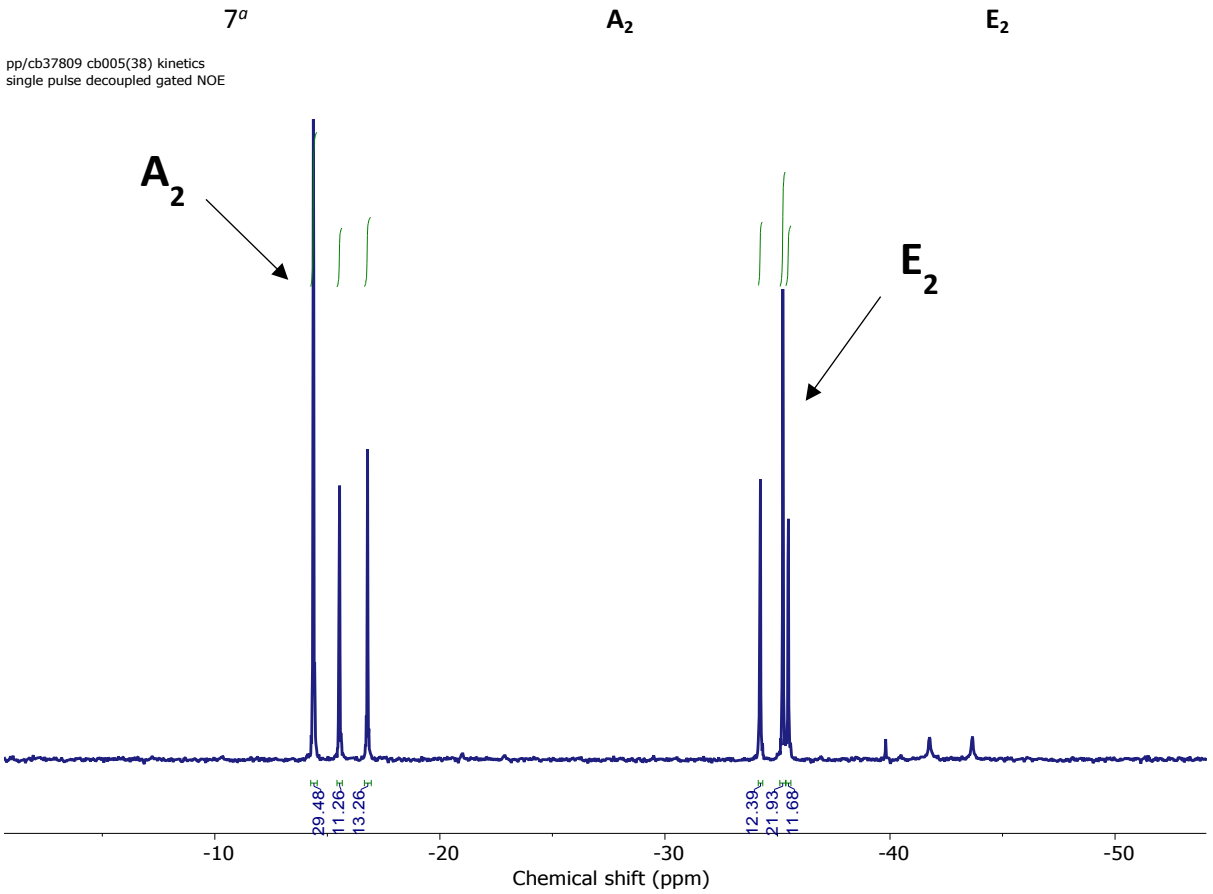

pp/cb37687 cb086(1)A
single pulse decoupled gated NOE
A2
13.76
20.15
30.20
21.54
14.35
0
-10
-20
-30
-40
Chemical shift (ppm)

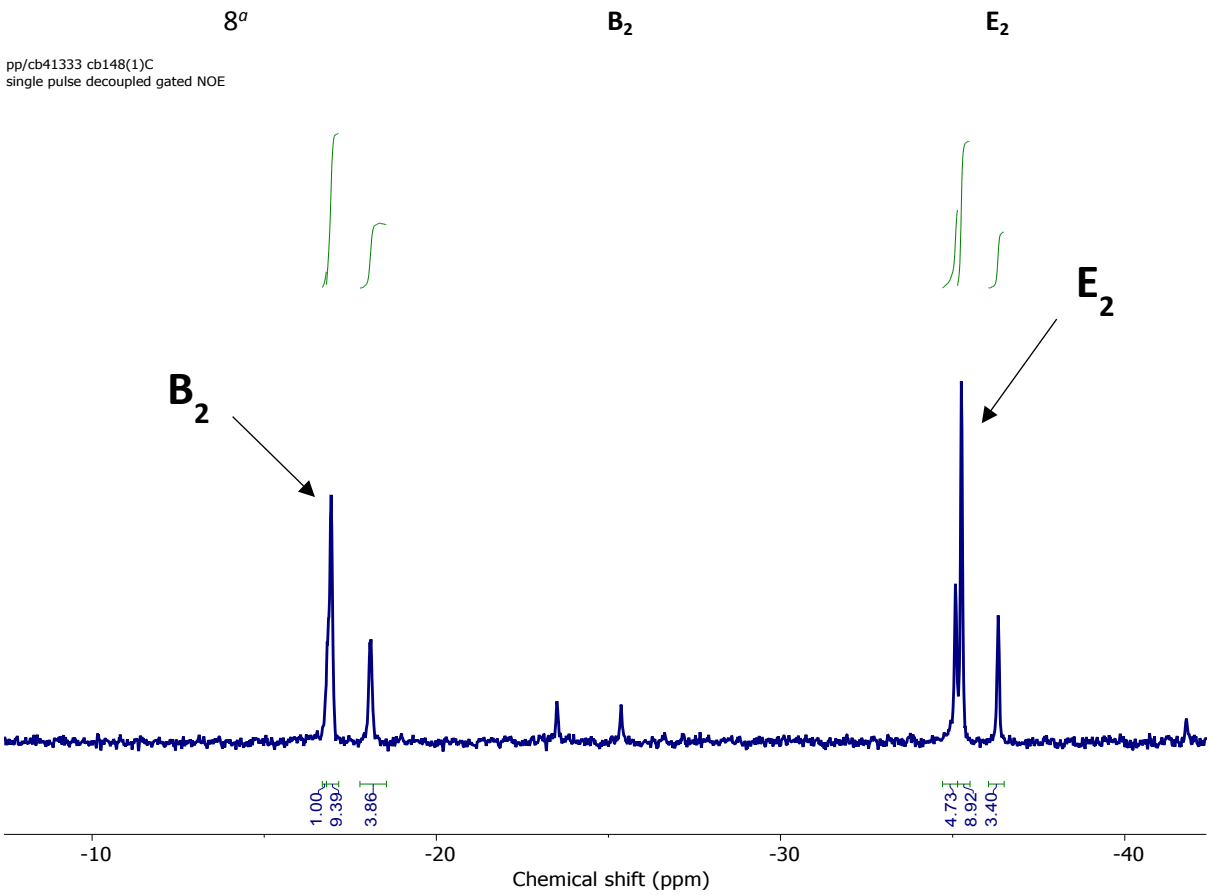
4^c B_2 C_2

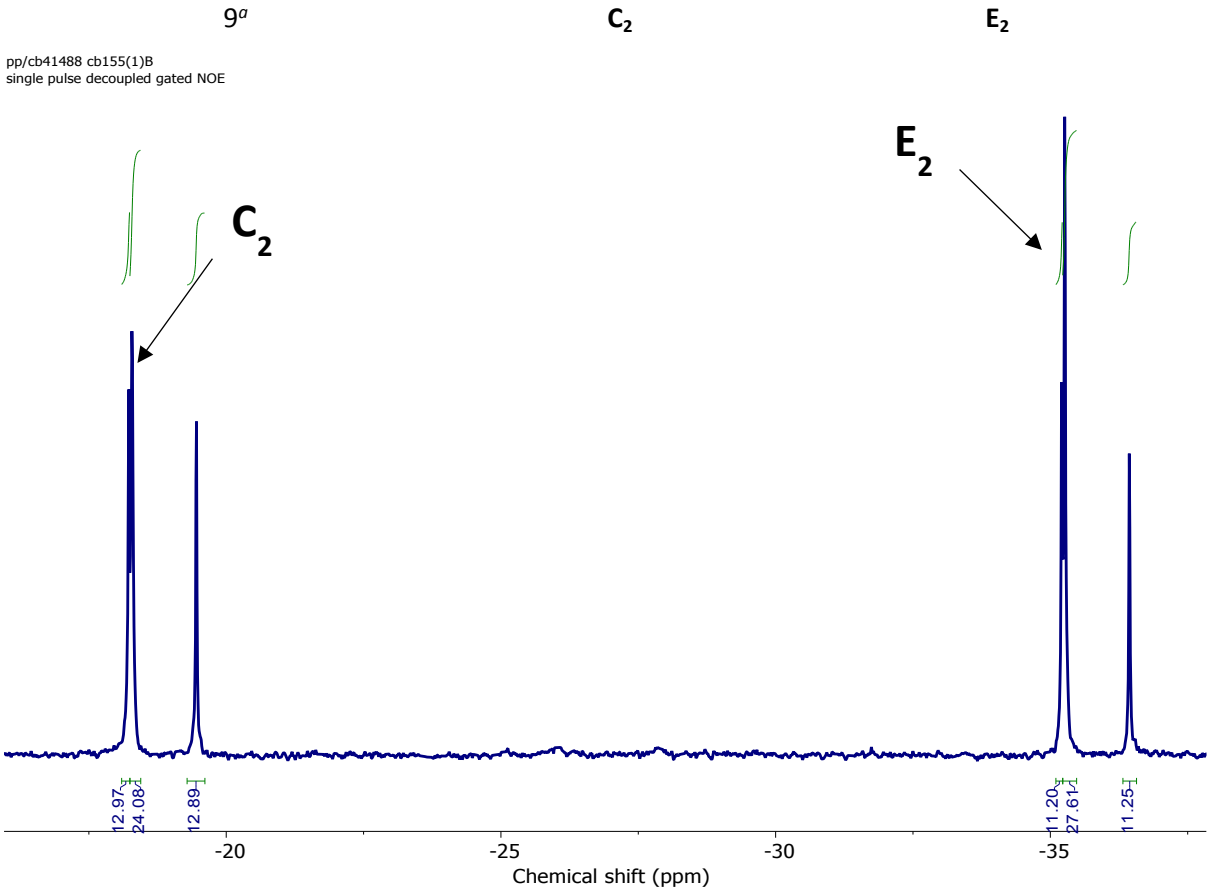

pp/cb37666 cb085(1)A
single pulse decoupled gated NOE
B2
C2
4.51
32.72
20.26
20.49
17.85
4.16
-15
-16
-17
-18
-19
-20
-21
Chemical shift (ppm)


5b
B2
D2
pp/cb37795 cb094(1)A
single pulse decoupled gated NOE
B2
D2
-9.77
-11.19
-11.45
-14.66
-16.08
5.15
10.09
7.07
11.50
5.69
60.50
-10
-15
Chemical shift (ppm)

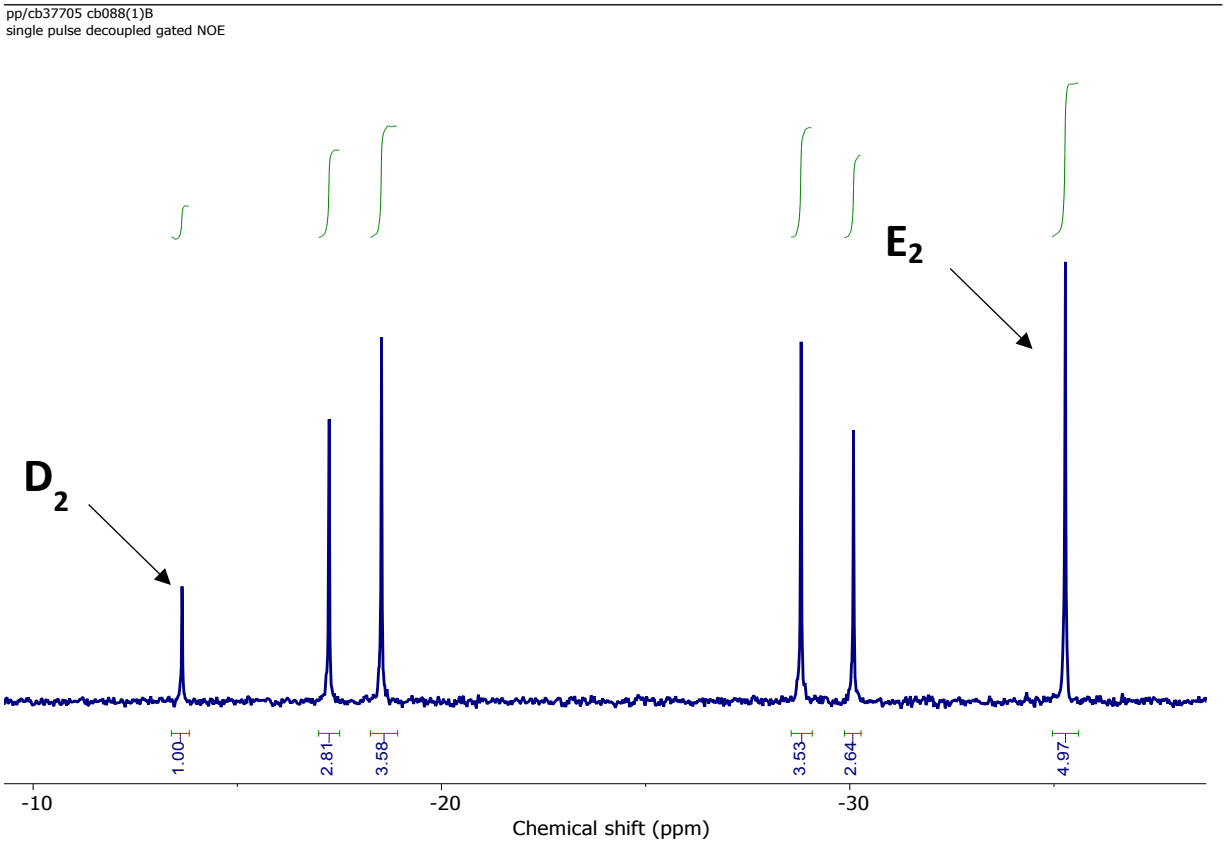

6b
C2
D2
pp/cb37796 cb095(1)A
single pulse decoupled gated NOE
C2
D2
9.24
4.02
17.23
16.10
9.10
44.31
-10
-12
-14
-16
-18
-20
Chemical shift (ppm)


7a
A2
E2
pp/cb37809 cb005(38) kinetics
single pulse decoupled gated NOE
A2
E2
29.48
11.26
13.26
12.39
21.93
11.68
-10
-20
-30
-40
-50
Chemical shift (ppm)


8a
B2
E2
pp/cb41333 cb148(1)C
single pulse decoupled gated NOE
B2
E2
1.00
9.39
3.86
4.73
8.92
3.40
-10
-20
-30
-40
Chemical shift (ppm)


9a
C2
E2
pp/cb41488 cb155(1)B
single pulse decoupled gated NOE
C2
E2
12.97
24.08
12.89
11.20
27.61
11.25
-20
-25
-30
-35
Chemical shift (ppm)

10[a]	D_2	E_2


pp/cb37705 cb088(1)B
single pulse decoupled gated NOE
D2
E2
1.00
2.81
3.58
3.53
2.64
4.97
-10
-20
-30
Chemical shift (ppm)

3 – Qualitative kinetics studies

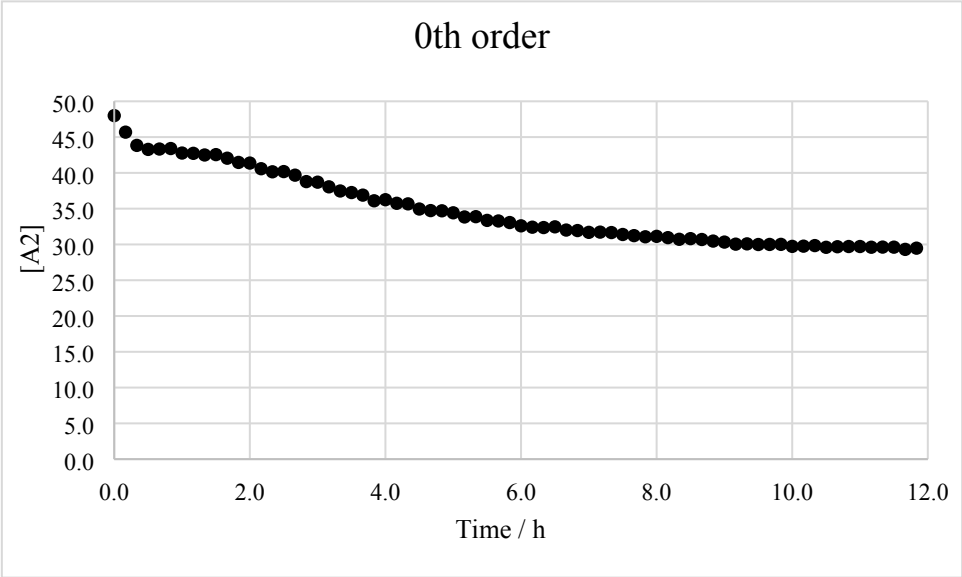
3.1 – Kinetics of A_2 + E_2

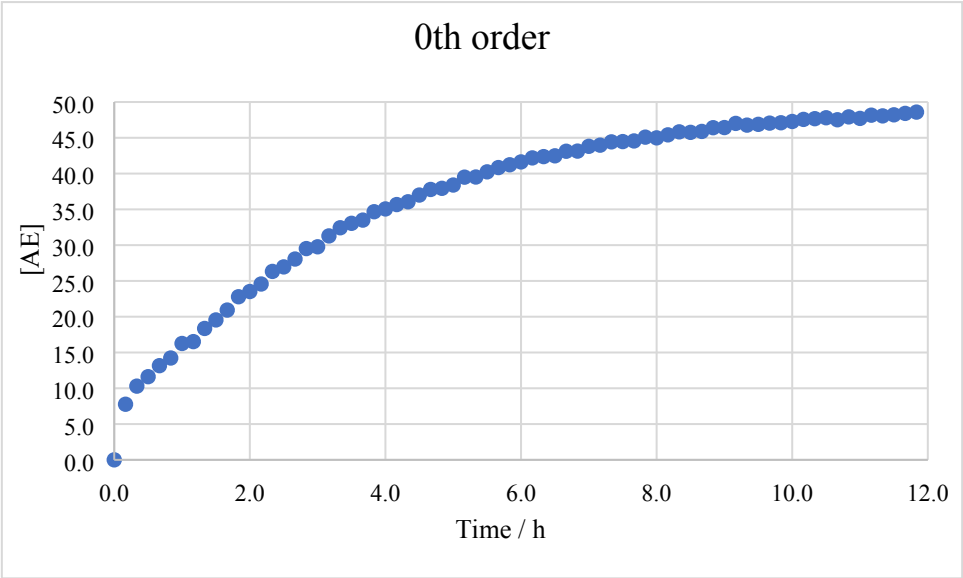
Experimental procedure for A_2/E_2 kinetics investigation.

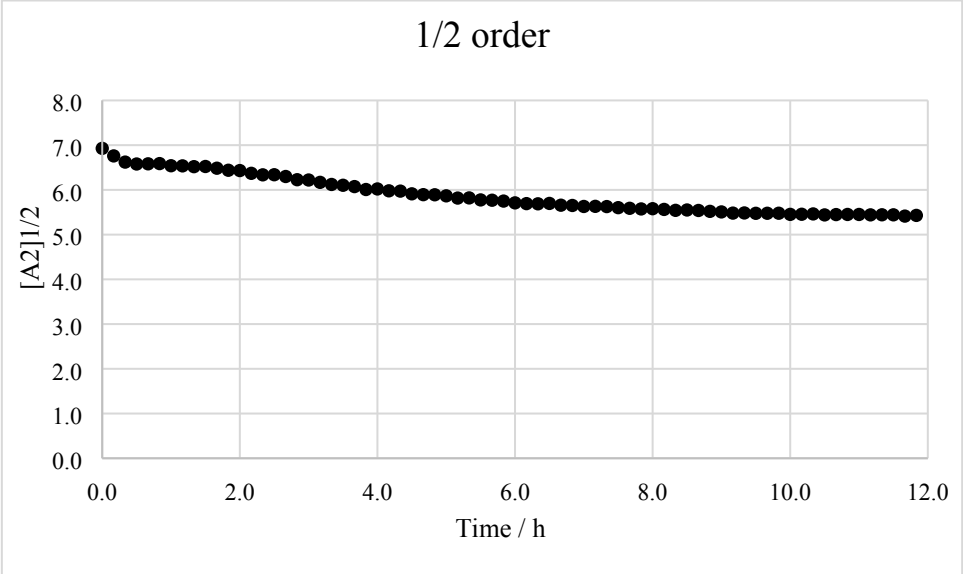
To an oven-dried NMR tube, **A_2** (10 mg, 0.025 mmol) and **E_2** (11.5 mg, 0.025 mmol) were added under an Ar atmosphere. The NMR tube was then sealed, removed from the glovebox and cycled onto a Schlenk line. Then, under a dry N_2 atmosphere 0.5 ml of solvent ($CDCl_3$ or toluene) was added and the diphosphanes dissolved. In the $CDCl_3$ case, the reaction mixture was immediately cooled to -78 °C using a dry ice/acetone bath. The toluene reaction was left at ambient temperature* and remained unchanged for a period of 3–4 days. The cooled $CDCl_3$ sample was then loaded into a JEOL ECS300 spectrometer, allowed to warm to ambient. A 64 scan $^{31}P\{^1H\}$ NMR spectrum was then recorded at 10 min intervals for 12 h, using inverse-gated decoupling.

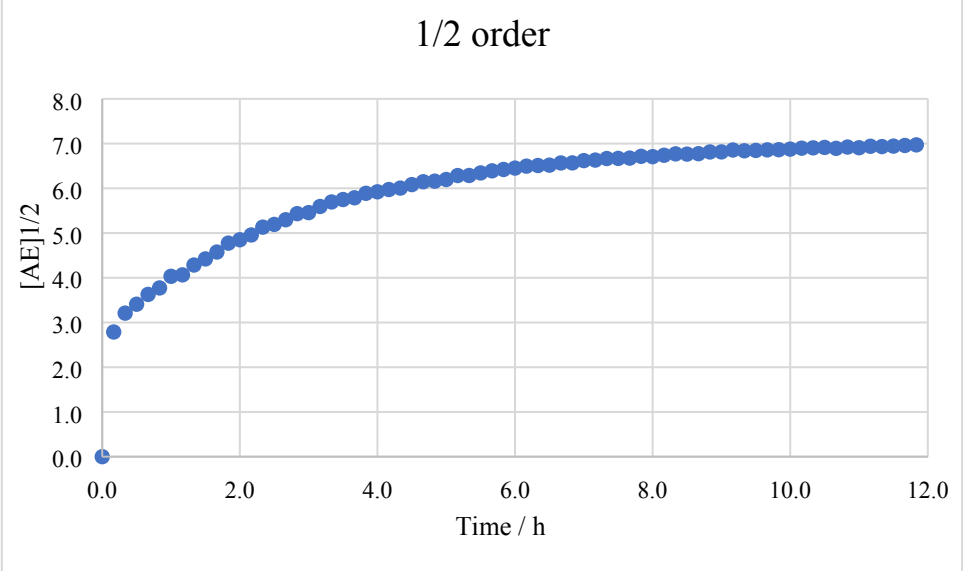
*In a subsequent experiment no metathesis was observed in the toluene reaction even when heated to 100 °C for 24 h.

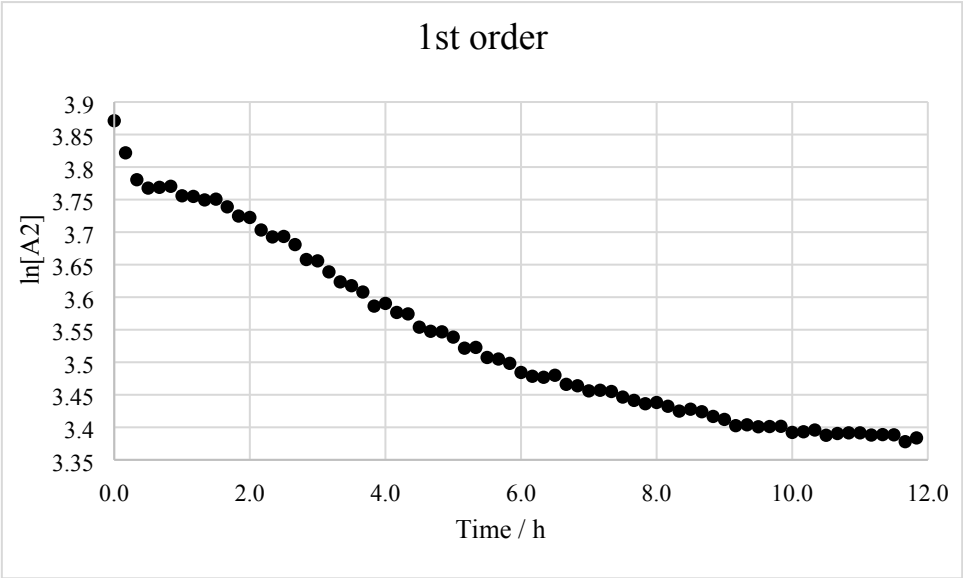
The following graphs show the lack of fit of the kinetics data for diphosphane metathesis and conventional (0th, ½, 1st and 2nd-order) kinetics, both in terms of a starting material **A_2** *and the product* **AE**.

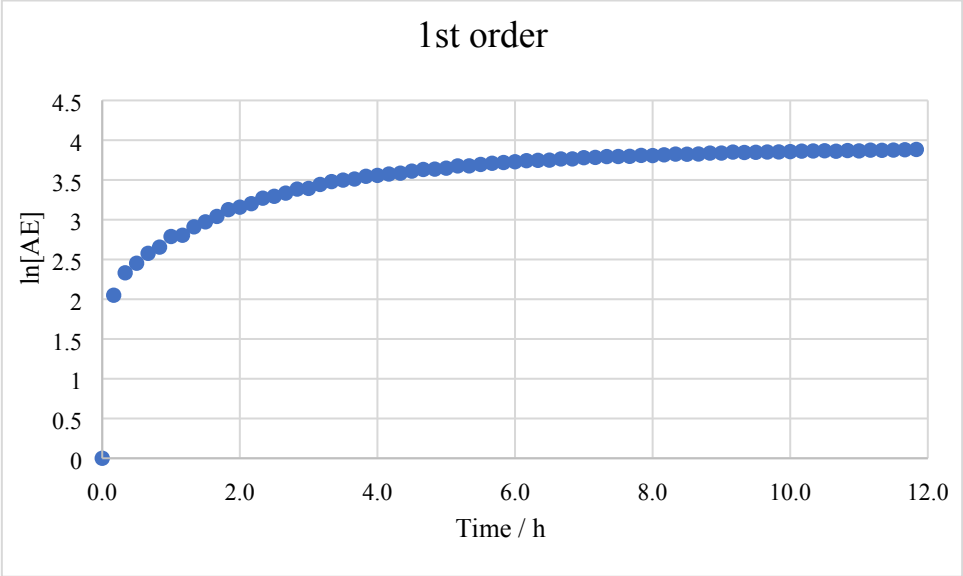


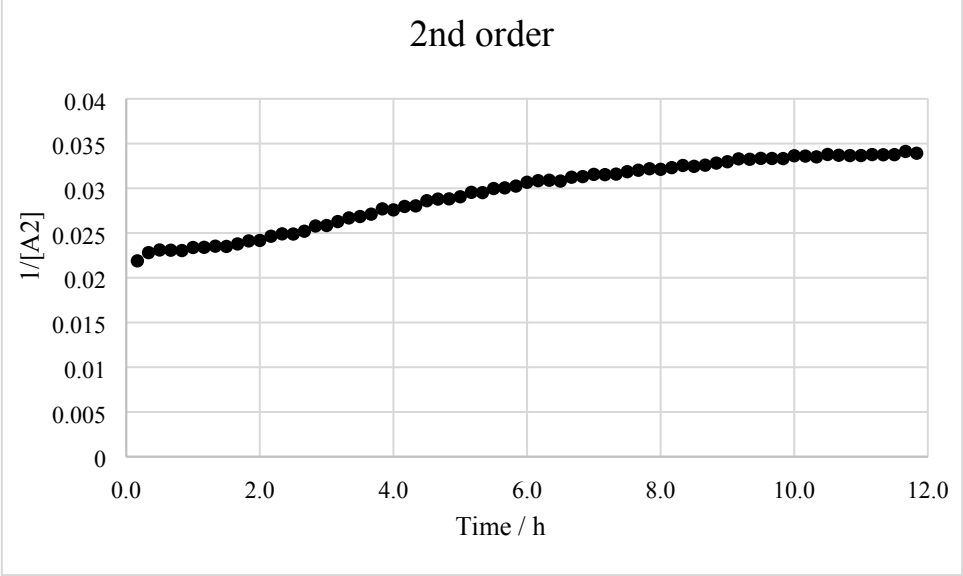

0th order
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
[AE]
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h

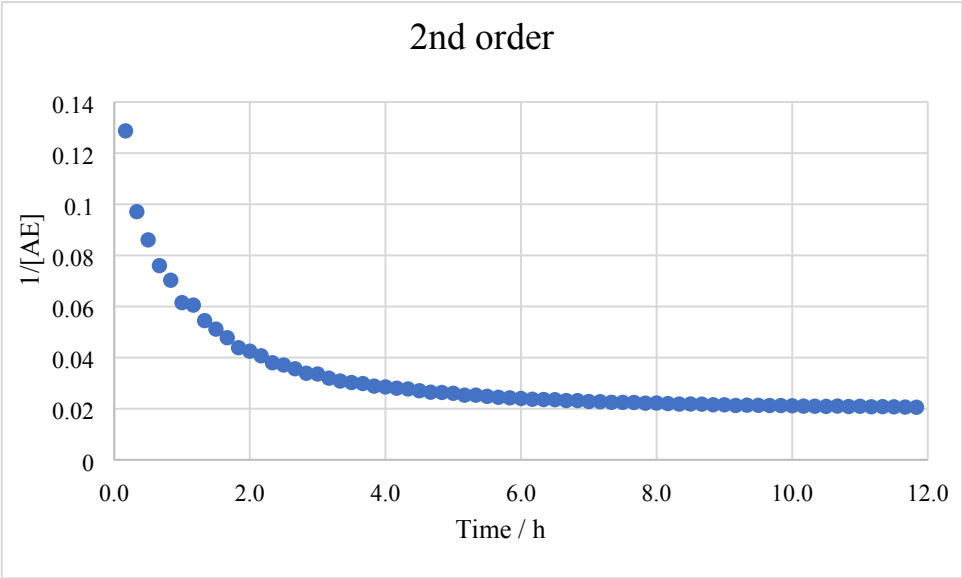

1/2 order
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
[A2]1/2
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h


1/2 order
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
[AE]1/2
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h


1st order
ln[A2]
3.9
3.85
3.8
3.75
3.7
3.65
3.6
3.55
3.5
3.45
3.4
3.35
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h

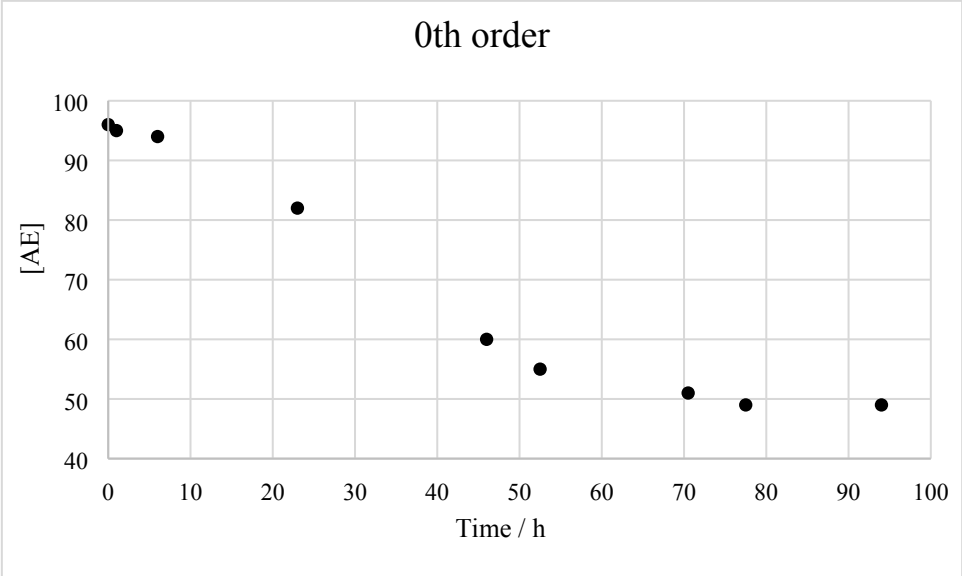

1st order
ln[AE]
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h

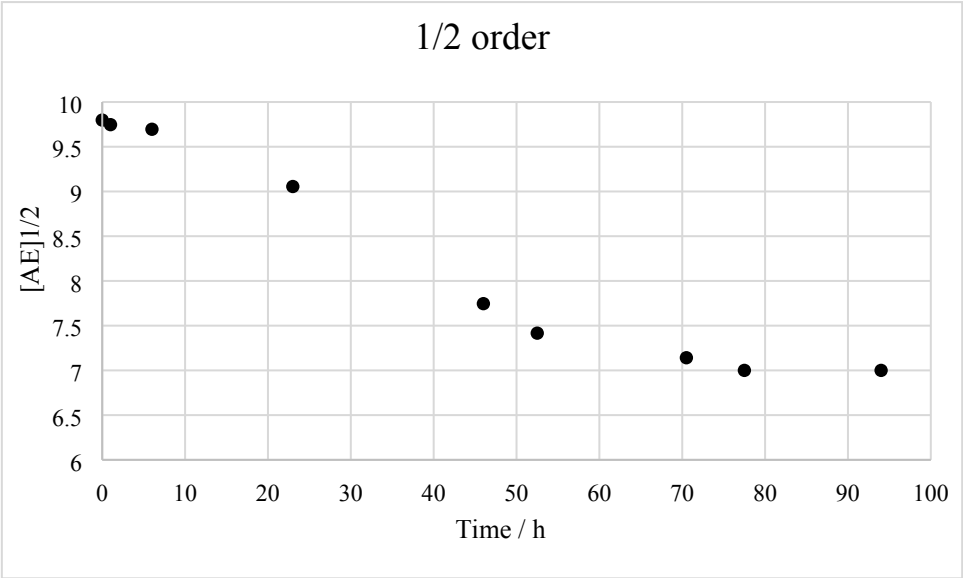

2nd order
1/[A2]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time / h

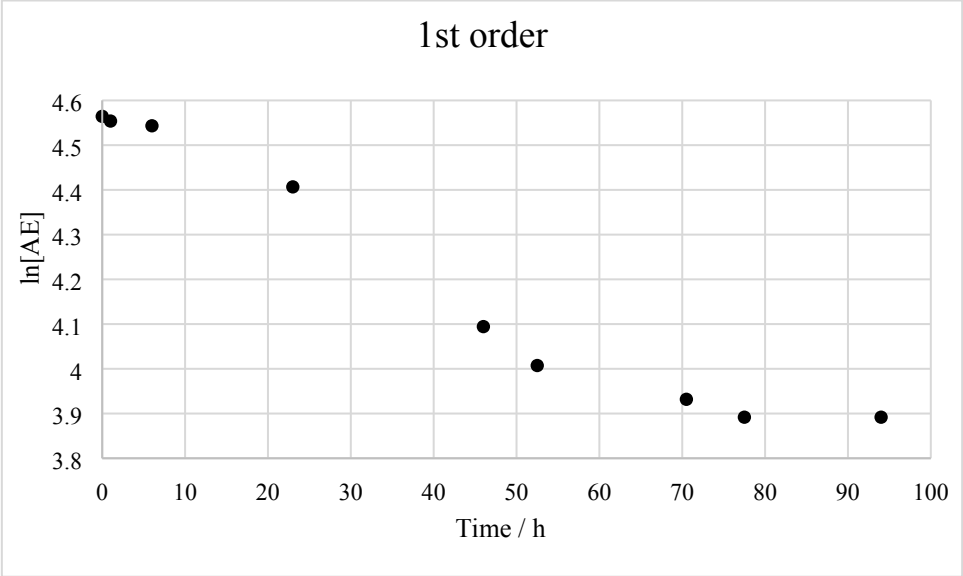


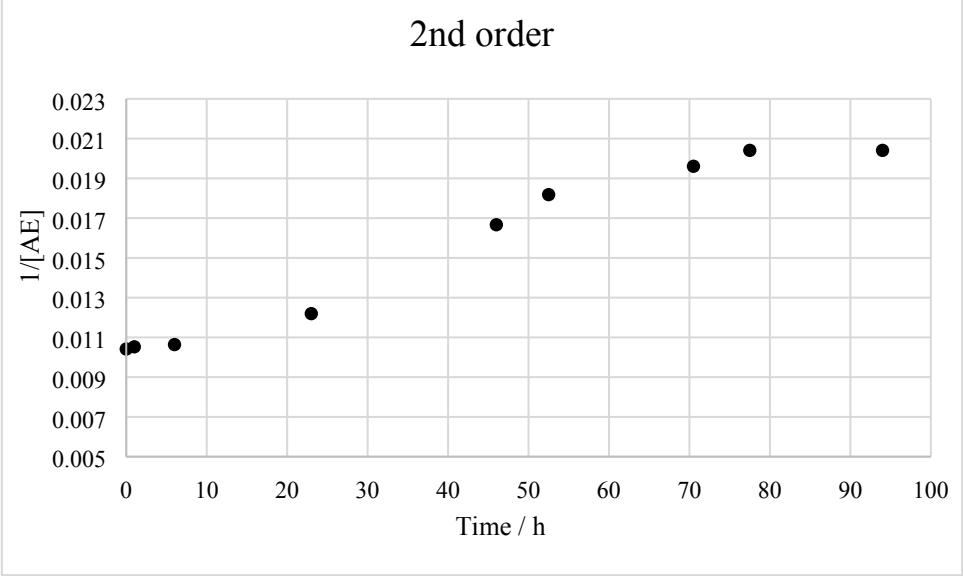
3.2 – Kinetics of reverse AE metathesis

The following plots show the kinetic fits of the reverse reaction, starting with pure **AE** (10 mg, in 0.5 ml $CDCl_3$)*, following an analogous procedure to the forward reaction.*



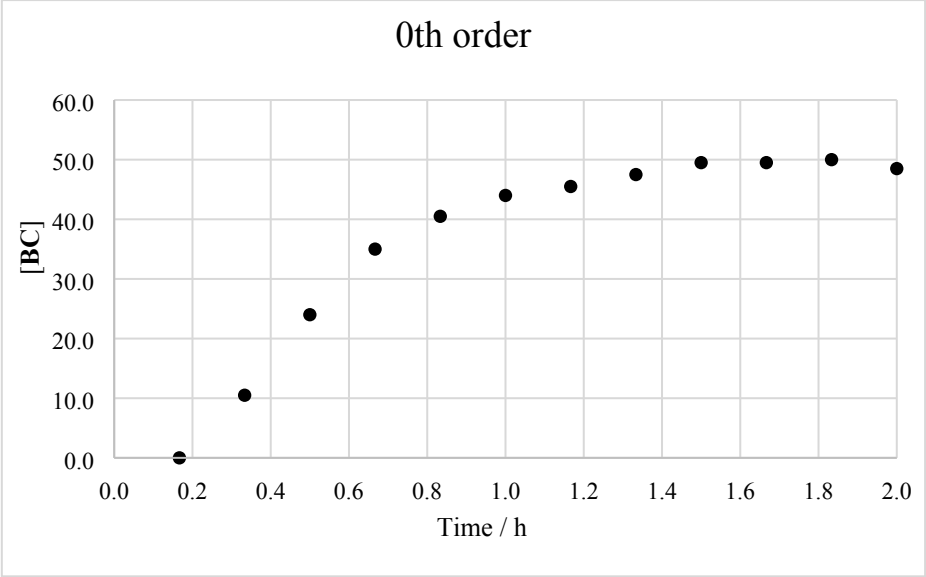

1/2 order
[AE]1/2
10
9.5
9
8.5
8
7.5
7
6.5
6
0
10
20
30
40
50
60
70
80
90
100
Time / h

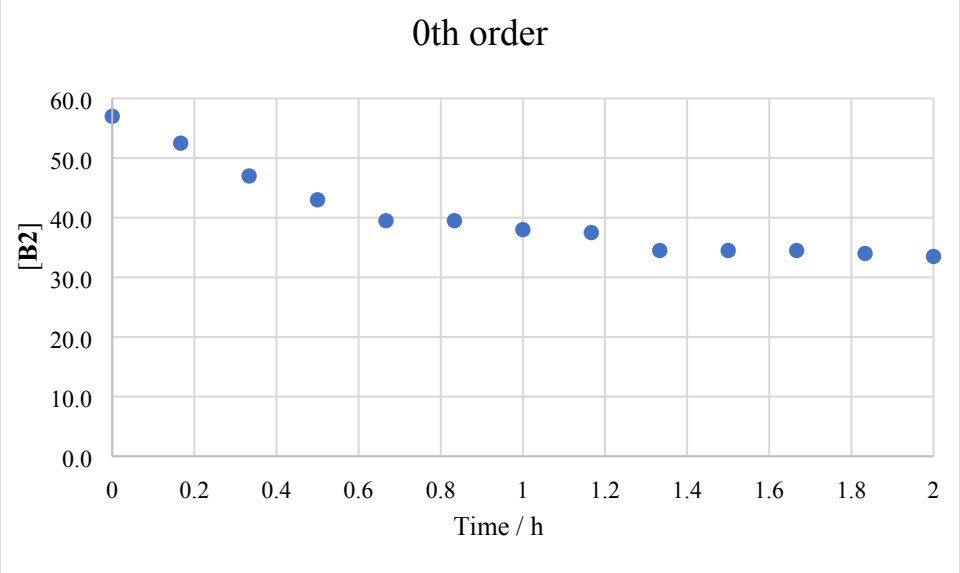

1st order
ln[AE]
4.6
4.5
4.4
4.3
4.2
4.1
4
3.9
3.8
0
10
20
30
40
50
60
70
80
90
100
Time / h

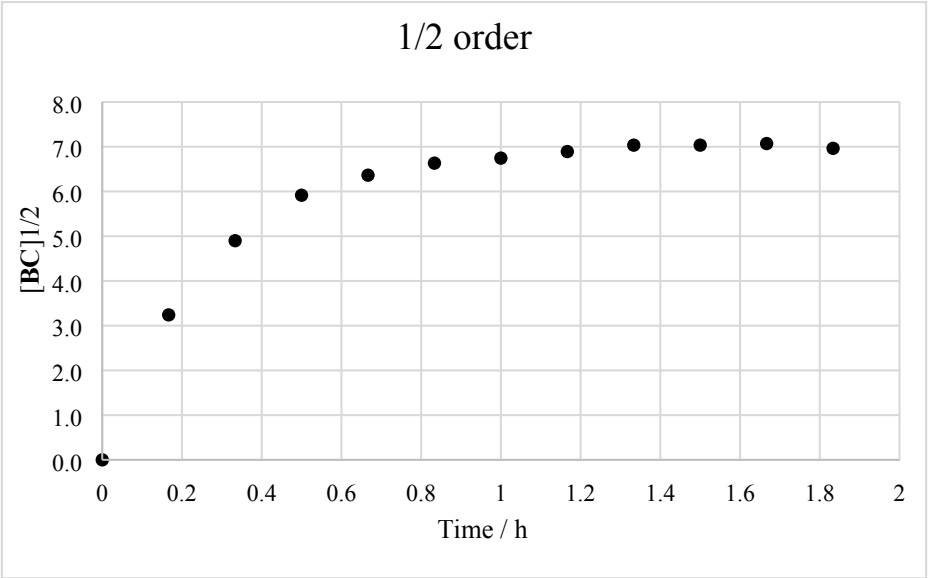

2nd order
1/[AE]
0.023
0.021
0.019
0.017
0.015
0.013
0.011
0.009
0.007
0.005
0
10
20
30
40
50
60
70
80
90
100
Time / h

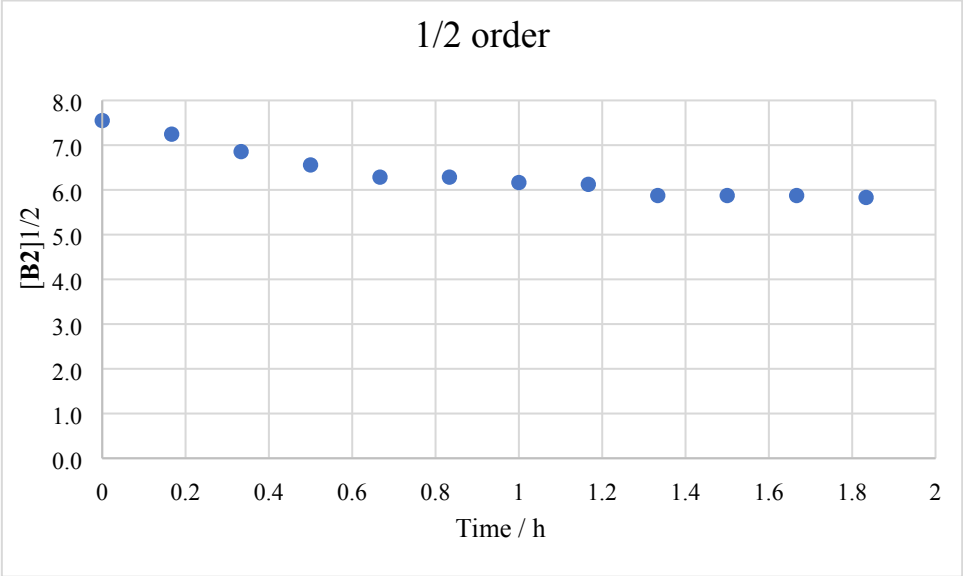
3.3 – Kinetics of B_2 + C_2

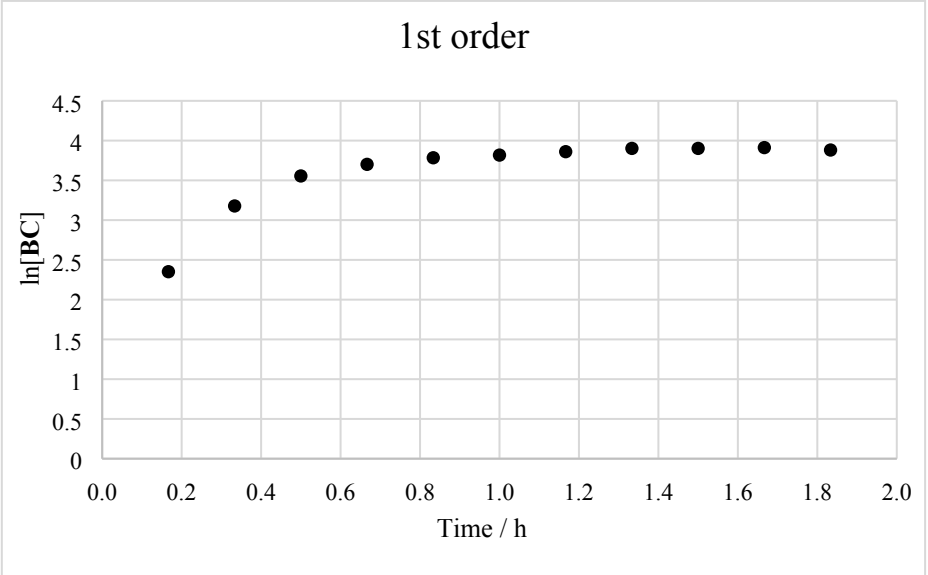
The same procedure used for the **AE** reactions was used in monitoring the kinetics of **BC** formation, though instead of warming the NMR tubes from -78 °C to room temperature, in this experiment the NMR tube was only warmed to -20 °C, where it was held for the duration of the experiment.

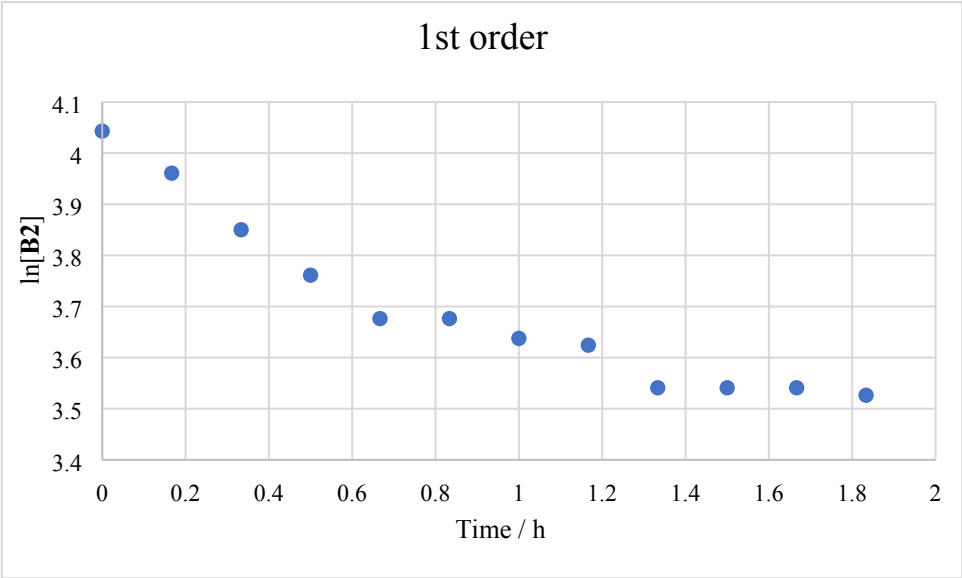


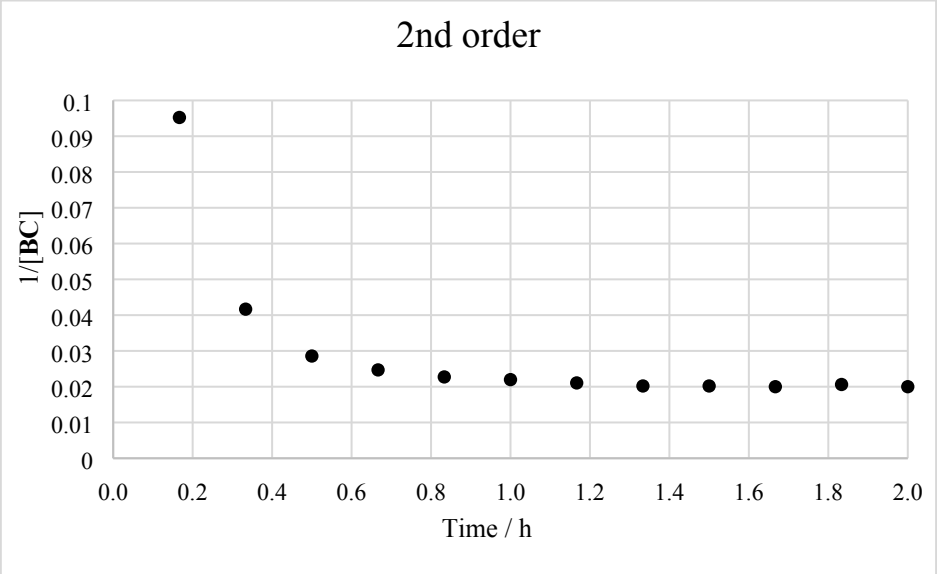


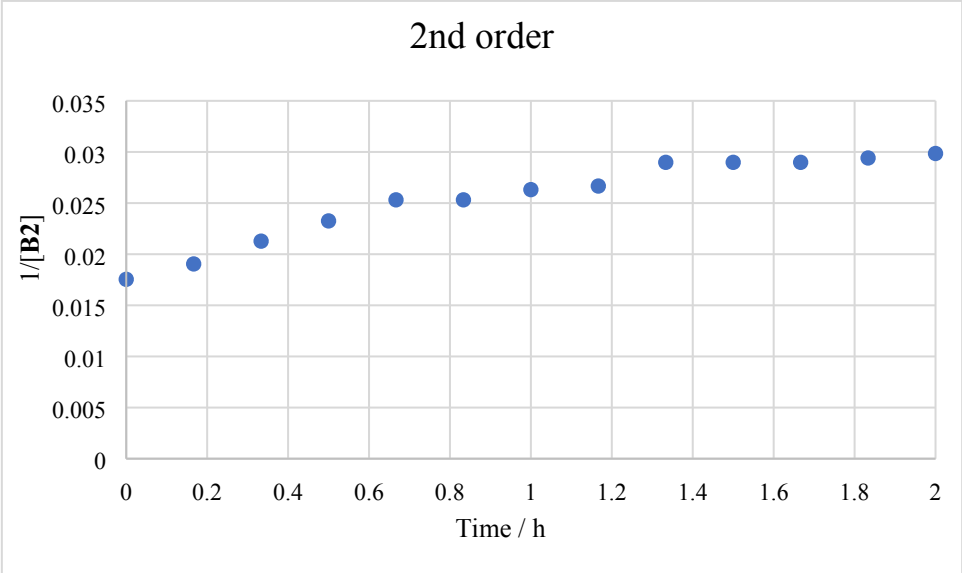

1/2 order
[BC]1/2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Time / h


1/2 order
[B2]1/2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Time / h


1st order
ln[BC]
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Time / h


1st order
ln[B2]
4.1
4
3.9
3.8
3.7
3.6
3.5
3.4
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Time / h


2nd order
1/[BC]
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Time / h


2nd order
1/[B2]
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Time / h

4 –^{31}P NMR spectra for mechanistic investigations

General procedure for additional mechanistic reactions.

Reactions involving additive inhibitors (e.g. water, $^{i}Pr_2NH$, TEMPO) or other non-diphosphane metathesis partners (e.g. Ar_2PCl/Ar_2PH) were performed analogously to the aforementioned equilibrium studies via the following procedure.

To an oven-dried NMR tube 0.025 mmol of $\mathbf{X_2}$ and 0.025–0.1 mmol of $\mathbf{Y_2}$ (or Ar_2PCl/Ar_2PH) was added under an Ar atmosphere. A 1:1 stochiometric balance was used unless otherwise stated. At this stage, any solid additives (e.g. TEMPO, TTBP) were added in excess (0.1–0.2 mmol). The NMR tube was then sealed, removed from the glovebox and cycled onto a Schlenk line under a dry N_2 atmosphere. At this stage, any liquid additives (e.g. H_2O) were syringed into the NMR tube prior to the addition of 0.5 ml of dry, degassed solvent ($CDCl_3$, CD_2Cl_2, C_6D_6, PhMe, PhCl, PhF or THF). The NMR tube was then re-sealed with a parafilm wrap around the cap to prevent the ingress of air into the tube. Generally, a $^{31}P\{^{1}H\}$ NMR spectrum was recorded within 20 min of solvent addition.

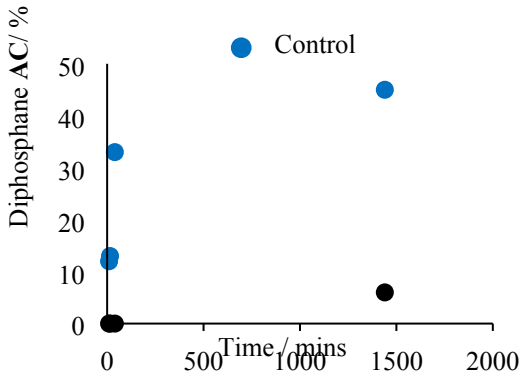
In experiments with **AE**, the same procedure was followed without the addition of a second diphosphane.

In photolysis experiments, the NMR tube was illuminated with a 5 W, 365 nm handheld UV lamp. Control experiments were wrapped in aluminium foil and placed in a dark cupboard.

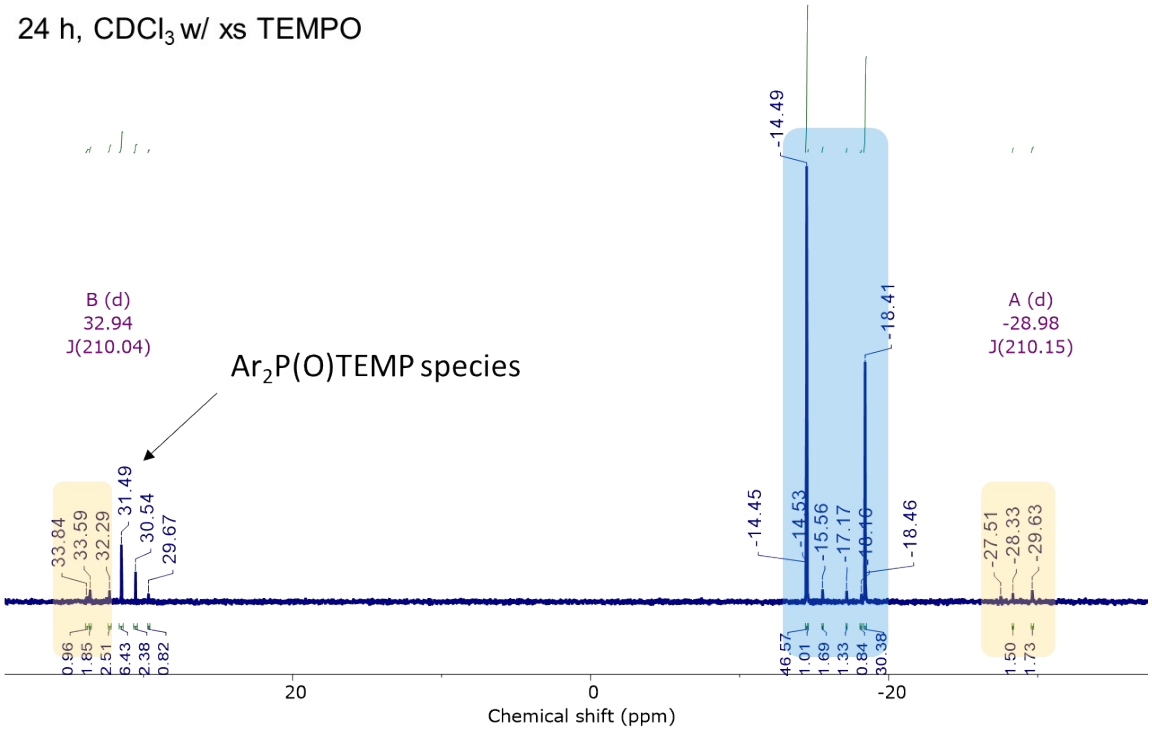
In sonication experiments a modified procedure was employed:

To an oven-dried Schlenk tube equipped with a magnetic stirrer, $\mathbf{A_2}$ (93 mg, 0.25 mmol) and $\mathbf{E_2}$ (107 mg , 0.25 mmol) were added under an Ar atmosphere. The Schlenk tube was removed from the glovebox and cycled onto a Schlenk line under an N_2 atmosphere. To the Schlenk, 5 ml of solvent (CH_2Cl_2, $CHCl_3$, THF or PhMe) was added and the diphosphanes were stirred until dissolution. Immediately thereafter the reaction mixture was syringed into a custom-built Suslick vessel (previously cycled onto the Schlenk line) whilst under a positive pressure of N_2. The Suslick vessel was then sealed and sonicated under pulse sonication mode (1 s on, 1 s off) at 20 kHz at 0 °C for 9 h. 0.5 ml aliquots of the reaction mixture were then removed from the reaction mixture at regular intervals into oven-dried tubes for $^{31}P\{^{1}H\}$ NMR examination.

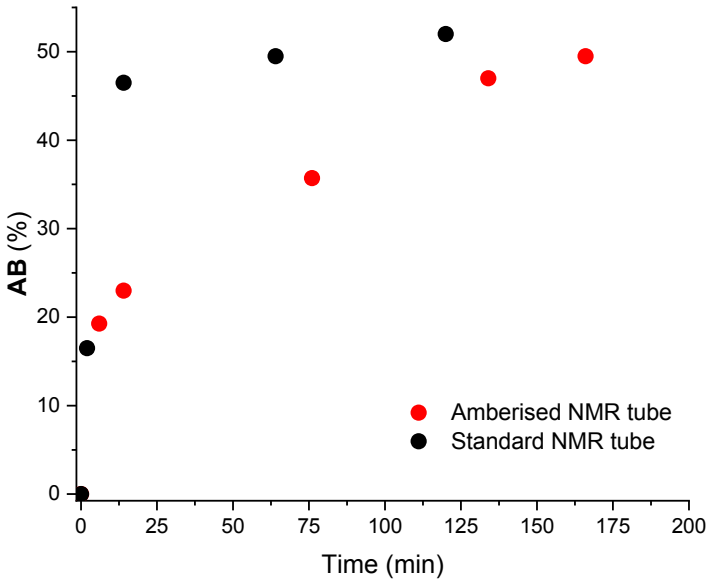
4.1 – Metathesis reactions not involving E_2



ESI 4.1.1. The metathesis reaction of tetraphenyldiphosphane (**A_2**) and tetra(p-anisyl)diphosphane (**C_2**) at -20 °C, with and without 5 equivalents of TEMPO (percentages determined by $^{31}P\{^1H\}$ NMR integration). After 1 h (the 3rd data point) the temperature was allowed to warm to ambient.

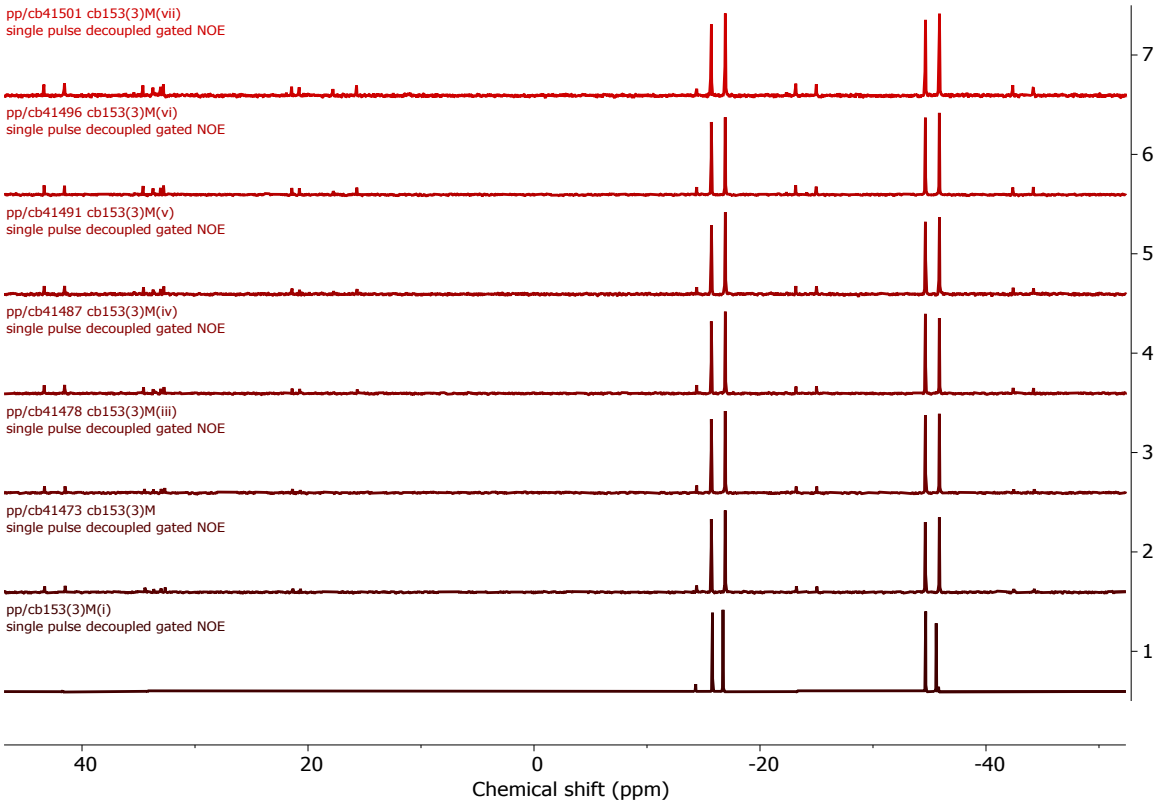


ESI 4.1.2. TEMPO inhibition of the **A_2/C_2** metathesis. Diphosphanes are highlighted in blue and oxides in yellow. The resonances at +30.54 and +31.49 are attributed to diphenylphosphino-TEMPO and di(*p*-anisyl)phosphino-TEMPO adducts respectively.

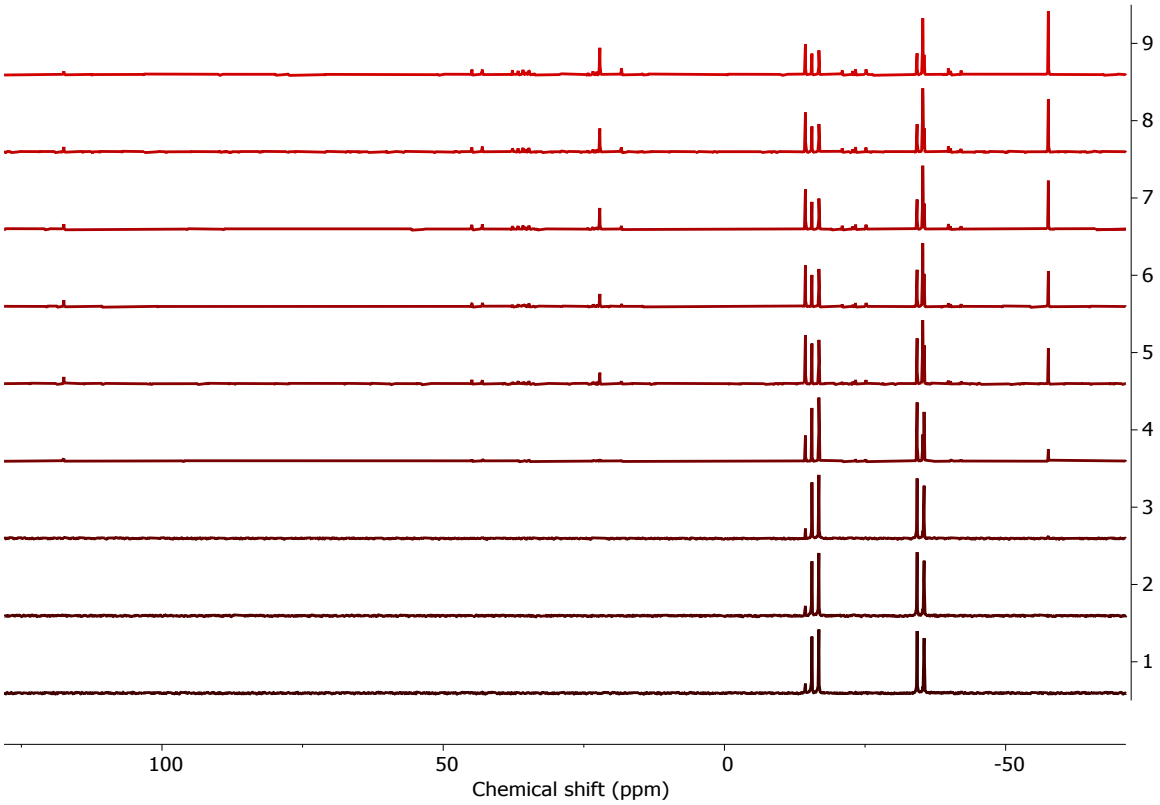


ESI 4.1.3. Amberised NMR-tube inhibition of $\mathbf{A_2/B_2}$ metathesis.

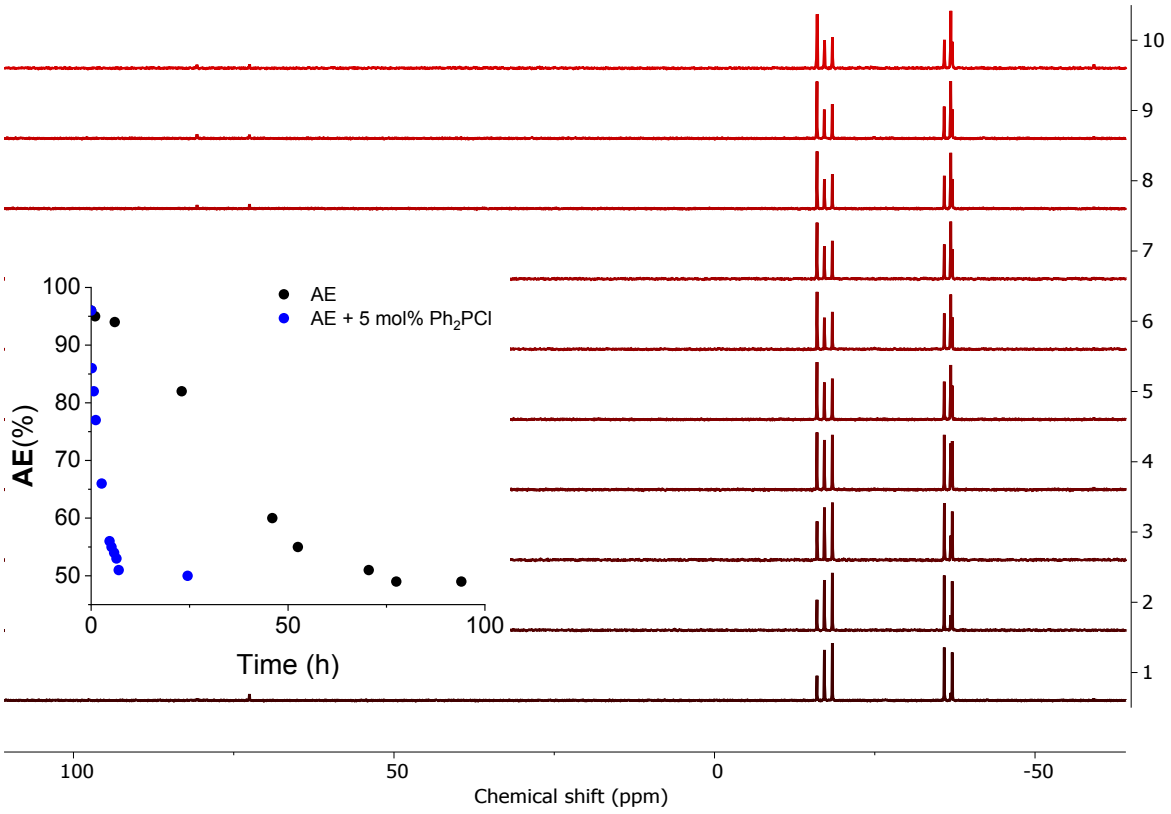
4.2 – Metathesis reactions involving AE or E_2



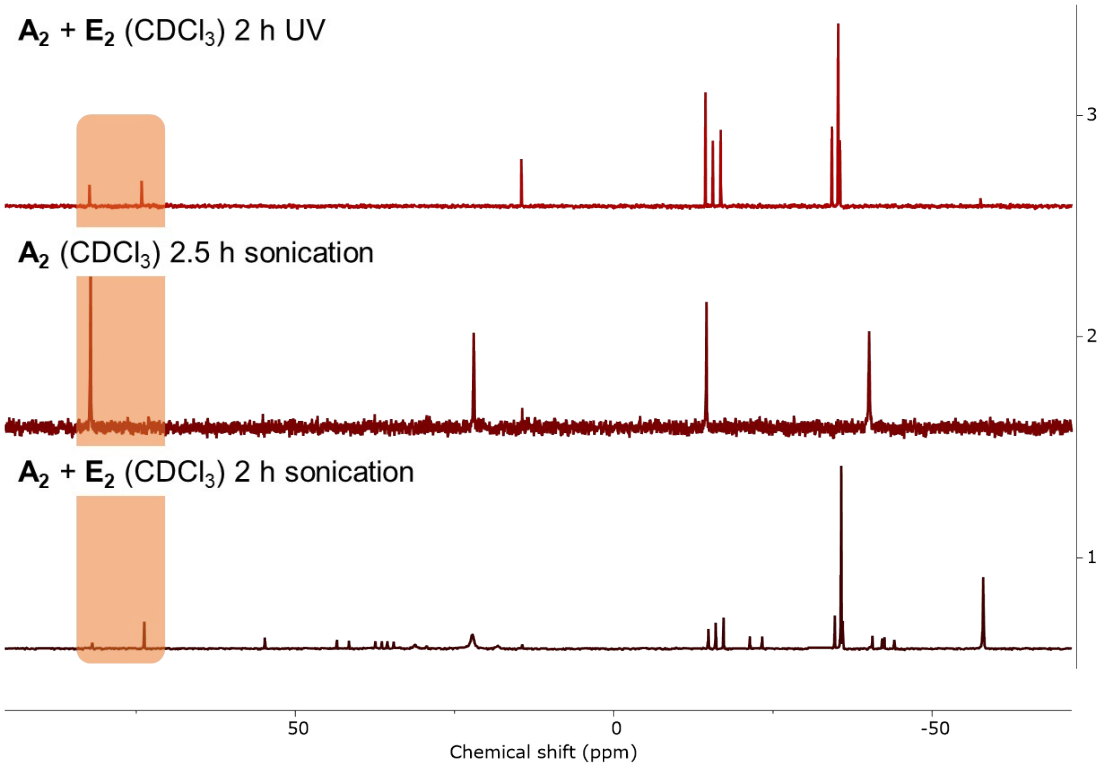
ESI 4.2.1. Pure diphosphane **AE** in benzene-d6. 1 – 1.5 h, 2 – 18.5 h, 3 – 24.5 h, 4 – 42.5 h, 5 – 49.5 h, 6 – 66 h, 7 – 71.5 h. The small doublet resonances correspond to $R_2P(O)PR'_2$ species.



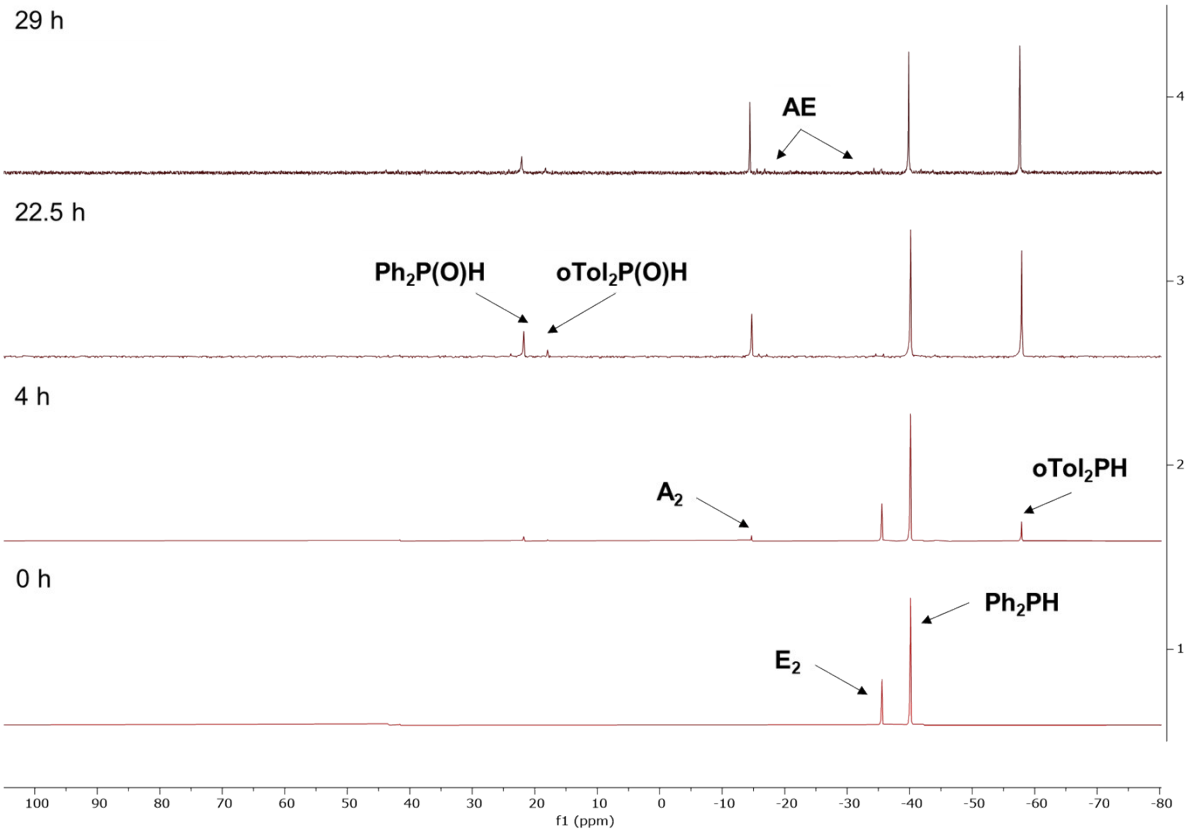
ESI 4.2.2. Reverse metathesis of AE (10 mg) in $CDCl_3$ (0.5 ml). The resonance at ca. -15 ppm corresponds to $\mathbf{A_2}$ and the resonance at ca. -35 ppm corresponds to $\mathbf{E_2}$. Formation of $oTol_2PH$ is observable at ca. -60 ppm. 1 – 0 h, 2 – 1 h, 3 – 6 h, 4 – 23 h, 5 – 46 h, 6 – 52.5 h, 7 – 70.5 h, 8 – 77.5 h, 9 – 94 h.



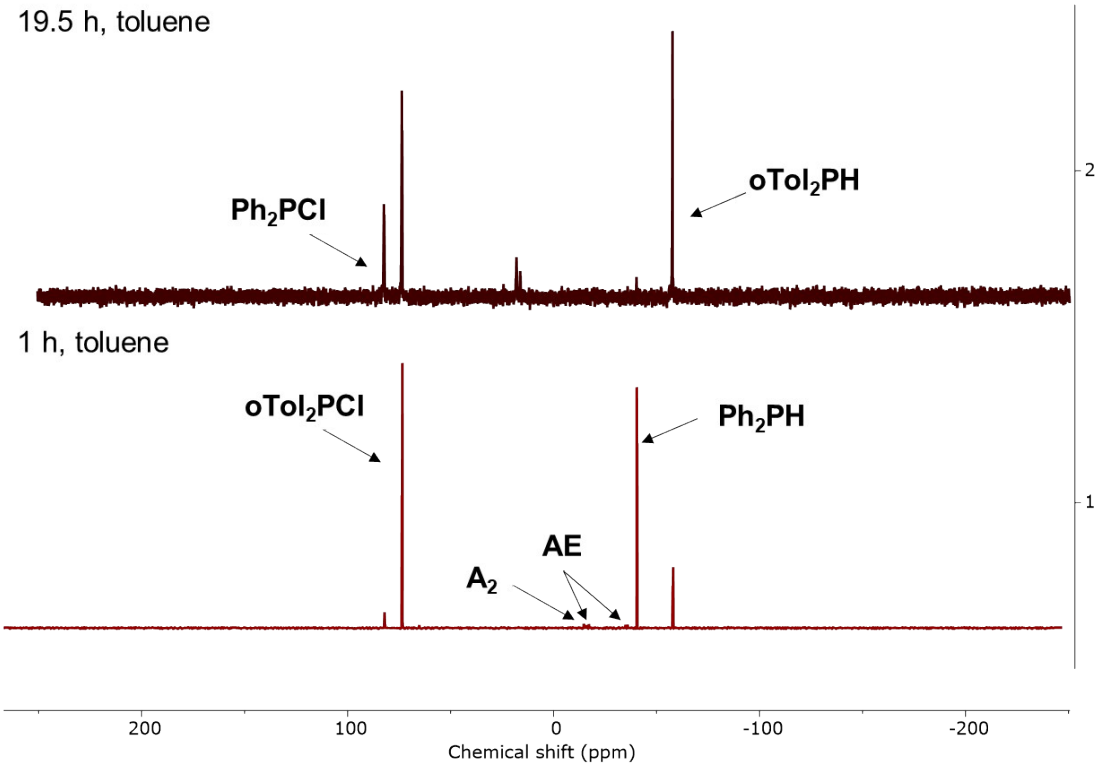
ESI 4.2.3. Reverse metathesis of AE (10 mg) in $CDCl_3$ (0.5 ml) catalysed with 5 mol% of Ph_2PCl. 1 – 10 min, 2 – 40 min, 3 – 70 min, 4 – 160 min, 5 – 280 min, 6 – 310 min, 7 – 350 min, 8 – 385 min, 9 – 420 min, 10 – 1470 min.



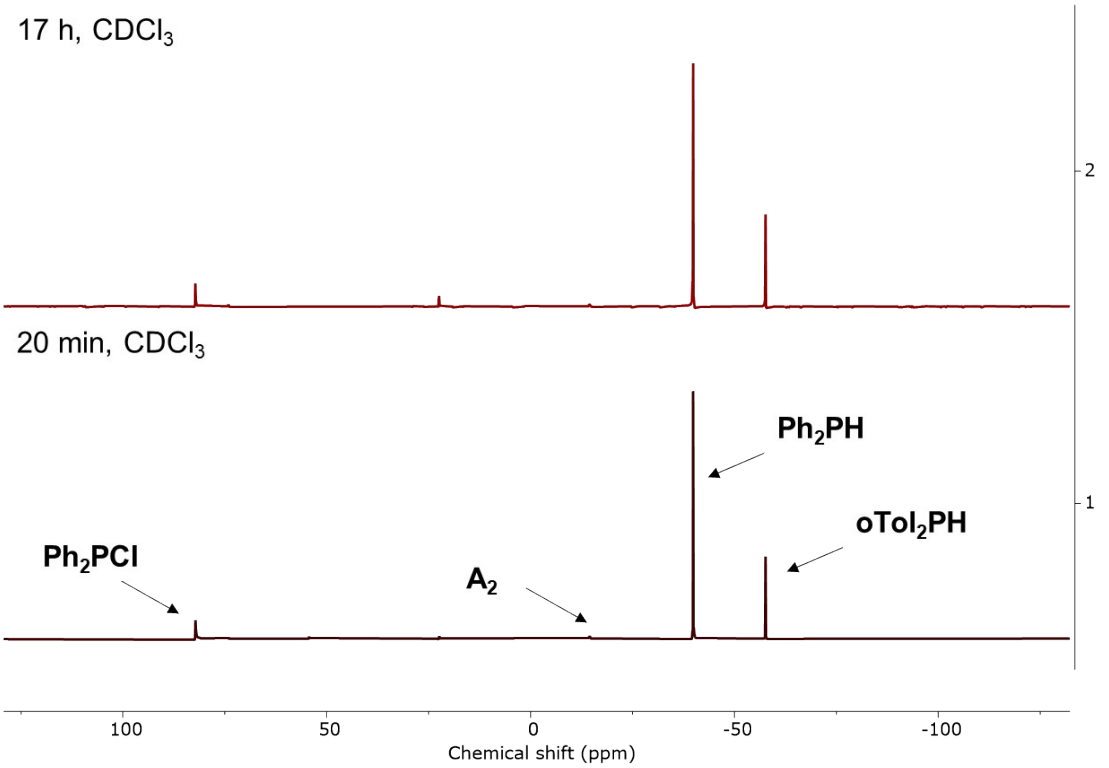
ESI 4.2.4. 1 – **AE** metathesis in $CDCl_3$, 2 – $\mathbf{A_2}$ sonolysis in CDCl3, and 3 – UV photolysis during **AE** metathesis. Chlorophosphine resonances are highlighted in orange.



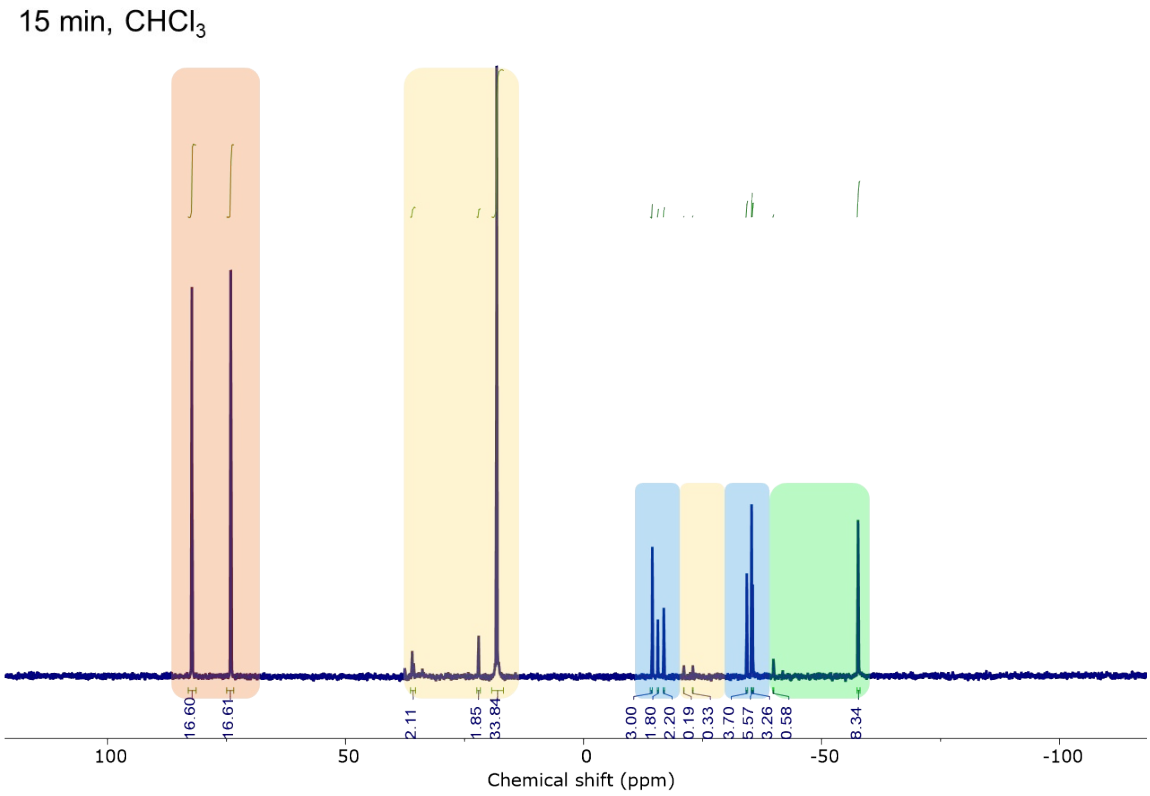
ESI 4.2.5. The reaction between $\mathbf{E_2}$ and Ph_2PH in $CDCl_3$.



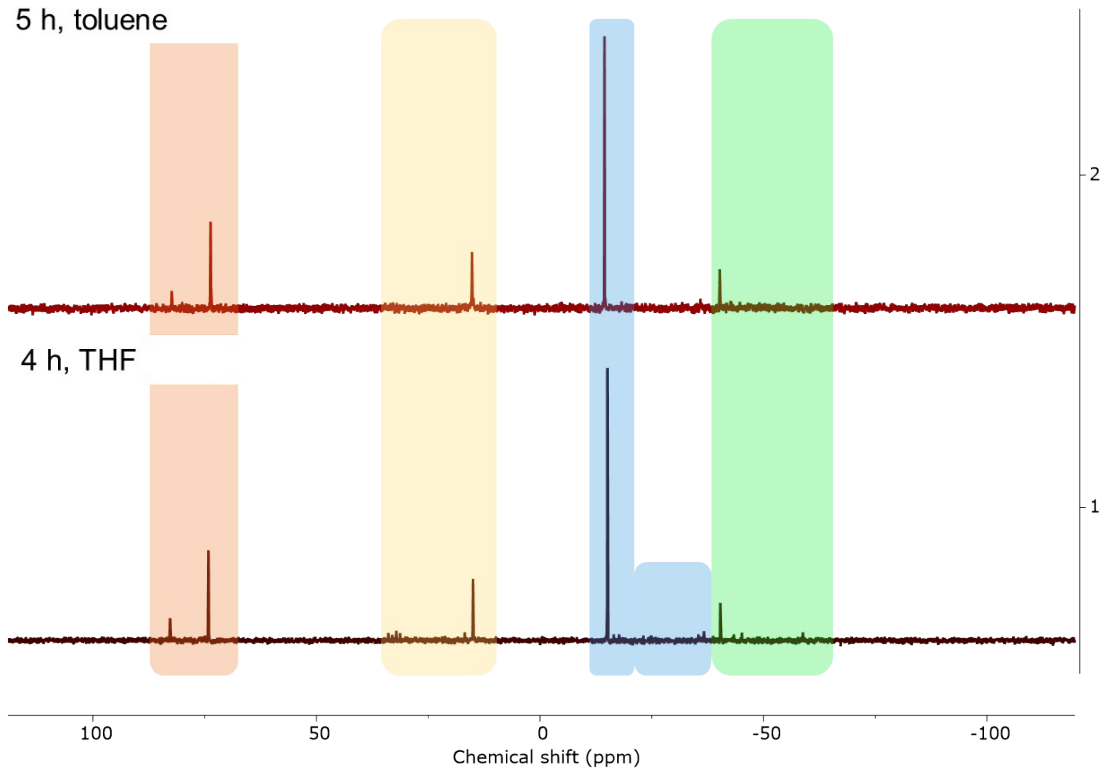
ESI 4.2.6. The reaction between *o*Tol_2PCl and Ph_2PH in toluene.



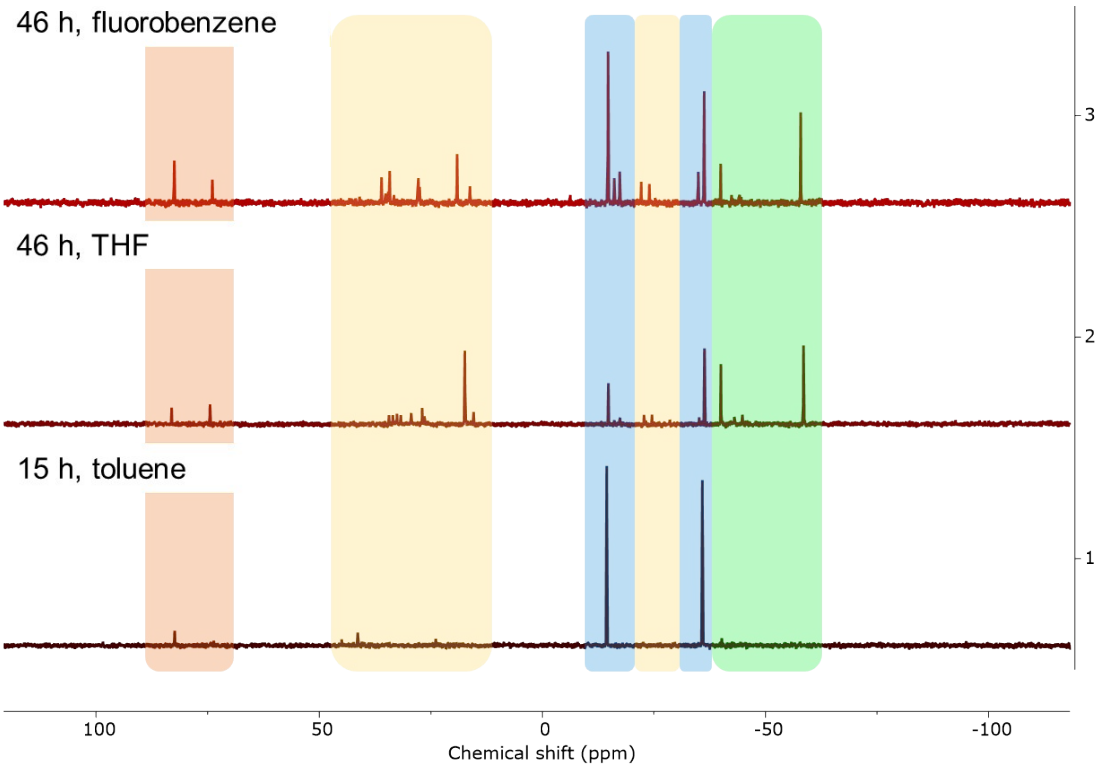
ESI 4.2.7. The reaction between $oTol_2PCl$ and Ph_2PH (ca. 3-fold excess) in $CDCl_3$. Note the immediate consumption of the starting chlorophosphine via H/Cl exchange. A trace resonance of A_2 is observed here as it is in toluene.



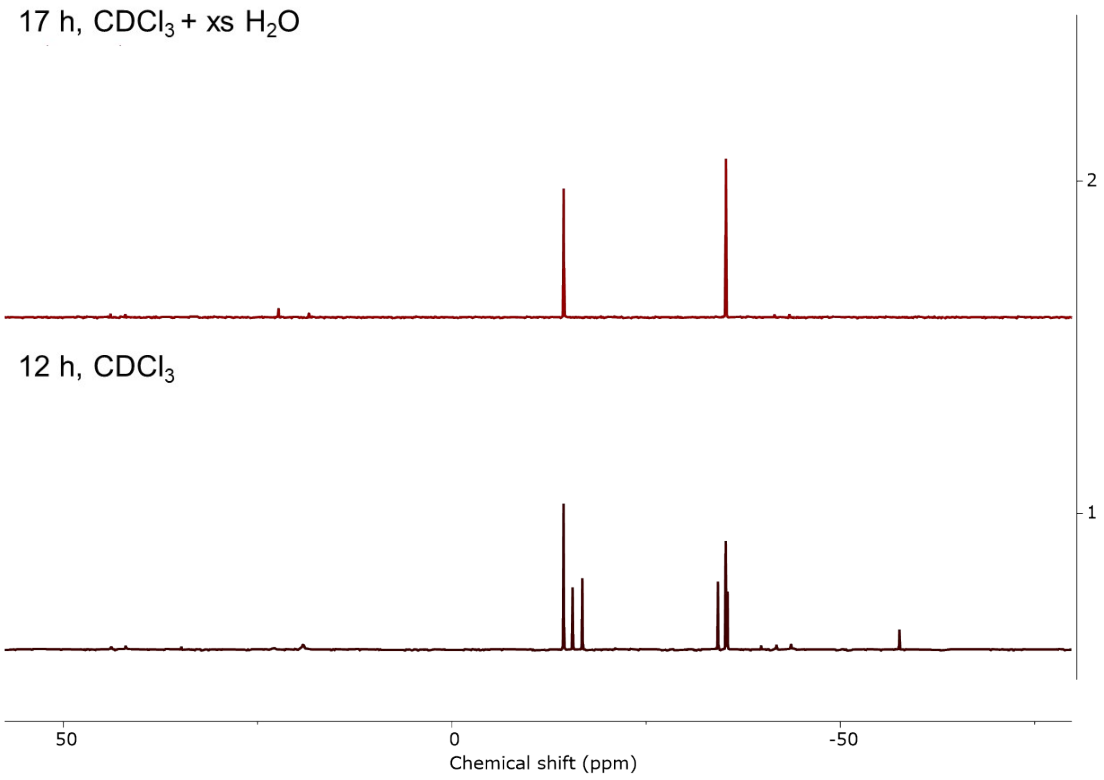
ESI 4.2.8. The reaction between **A_2** and $oTol_2PCl$ in chloroform. Chlorophosphines are highlighted in orange, oxides in yellow, diphosphanes in blue and secondary phosphines in green.



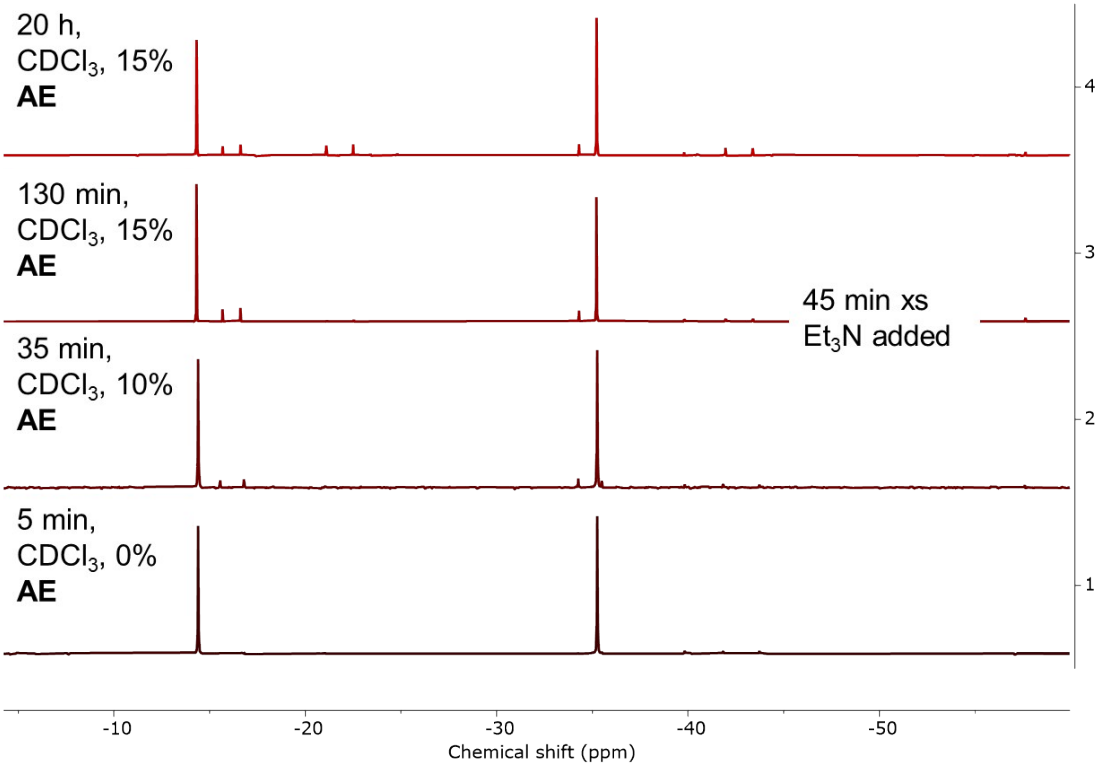
ESI 4.2.9. The reaction between **A_2** and $oTol_2PCl$ in THF. Chlorophosphines are highlighted in orange, oxides in yellow, diphosphanes in blue and secondary phosphines in green.



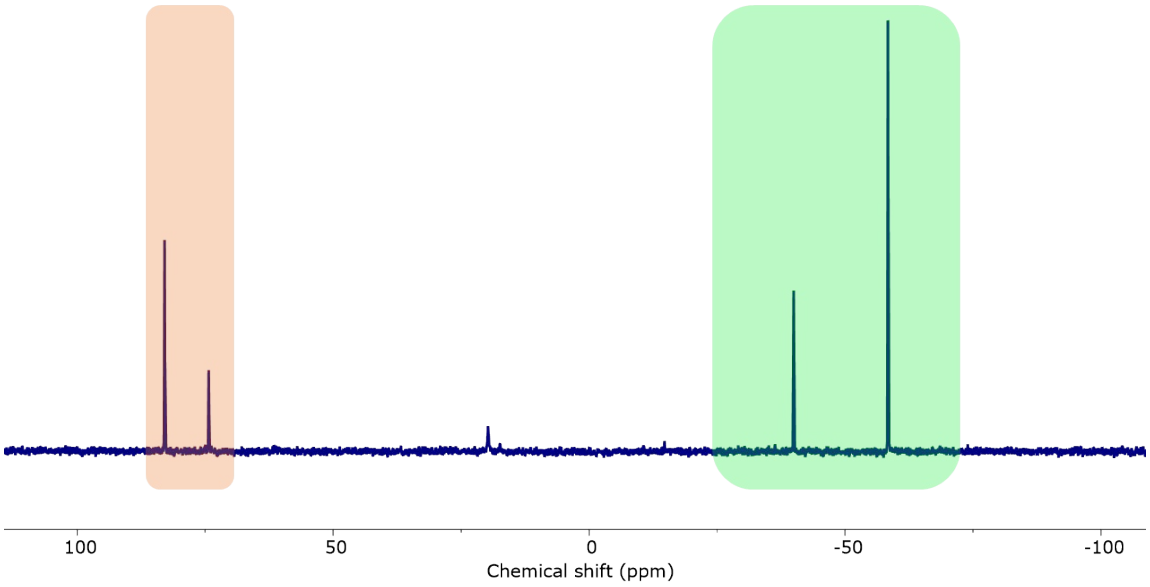
ESI 4.2.10. The reactions between $\mathbf{A_2}$ and $\mathbf{E_2}$ in the presence of N-chlorosuccinimide (NCS). NCS reacts with diphosphanes to produce chlorophosphines. Chlorophosphines are highlighted in orange, oxides in yellow, diphosphanes in blue and secondary phosphines in green. As with the direct reaction between $\mathbf{A_2}$ and $oTol_2PCl$, the reaction is very slow in THF/PhF and does not proceed at all in toluene.



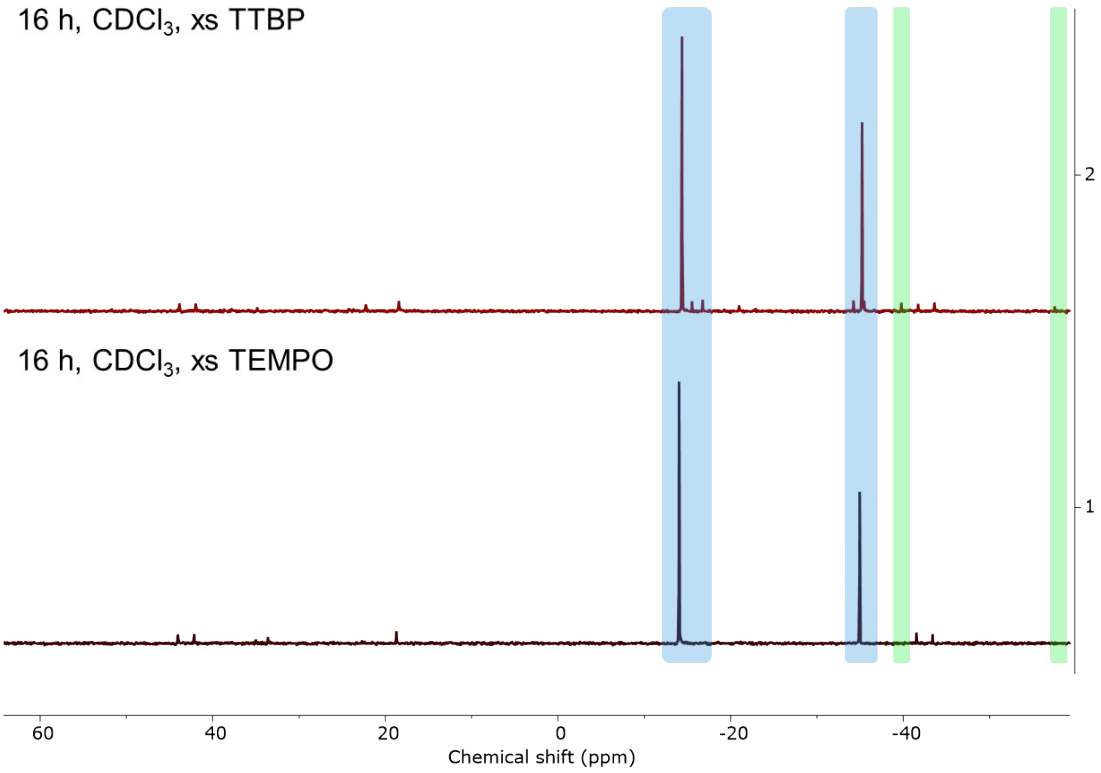
ESI 4.2.11. The water inhibited (top) reaction between $\mathbf{A_2}$ and $\mathbf{E_2}$ in $CDCl_3$. After ~40 h, approximately 2% of the diphosphanes had reacted to form **AE** in the water inhibited reaction (not shown).



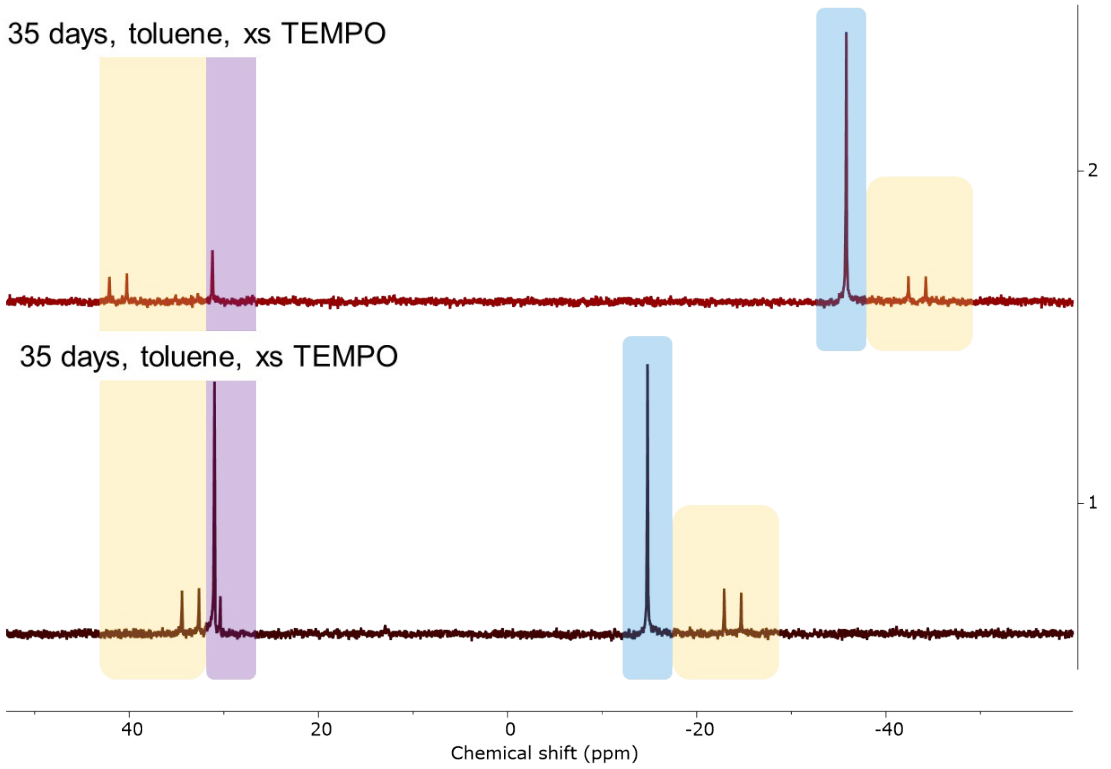
ESI 4.2.12. Amine (Et_3N, ~3-fold excess) inhibition in the $\mathbf{A_2}/\mathbf{E_2}$ metathesis reaction. No change in the proportion of $\mathbf{A_2}/\mathbf{E_2}/\mathbf{AE}$ within 20 h of amine addition, though minor oxidation is observed.



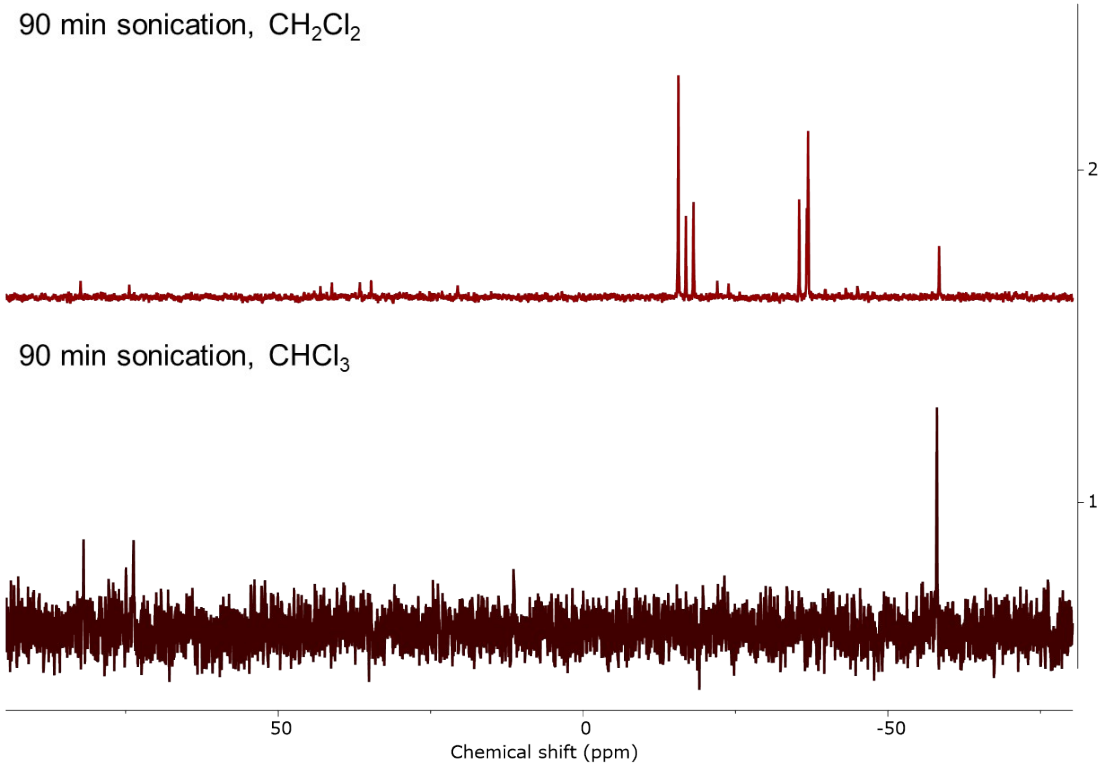
ESI 4.2.13. HCl (~5-fold excess) cleavage of $\mathbf{A_2/E_2}$ in THF. Chlorophosphines are highlighted in orange and secondary phosphines in green. The addition of sub-stoichiometric quantities of HCl resulted in proportionate cleavage of the PP bond.



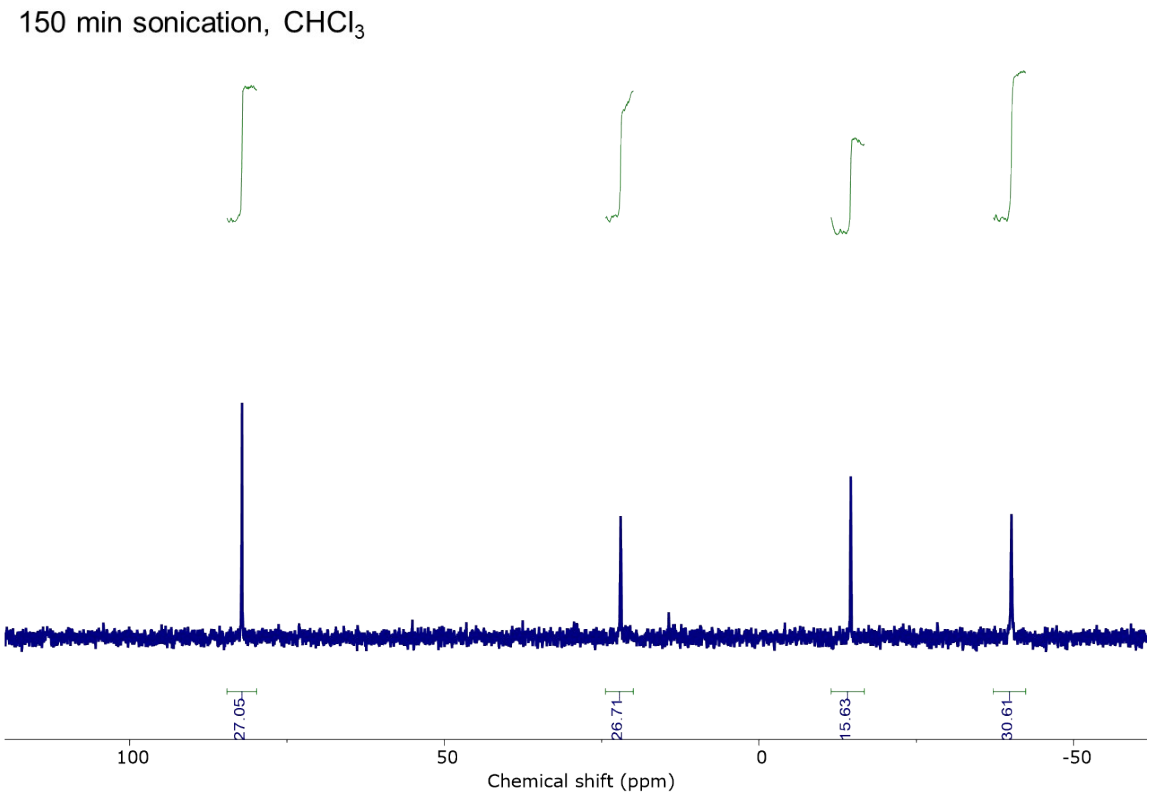
ESI 4.2.14. TTBP/TEMPO (4-fold excesses) radical inhibition of $\mathbf{A_2/E_2}$ metathesis in chloroform. Diphosphanes are highlighted in blue and secondary phosphines in green. Other, non-highlighted, resonances correspond to oxides. Note equilibrium is normally fully established (with 50% **AE**) within 12 h.



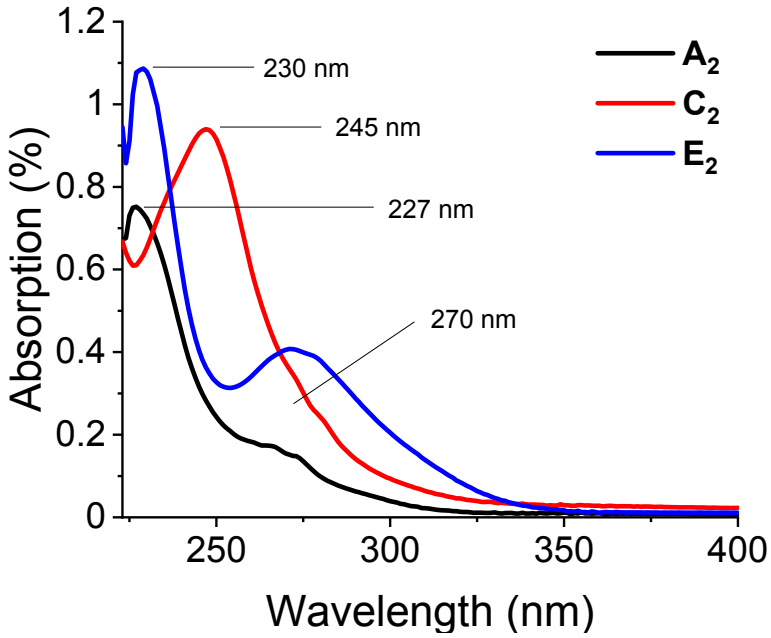
ESI 4.2.15. The reaction of $\mathbf{A_2}$ (bottom) and $\mathbf{E_2}$ (top) with TEMPO (~4-fold excess).



ESI 4.2.16. Pulse-sonicated $\mathbf{A_2}$/$\mathbf{E_2}$ metathesis in chloroform (bottom) and DCM (top). Note, after 90 mins no diphosphanes remain in the chloroform sample, all that is visible are the two chlorophosphines and oTolyl$_2$PH (-58 ppm).



ESI 4.2.17. Ultrasonication of pure A_2 in chloroform for 2.5 h. Left to right: Ph_2PCl, $Ph_2P(O)H$, A_2 and Ph_2PH.



ESI 4.3. UV-vis spectra of **A_2**, **C_2** and **E_2**.

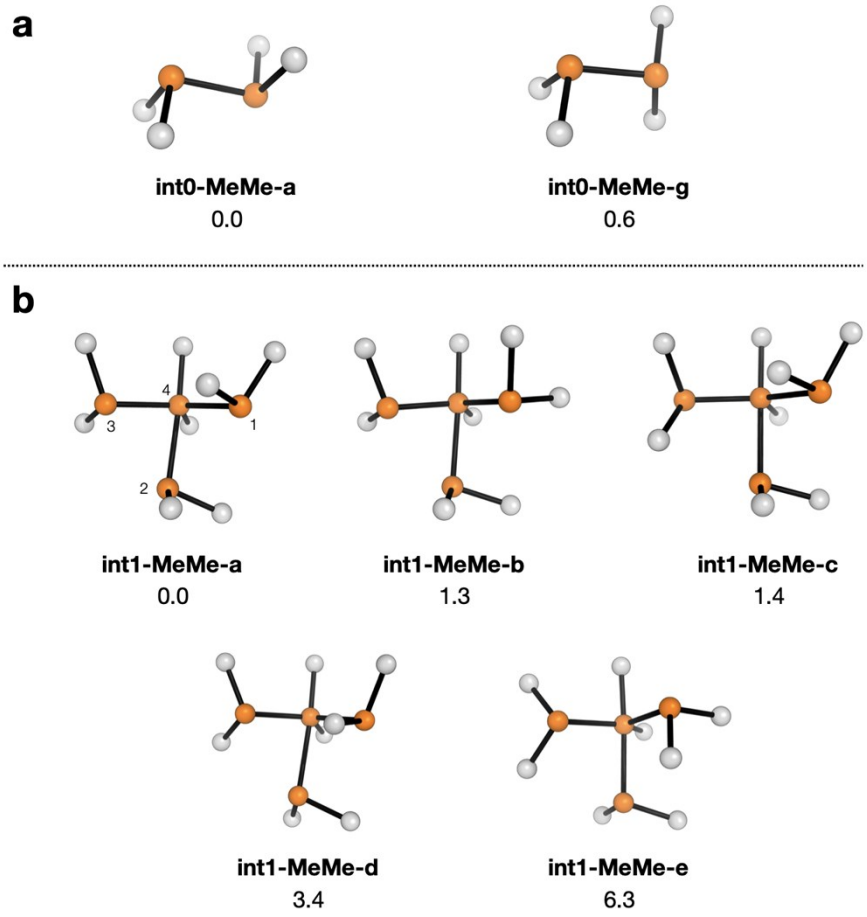
5 – Computational details

5.1 – Computational methods

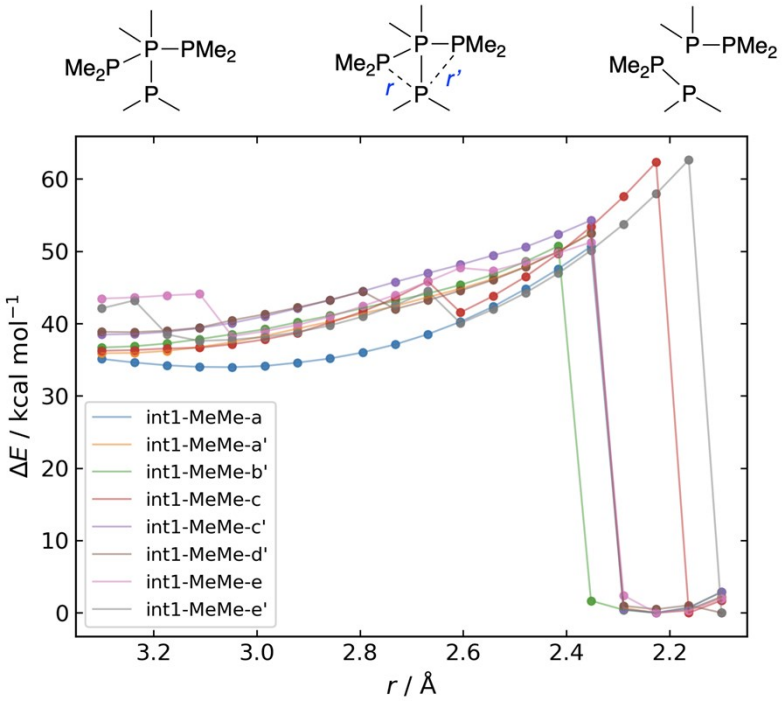
All calculations were performed in ORCA v. 4.1.1.[1] Unless otherwise specified calculations utilised the resolution of identity with the chain of spheres approximation for the exchange integrals (RIJCOSX) with the default auxiliary basis sets (*AutoAux* keyword).[2] Geometry optimisations were performed with the hybrid PBE0 functional,[3] D3BJ dispersion correction,[4,5] and the def2-SVP basis set.[6] Vibrational frequencies were calculated at the same level of theory to assign stationary points as either minima or transition structures, as characterised by the presence of none or a single imaginary frequency respectively. Thermodynamic corrections were calculated at 298.15 K in a 1 M standard state using the quasi-rigid rotor harmonic oscillator (q-RRHO) approximation.[7] Where applicable solvent effects were accounted for with the SMD implicit solvent model[8] using parameters appropriate for tetrahydrofuran (THF) or chloroform at the single point level of theory. Single point energies were calculated using the same dispersion corrected functional (PBE0-D3BJ) in conjunction with the larger def2-TZVPP basis set on all atoms.[6] Transition state searches and combinatorial reaction energy calculations were performed with autodE.[9] TD-DFT calculations additionally employed CAM-B3LYP[10] and M06-2X[11] functionals.

5.2 – Closed shell mechanistic possibilities

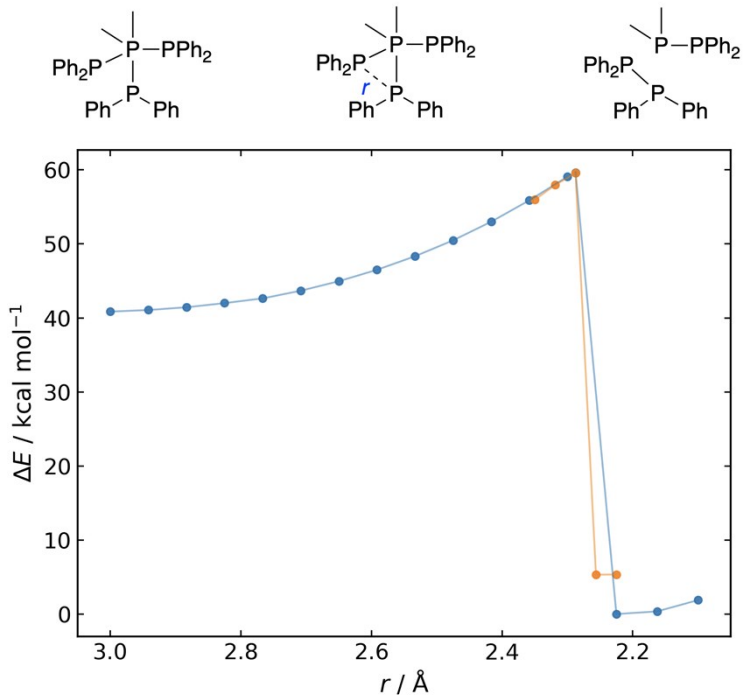
To limit the conformational flexibility and thus the conformational noise in the calculations we first explored the mechanism of PP metathesis in Me_2PPMe_2. Then, having established the lowest energy conformation of the intermediates and transitions state(s) (shown in Figure 6.2.1, 6.2.2), obtained the mechanism for the analogous aryl systems assuming the same P–P dihedrals (Figure 6.2.3, 6.2.4). The high energy P(V) intermediate **int1-MeMe** can be viewed in two resonance forms: either a covalent or ionic form (Figure 6.2.5). A selection of 'wavefunction' (Kohn–Sham orbital and density) analysis tools suggest a reasonably consistent picture that the covalent form is the more accurate representation (Figure 6.2.3, Table 6.2.1). The Laplacian of the electron density is negative at the bond critical point between the central phosphorus (P_4) and the 'bonded' PMe_2 moiety (P_2), indicating a local concentration of electron density and is generally considered to indicate a covalent bond.[12]



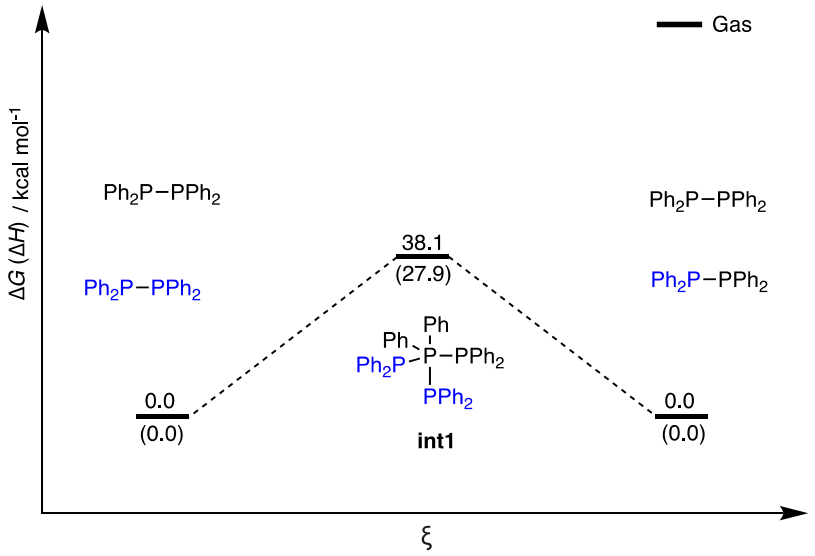
ESI 6.2.1. Conformations and relative free energies (ΔG) in kcal mol^{-1} of (a) Me_2PPMe_2 (**int0-MeMe**) and (b) **int1-MeMe**. Calculations performed at the PBE0-D3BJ/def2-TZVPP//PBE0-D3BJ/def2-SVP level of theory. Hydrogens are omitted for clarity.



ESI 6.2.2. Relaxed potential energy surface scans from **int1-MeMe** to **int0-MeMe** over **ts1-MeMe**. Scans performed from left(*r*) and right(*r'*) migration of PMe_2 from **int1-MeMe** conformers shown in **Figure 6.2.1**. **int1-MeMe-b** and **int1-MeMe-d** did not converge after 250 geometry optimisation cycles.

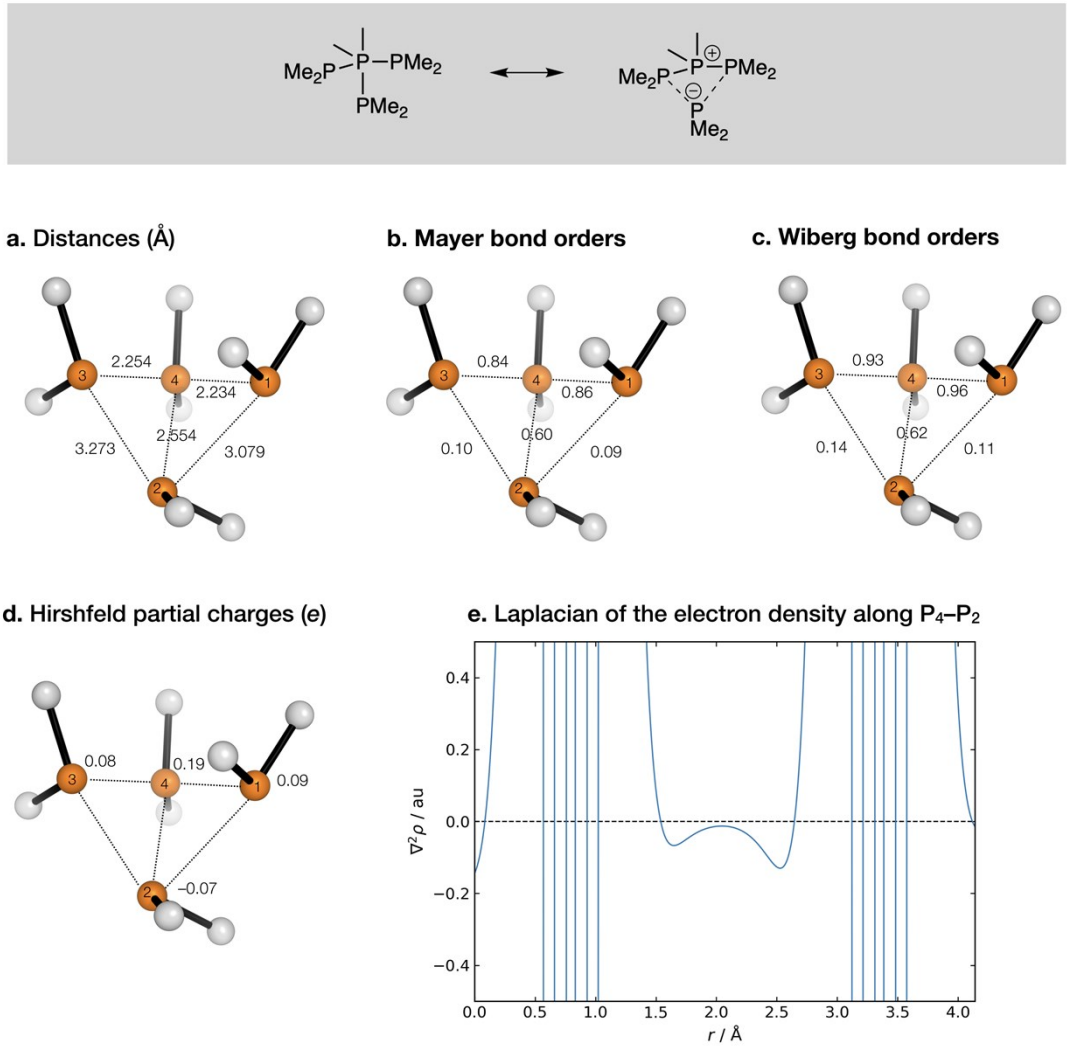


ESI 6.2.3. **int1-PhPh** equivalent of Figure 6.2.2 for the lowest energy **int1** conformer. Colours correspond to differing spacings between points in the PES scan.



Solvent	ΔG
CPCM(DCM)	44.1
CPCM(THF)	41.9
SMD(DCM)	45.9
SMD(THF)	42.1

ESI 6.2.4. Partial reaction profile excluding transition states for the homo-metathesis of Ph_2PPPh_2 via **int1-PhPh**. Free energies quoted at the PBE0-D3BJ/def2-TZVPP//PBE0-D3BJ/def2-SVP. Transition state could not be located due to the extremely flat imaginary mode, but must be above **int1-PhPh** in energy.



ESI 6.2.5. Distance and population/density analysis on **int1-MeMe** performed using MultiWfn v. 3.6.[13] P_2–P_8 line contains a bond critical point (BCP).

Table 6.2.1. Partial atomic charges (*e*) of phosphorus atoms in **int1-MeMe-a** calculated at PBE0-D3BJ/def2-SVP using different schemes. Numbering as **Figure CX12**.

Scheme	P_1	P_2	P_3	P_4
Mulliken	0.07	-0.14	0.05	0.00
Löwdin	0.32	0.12	0.30	0.49
Hirshfeld	0.09	-0.07	0.08	0.19

5.3 – Radical mechanistic possibilities

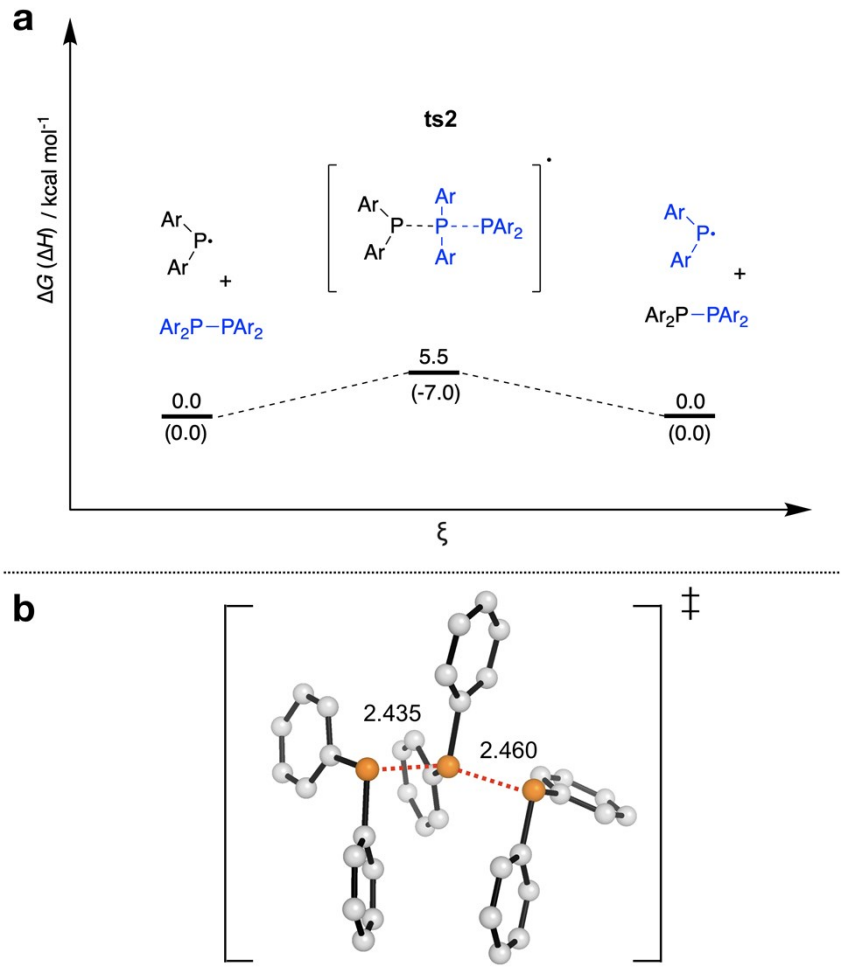
To probe the possibility of thermally generated P-based radicals from aryl diphosphanes the relative stability of the corresponding $Ar_2P•$ radicals are computed in the gas phase (**Table 6.3.1**). Identical aryl conformations are utilised as to remove the conformational noise associated with the multiple CCPC dihedral angles possible. Even with the entropic favourability associated with the 1→2 molecularity change, homolytic cleavage of the PP bond is endergonic by some 35 kcal mol^{-1} and not thermally feasible under the reaction conditions.

Table CX1. Reaction energetics for $R_2PPR_2 \rightarrow R_2P•$. *a*. Diphosphane contained 1 or 2 imaginary modes associated with aryl rotation (<20*i* cm^{-1}). *b*. Convergence to RMSD(gradient) < 0.005 au (*Loose* threshold in ORCA) could not be achieved but the computed frequencies were all real.

	kcal mol^{-1}		
R	**Δ*E***	**Δ*H***	**Δ*G***
3,5-diCF_3Ph[b]	55.8	53.2	39.2
o-tolyl	54.7	52.3	36.1
p-tolyl[a]	52.3	48.6	38.9
p-OMePh[a]	51.4	50.2	35.9
Ph[a]	52.2	51.4	36.0

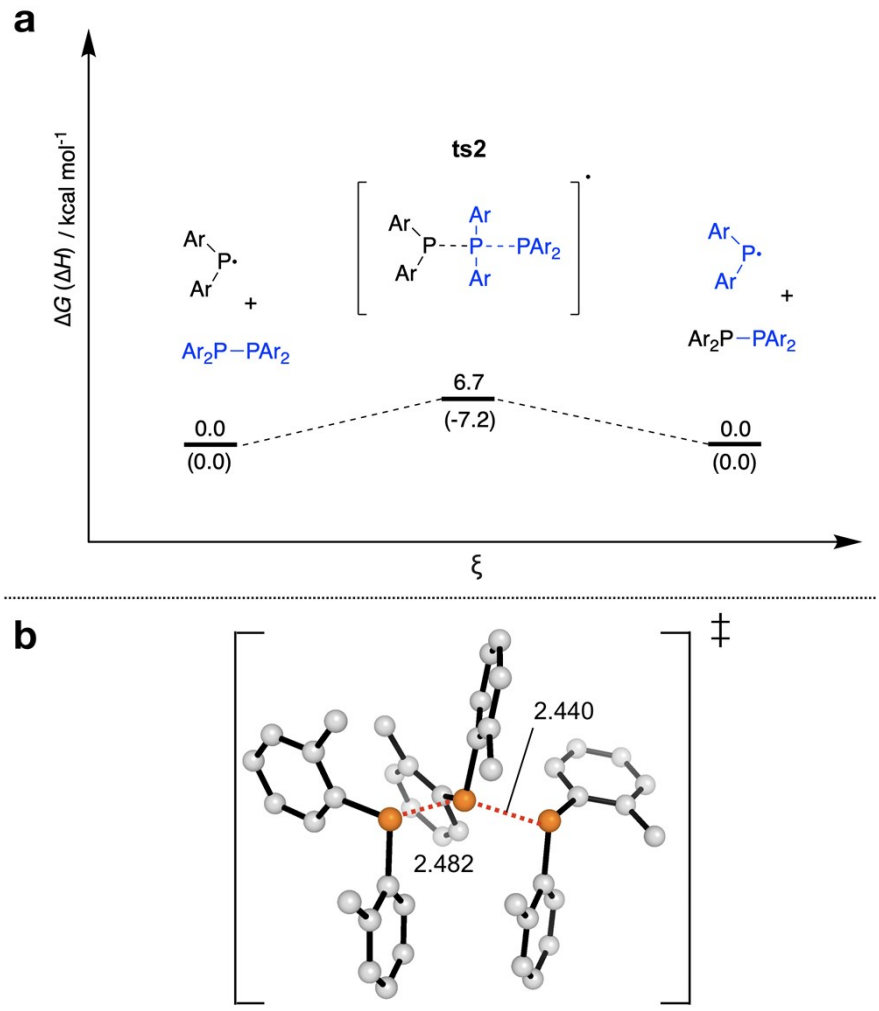
Given the possibility of photochemical PP homolysis to deliver phosphinyl radicals ($Ar_2P•$) the metathesis reaction $Ar_2P• + Ar'_2PPAr'_2 \rightarrow Ar_2PPAr'_2 + Ar'_2P•$ was investigated following the model methyl-substituted system. The reaction is found to be energetically viable at room temperature given some initial non-zero concentration of radical, for both Ar = Ph (Figure 6.3.1) and Ar = *o*-tolyl (Figure 6.3.2). Note that the TS barrier for the *o*-tolyl variant has not been extensively conformationally sampled due more than (2 Ar rotations)^6 × (2 methyl positions)^6 = 4,096 possibilities for the six equivalent aryls. Nevertheless, the low barrier suggests that any phosphinyl in solution would react quickly with PP species. Interestingly, the model methyl-substituted diphosphane exhibits slightly different reactivity, with the symmetric $[Me_2PP(Me)_2–PMe_2]•$ species now a shallow minima on the potential energy surface rather than a transition state (Figure 6.3.3), but also would proceed rapidly at room temperature given an initial concentration of $Me_2P•$. Steric

bulk at the ortho position of the aryl substituent can increase the barrier significantly (Figure 6.3.4) while the attack of solvent-generated Cl• on Ar_2PPAr_2 is highly exergonic and rapid (Figure 6.3.5). The intramolecular H-transfer to form a benzyl radical from $(o\text{-tol})_2P$• is endergonic with a free barrier of 28.8 kcal mol^{-1} (Figure 6.3.6), which is out of reach for a thermal reaction at room temperature. However, following excitation to S_1, intersystem crossing to T_1 and relaxation to the minimum there is ~33 kcal mol^{-1} of excess energy (Figure 6.3.6) that may facilitate hydrogen abstraction to form a benzylic radical. Coupled with the non-negligible quantum tunnelling in H-transfer reactions accelerating the relative rate this reaction is feasible, which – upon thermalisation with the solvent – would give a reasonably slow backwards reaction to $(o\text{-tol})_2P$•, thus may explain the slow rate with *o*-tolyl substituted aryls.

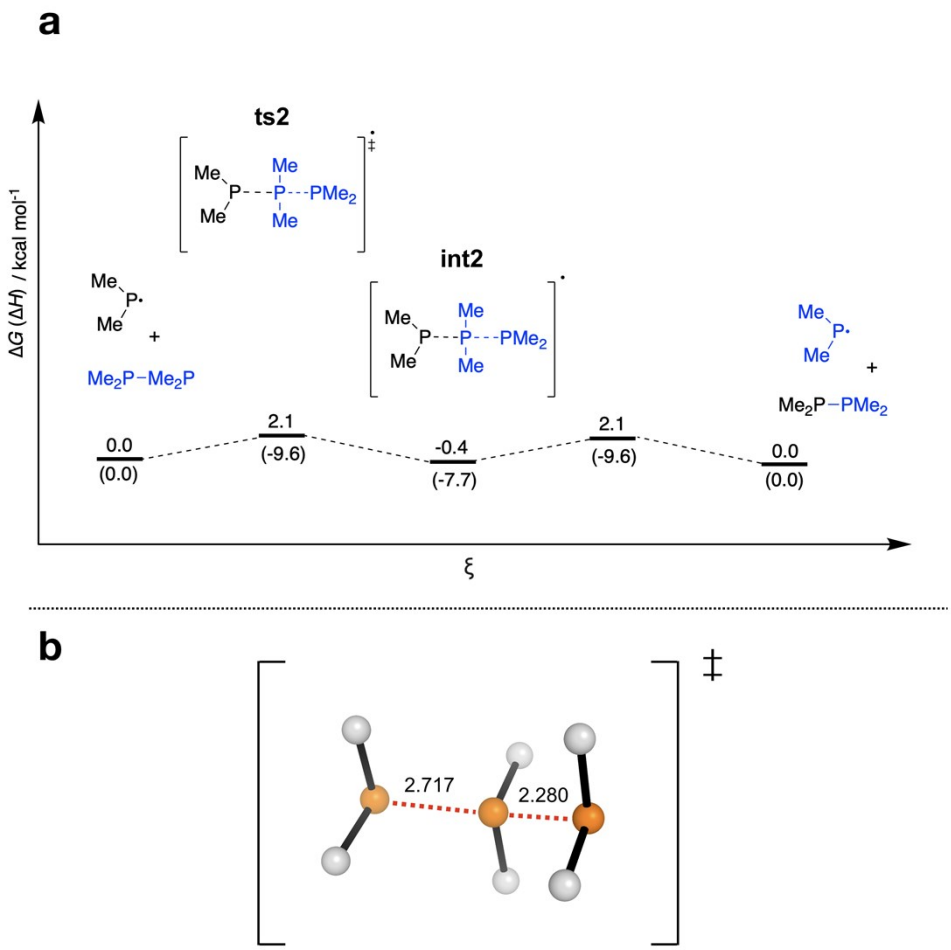


ESI 6.3.1. (a) Reaction free energy profile for the PP homo-metathesis of Ph_2PPPh_2 via Ph_2P•, where Ar = Ph and (b) **ts2-PhPh** geometry. TS contained a second spurious imaginary frequency corresponding to phenyl

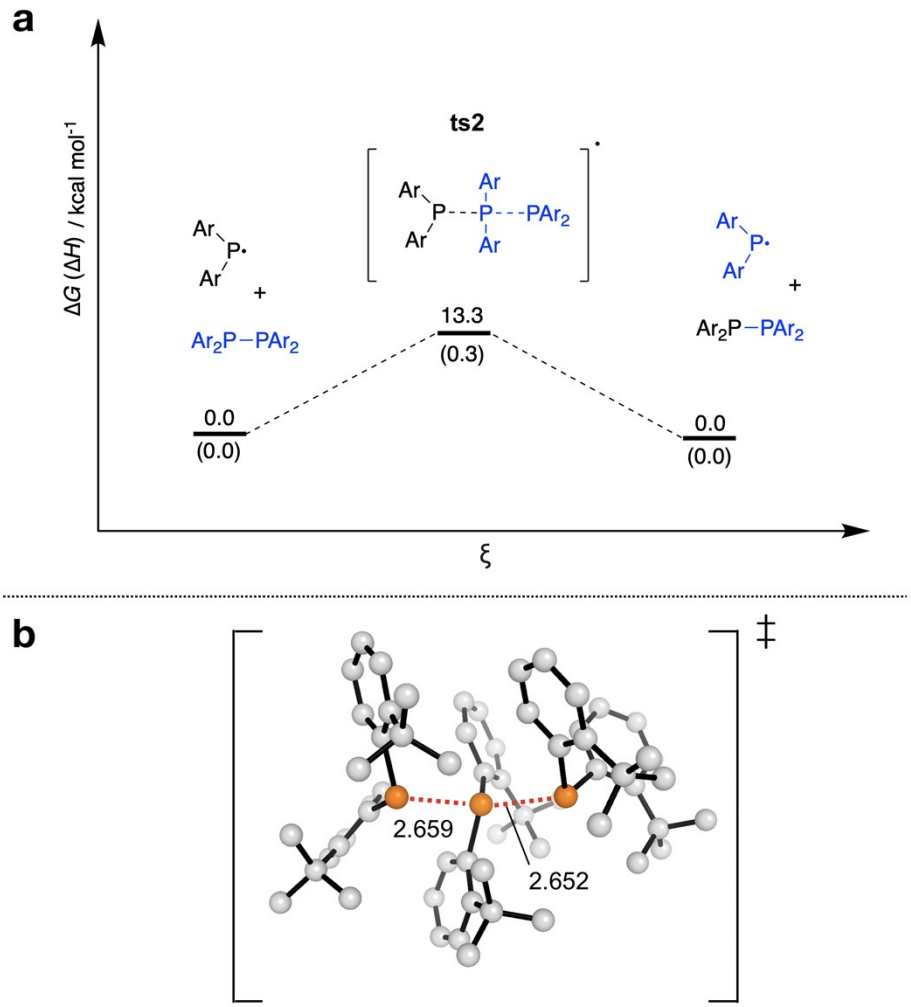
rotation ν = 10.69*i* cm^{-1}. Potential energy barrier from association complex at PBE0-D3BJ/def2-SVP is ~3.0 kcal mol^{-1}. Key distances are shown in Å and hydrogens omitted for clarity.



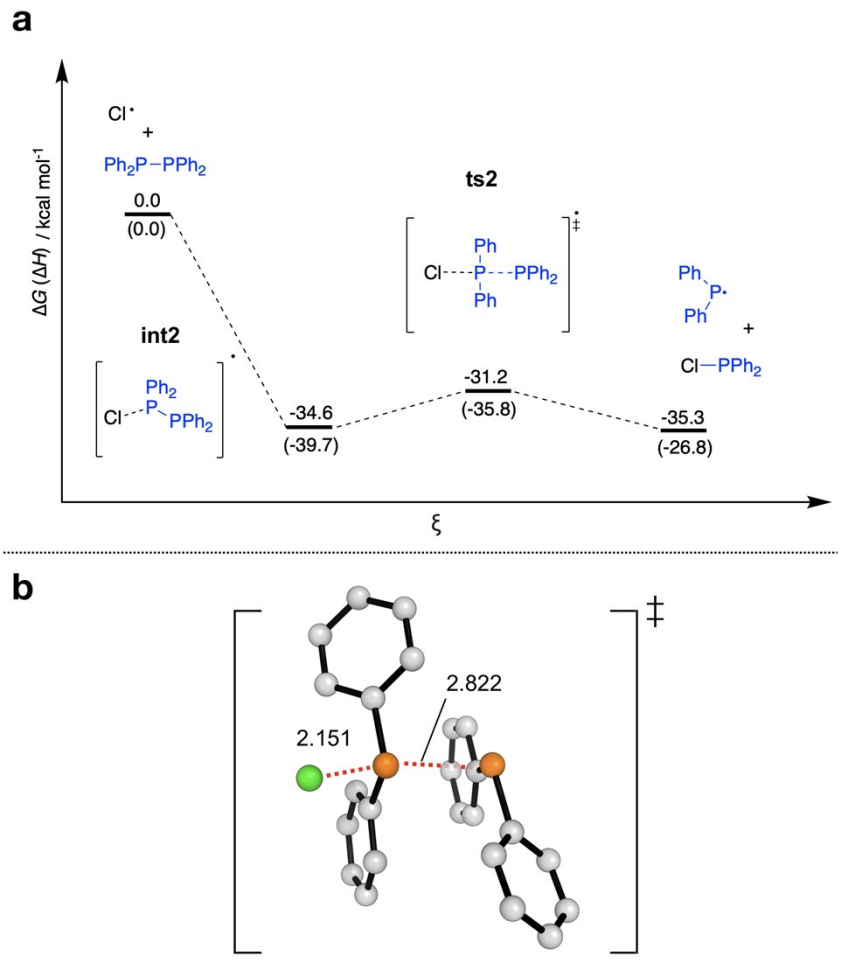
ESI 6.3.2. As Figure 6.3.1 for Ar = *o*-Tol. TS contained a second spurious imaginary frequency ν = 46.53*i* cm^{-1}.



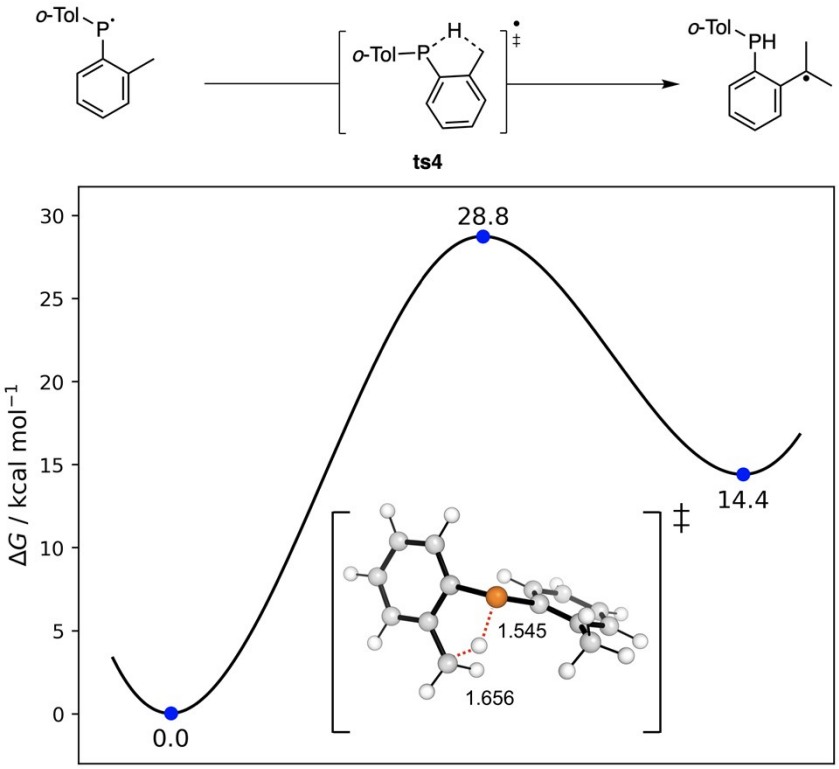
ESI 6.3.3. As Figure 6.3.1 for Me_2PPMe_2 + Me_2P•.



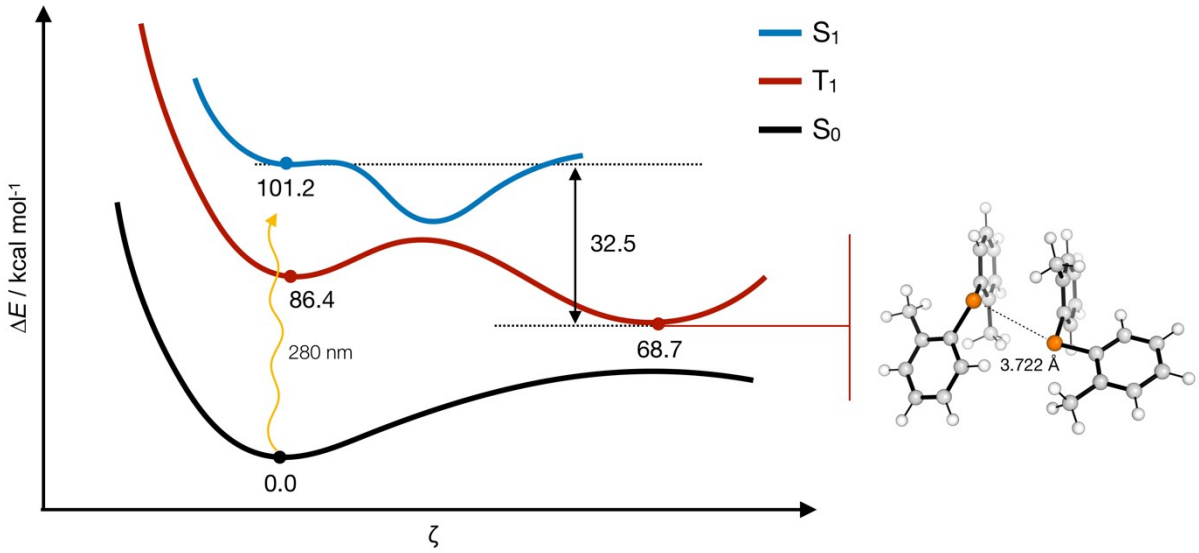
ESI 6.3.4. As Figure 6.3.1 with Ar=*o*-^{t}Bu-C_5H_4.



ESI 6.3.5. As Figure 6.3.1 for for Ph_2PPPh_2 + Cl•.



ESI 6.3.5. Free energy profile for the intramolecular H-transfer from a phosphorus to benzyl radical in (*o*-tol)$_2$P• obtained directly from autodE. Geometry of the optimised TS with key distances in Å overlaid.



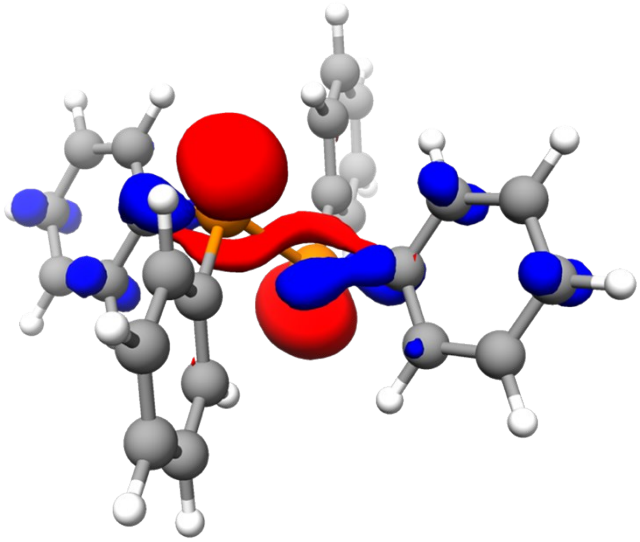
ESI 6.3.6. Schematic excited state energy level diagram of (*o*-tol)$_2$PP(*o*-tol)$_2$ calculated at CAM-B3LYP/def2-TZVP//PBE0-D3BJ/def2-SVP. Functional chosen based on the data in Table 6.4.1 to match the experimental UV-vis spectrum of Ph_2PPh_2.

5.4 – UV-Vis interpretation

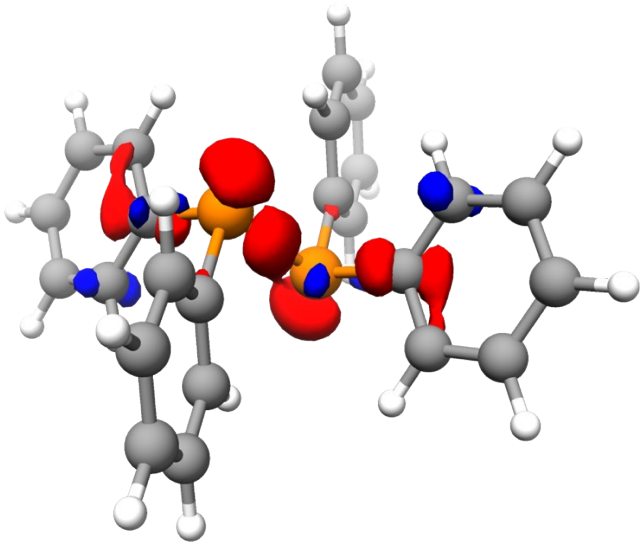
Time-dependent density functional theory (TD-DFT) calculations were performed using a selection of functionals to test the functional dependence of vertical electronic excitation energies on Ph_2PPh_2, which are known to be fairly functional dependent (RMSE ~0.5 eV).[14,15] **Table 6.4.1** outlines the obtained results with three well performing functionals in TD-DFT calculations on organic molecules. The range of excitation predictions is around 0.5 eV with little effect of solvent and the range separated CAM-B3LYP functional comparing favourably to experiment. Transition density difference plots (Figure 6.4.1, 6.4.2) suggest the transitions have dominant $n \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) and $\sigma \rightarrow \sigma^*$ ($S_0 \rightarrow S_2$) character with little qualitative variation between functionals. Optimisation of the triplet state led to fragmentation into two $Ph_2P\bullet$ radicals.

Table 6.4.1. Excitation energies to the first two excited states (S_1, S_2) with significant transition dipole oscillator strengths. All calculations used the def2-TZVPP basis set at PBE0-D3BJ/def2-SVP geometries.

Method	Excitation energy / eV		λ / nm	
	S_1	S_2	S_1	S_2
PBE0	3.946	5.038	314.2	246.1
SMD(DCM)-PBE0	4.011	5.030	309.1	246.5
CAM-B3LYP	4.404	5.575	281.5	222.4
M06-2X	4.242	5.443	292.3	227.8



ESI 6.4.1. Transition electron density difference calculated with orca_plot between the S_0 and S_1 states at the CAM-B3LYP/def2-TZVPP//PBE0-D3BJ/def2-SVP level of theory. Red/blue corresponds to depleted/excess electron density respectively. Isosurface plotted at a contour of 0.003 au.



ESI 6.4.2. As Figure 6.4.1 for the S_0 and S_2 states.

5.5 – Cartesian coordinates

Optimised cartesian coordinates (Å), total potential energies (*E*) and thermal contributions (H_{cont}, G_{cont}) calculated at PBE0-D3BJ/def2-SVP, and single point energies (E_{sp}) at PBE0-D3BJ/def2-TZVPP// PBE0-D3BJ/def2-SVP all in Hartrees. Note the latter do not include the 1 atm → 1 M standard state correction.

int0-MeMe

E: -841.6014756

H_{cont}: 0.16317247

G_{cont}: 0.11725234

E_{sp}: -842.0159307

P	-3.1471	-0.8025	-0.8025
P	-1.0344	-0.2239	-0.2239
C	-3.7368	0.8496	0.8496
C	-3.7553	-0.7178	-0.7178
C	-0.4266	-0.3077	-0.3077
C	-0.4446	-1.8763	-1.8763
H	-3.3298	1.0375	1.0375
H	-3.4404	1.6756	1.6756
H	-4.8344	0.8327	0.8327
H	-3.3082	-1.5350	-1.5350
H	-4.8472	-0.8625	-0.8625
H	-3.5132	0.2408	0.2408
H	-0.8737	0.5098	0.5098
H	-0.6688	-1.2660	-1.2660
H	0.6653	-0.1631	-0.1631
H	-0.8514	-2.0648	-2.0648
H	0.6530	-1.8594	-1.8594
H	-0.7410	-2.7020	-2.7020

int1-MeMe

E: -1683.15383389

H_{cont}: 0.32782527

G_{cont}: 0.25911768

E_{sp}: -1683.982137

P	-1.7807	0.4217	0.4217
P	-1.2662	-2.3657	-2.3657
C	-2.8450	-0.3527	-0.3527
C	-2.3010	2.1886	2.1886
C	-0.9951	-2.9754	-2.9754
C	0.3901	-1.5540	-1.5540
P	-4.3315	-2.1577	-2.1577
P	-2.9140	-0.4170	-0.4170
C	-4.4147	-2.7159	-2.7159
C	-6.0490	-1.4637	-1.4637
C	-4.2131	0.9687	0.9687
C	-2.1823	-0.1120	-0.1120
H	-1.9349	-1.0690	-1.0690
H	-1.2538	0.4608	0.4608
H	-2.8698	0.4660	0.4660
H	-4.8943	0.7548	0.7548
H	-3.7059	1.9250	1.9250
H	-4.8181	1.0874	1.0874
H	-1.9264	2.8172	2.8172
H	-1.8005	2.5293	2.5293
H	-3.3844	2.3388	2.3388
H	-2.8908	-1.4405	-1.4405
H	-3.8689	0.0535	0.0535
H	-2.3821	-0.1510	-0.1510
H	0.4933	-1.1983	-1.1983
H	1.1808	-2.3027	-2.3027
H	0.5556	-0.7062	-0.7062
H	-1.9355	-3.3894	-3.3894
H	-0.6191	-2.2005	-2.2005
H	-0.2599	-3.7972	-3.7972
H	-5.1419	-3.5416	-3.5416
H	-3.4298	-3.1030	-3.1030
H	-4.7376	-1.9226	-1.9226
H	-6.7310	-2.3290	-2.3290
H	-6.3538	-0.8254	-0.8254
H	-6.1658	-0.9034	-0.9034

ts1-MeMe

E: -1683.135903

H_{cont}: 0.32623367

G_{cont}: 0.25681999

E_{sp}: -1683.965515

P	-1.7939	0.7414	0.7414

P	-1.2026	-1.9232	-1.9232
C	-2.3750	-0.1414	-0.1414
C	-2.6946	2.3784	2.3784
C	-1.1503	-3.4606	-3.4606
C	0.4464	-1.9640	-1.9640
P	-4.1472	-1.9134	-1.9134
P	-3.1680	0.0220	0.0220
C	-4.0598	-2.7275	-2.7275
C	-5.9617	-1.4294	-1.4294
C	-4.4923	1.2747	1.2747
C	-2.3137	0.0880	0.0880
H	-1.6440	-0.7768	-0.7768
H	-1.7321	1.0214	1.0214
H	-3.0562	0.0805	0.0805
H	-5.1401	0.9458	0.9458
H	-4.0432	2.2420	2.2420
H	-5.1060	1.4074	1.4074
H	-2.6191	3.0714	3.0714
H	-2.1233	2.8310	2.8310
H	-3.7474	2.3053	2.3053
H	-1.5902	-0.8521	-0.8521
H	-3.2967	-0.7178	-0.7178
H	-2.5557	0.5963	0.5963
H	0.5682	-1.0434	-1.0434
H	0.5664	-2.8257	-2.8257
H	1.2732	-1.9871	-1.9871
H	-2.1034	-3.5440	-3.5440
H	-0.3323	-3.4390	-3.4390
H	-1.0315	-4.3720	-4.3720
H	-4.6810	-3.6355	-3.6355
H	-3.0144	-3.0131	-3.0131
H	-4.4374	-2.1011	-2.1011
H	-6.5333	-2.3611	-2.3611
H	-6.2905	-0.9684	-0.9684
H	-6.2188	-0.7646	-0.7646

int0-PhPh

E: -1607.155428

H_{cont}: 0.39097614

G_{cont}: 0.32191687

E_{sp}: -1608.358873

H	1.4109	1.8726	1.8726
H	3.1461	3.5070	3.5070
H	3.8009	3.6282	3.6282
H	2.7258	2.1255	2.1255
H	0.3446	0.3689	0.3689
C	1.7120	1.9235	1.9235
C	2.6810	2.8407	2.8407
C	3.0483	2.9079	2.9079
C	2.4458	2.0604	2.0604
C	1.1151	1.0729	1.0729
C	1.4800	1.1252	1.1252
H	2.4463	-3.7803	-3.7803
H	2.5998	-5.2885	-5.2885
H	2.0029	-4.4388	-4.4388
H	1.2368	-2.0945	-2.0945
H	1.6868	-1.4391	-1.4391
C	1.7427	-2.0955	-2.0955
C	2.1691	-3.4119	-3.4119
C	2.2544	-4.2598	-4.2598
C	1.9197	-3.7854	-3.7854
C	1.4945	-2.4685	-2.4685
H	-2.9806	3.6499	3.6499
H	-3.1318	5.1639	5.1639
H	-2.5362	4.3197	4.3197
H	-1.7734	1.9749	1.9749
H	-2.2240	1.3081	1.3081
C	-2.7040	3.2838	3.2838
C	-2.7881	4.1349	4.1349
C	-2.4542	3.6636	3.6636
C	-2.0308	2.3465	2.3465
C	-2.2795	1.9672	1.9672
H	-4.3377	-3.7584	-3.7584
H	-3.6787	-3.6499	-3.6499
H	-1.9442	-2.0192	-2.0192
H	-0.8815	-0.5043	-0.5043
H	-3.2649	-2.2470	-2.2470
C	-2.9838	-2.1872	-2.1872
C	-3.5849	-3.0397	-3.0397
C	-3.2155	-2.9795	-2.9795
C	-2.2465	-2.0639	-2.0639
C	-1.6516	-1.2077	-1.2077
C	1.3917	-1.6117	-1.6117
C	-1.9292	1.4866	1.4866
C	-2.0177	-1.2537	-1.2537
P	0.7567	0.0824	0.0824
P	-1.2945	-0.2068	-0.2068

int1-PhPh

E: -3214.280709

H_{cont}: 0.78765747

G_{cont}: 0.66999483

E_{sp}: -3216.679038

P	-1.5670	0.6627	0.6627
P	-1.2457	-2.3029	-2.3029
P	-4.3246	-2.2917	-2.2917

P	-2.9771	-0.3327	-0.3327
C	-8.4610	-0.8849	-0.8849
C	-8.1643	-0.6441	-0.6441
C	-6.9626	-1.0813	-1.0813
C	-6.0157	-1.7457	-1.7457
C	-6.3476	-2.0179	-2.0179
C	-7.5572	-1.5951	-1.5951
H	-9.4008	-0.5270	-0.5270
H	-8.8756	-0.1012	-0.1012
H	-6.7608	-0.8817	-0.8817
H	-5.6407	-2.5774	-2.5774
H	-7.7959	-1.8277	-1.8277
C	-4.1544	-3.4779	-3.4779
C	-4.7474	-2.2601	-2.2601
C	-4.8205	-1.8525	-1.8525
C	-4.3323	-2.6712	-2.6712
C	-3.7308	-3.8917	-3.8917
C	-3.6364	-4.2888	-4.2888
H	-4.0854	-3.7944	-3.7944
H	-5.1385	-1.6100	-1.6100
H	-5.2234	-0.8676	-0.8676
H	-3.3052	-4.5173	-4.5173
H	-3.1527	-5.2356	-5.2356
C	-6.6967	2.5434	2.5434
C	-6.1673	1.9708	1.9708
C	-5.0485	1.1465	1.1465
C	-4.4261	0.8731	0.8731
C	-4.9830	1.4377	1.4377
C	-6.1011	2.2693	2.2693
H	-7.5724	3.1938	3.1938
H	-6.6270	2.1690	2.1690
H	-4.6554	0.7122	0.7122
H	-4.5362	1.2379	1.2379
H	-6.5094	2.7069	2.7069
C	-2.2378	5.2405	5.2405
C	-3.0462	4.5138	4.5138
C	-2.8609	3.1426	3.1426
C	-1.8711	2.4741	2.4741
C	-1.0308	3.2262	3.2262
C	-1.2157	4.5980	4.5980
H	-2.4041	6.3125	6.3125
H	-3.8327	5.0203	5.0203
H	-3.4923	2.5828	2.5828
H	-0.2312	2.7152	2.7152
H	-0.5587	5.1680	5.1680
C	-0.9630	0.9035	0.9035
C	-1.3779	1.8680	1.8680
C	-2.0274	1.4861	1.4861
C	-2.2425	0.1291	0.1291
C	-1.8214	-0.8319	-0.8319
C	-1.1972	-0.4438	-0.4438
H	-0.4498	1.2051	1.2051
H	-1.1926	2.9275	2.9275
H	-2.3625	2.2526	2.2526
H	-1.9526	-1.8920	-1.8920
H	-0.8720	-1.2090	-1.2090
C	-3.0441	-0.7199	-0.7199
C	-2.0996	0.2971	0.2971
C	-1.7131	0.7210	0.7210
C	-2.2700	0.1400	0.1400
C	-3.2061	-0.8867	-0.8867
C	-3.5934	-1.3113	-1.3113
H	-3.3492	-1.0600	-1.0600
H	-1.6520	0.7657	0.7657
H	-0.9668	1.5143	1.5143
H	-3.6302	-1.3828	-1.3828
H	-4.3200	-2.1216	-2.1216
C	3.2201	-1.0953	-1.0953
C	2.2097	-0.2453	-0.2453
C	0.8709	-0.5661	-0.5661
C	0.5016	-1.7550	-1.7550
C	1.5347	-2.6092	-2.6092
C	2.8727	-2.2796	-2.2796
H	4.2694	-0.8368	-0.8368
H	2.4640	0.6846	0.6846
H	0.1068	0.1291	0.1291
H	1.2825	-3.5466	-3.5466
H	3.6500	-2.9597	-2.9597
C	-1.5135	-3.9692	-3.9692
C	-0.5696	-2.9822	-2.9822
C	-0.4556	-2.4761	-2.4761
C	-1.2779	-2.9506	-2.9506
C	-2.1976	-3.9701	-3.9701
C	-2.3206	-4.4685	-4.4685
H	-1.6187	-4.3528	-4.3528
H	0.0683	-2.5827	-2.5827
H	0.2656	-1.6836	-1.6836
H	-2.8326	-4.3636	-4.3636
H	-3.0470	-5.2580	-5.2580

Ph2P

E: -803.5357909

H_{cont}: 0.19489848

G_{cont}: 0.1460200

E_{sp}: -804.1373262

P	2.2490	0.1305	0.1305
C	2.0526	-1.5788	-1.5788
C	1.1946	-2.4313	-2.4313
C	1.0079	-3.7528	-3.7528

C	1.6929	-4.2535	-4.2535
C	2.5818	-3.4318	-3.4318
C	2.7622	-2.1081	-2.1081
H	3.4551	-1.4707	-1.4707
H	0.6545	-2.0438	-2.0438
H	0.3219	-4.3959	-4.3959
H	1.5318	-5.2846	-5.2846
H	3.1350	-3.8260	-3.8260
C	2.1810	1.1056	1.1056
C	1.6480	0.6637	0.6637
C	2.6208	2.4430	2.4430
C	2.5542	3.2929	3.2929
C	2.0387	2.8328	2.8328
C	1.5816	1.5173	1.5173
H	1.2665	-0.3549	-0.3549
H	3.0289	2.8109	2.8109
H	2.9127	4.3211	4.3211
H	1.9858	3.5013	3.5013
H	1.1544	1.1541	1.1541

ts2-PhPh

E: -2410.708661

H_{cont}: 0.58806998

G_{cont}: 0.494042812

E_{sp}: -2412.509492

H	-3.9087	-2.8882	-2.8882
H	-2.0545	-4.5458	-4.5458
H	0.3028	-3.7740	-3.7740
H	0.7971	-1.4087	-1.4087
H	-3.1849	-0.2408	-0.2408
H	-3.3129	2.1199	2.1199
H	-2.4296	3.9490	3.9490
H	-1.4523	3.4300	3.4300
H	4.7260	-1.7678	-1.7678
H	3.6339	-2.9798	-2.9798
H	1.4612	-2.1564	-2.1564
H	0.4134	-0.1214	-0.1214
H	1.6107	-0.0022	-0.0022
H	2.2391	0.4309	0.4309
H	2.7577	2.7517	2.7517
H	2.6365	4.6310	4.6310
H	-3.4149	-0.4974	-0.4974
C	-2.5932	-1.2183	-1.2183
C	-2.8737	-2.5622	-2.5622
C	-1.8357	-3.4913	-3.4913
C	-0.5210	-3.0595	-3.0595
C	-0.2399	-1.7146	-1.7146
C	-1.2714	-0.7725	-0.7725
H	-2.2017	-0.7666	-0.7666
C	-2.2482	0.2715	0.2715
C	-2.8017	0.5689	0.5689
C	-2.8745	1.8879	1.8879
C	-2.3853	2.9135	2.9135
C	-1.8348	2.6203	2.6203
C	-1.7599	1.2943	1.2943
P	-1.0445	1.0463	1.0463
H	3.6884	0.2672	0.2672
C	3.1968	-0.2579	-0.2579
C	3.7813	-1.4062	-1.4062
C	3.1685	-2.0858	-2.0858
C	1.9591	-1.6179	-1.6179
C	1.3713	-0.4729	-0.4729
C	1.9908	0.2271	0.2271
P	1.2039	1.7840	1.7840
C	1.8102	2.0639	2.0639
C	1.8536	1.0156	1.0156
C	2.1968	1.2617	1.2617
C	2.4822	2.5592	2.5592
C	2.4189	3.6112	3.6112
C	2.0852	3.3663	3.3663
H	2.0414	4.1949	4.1949
H	1.3918	5.5779	5.5779
H	-0.0138	5.7856	5.7856
H	-0.5583	3.7663	3.7663
H	0.3052	1.5399	1.5399
H	1.7181	1.3383	1.3383
H	4.7378	2.8174	2.8174
H	6.8364	1.5103	1.5103
H	7.4255	0.4291	0.4291
H	5.9238	0.7058	0.7058
H	3.8336	2.0147	2.0147
C	1.1541	4.6922	4.6922
C	0.3687	4.8086	4.8086
C	0.0661	3.6776	3.6776
C	0.5536	2.4321	2.4321
C	1.3426	2.3176	2.3176
C	4.9957	2.3458	2.3458
C	6.1718	1.6127	1.6127
C	6.5038	1.0077	1.0077
C	5.6572	1.1609	1.1609
C	4.4756	1.8906	1.8906
C	4.1124	2.4763	2.4763
P	2.5954	3.4248	3.4248
C	1.6552	3.4470	3.4470

oTol2P

E: -882.0219441

H_{cont}: 0.25300362

G_{cont}: 0.19669777

E_{sp}: -882.7053332

P	0.8296	0.0476	0.0476
C	1.5318	-1.5935	-1.5935
C	1.4862	-2.5352	-2.5352
C	1.9331	-3.8362	-3.8362
C	2.4275	-4.2253	-4.2253
C	2.5082	-3.2945	-3.2945
C	2.0757	-1.9904	-1.9904
H	2.1628	-1.2544	-1.2544
H	1.9013	-4.5609	-4.5609
H	2.7731	-5.2504	-5.2504
H	2.9243	-3.5859	-3.5859
C	1.5229	1.0520	1.0520
C	0.9319	1.1653	1.1653
C	2.6337	1.8468	1.8468
C	3.1830	2.7289	2.7289
C	2.6127	2.8305	2.8305
C	1.5014	2.0547	2.0547
H	3.0730	1.7732	1.7732
H	4.0500	3.3353	3.3353
H	3.0292	3.5172	3.5172
H	1.0533	2.1466	2.1466
C	1.0077	-2.1460	-2.1460
H	1.0974	-2.9890	-2.9890
H	1.5942	-1.3054	-1.3054
H	-0.0434	-1.8127	-1.8127
C	-0.2807	0.3635	0.3635
H	-1.0885	0.4988	0.4988
H	-0.6641	0.6617	0.6617
H	-0.0588	-0.7159	-0.7159

ts2-oToloTol

E: -2646.171457

H_{cont}: 0.7631705

G_{cont}: 0.65042506

E_{sp}: -2648.215005

C	1.3144	3.0723	3.0723
P	2.2296	3.4110	3.4110
C	3.9413	2.9895	2.9895
C	4.2769	2.0954	2.0954
C	5.6041	1.7980	1.7980
C	6.6246	2.4089	2.4089
C	6.3037	3.3085	3.3085
C	4.9782	3.6045	3.6045
C	0.8953	1.7917	1.7917
C	0.1697	1.5855	1.5855
C	-0.1594	2.6726	2.6726
C	0.2442	3.9525	3.9525
C	0.9823	4.1798	4.1798
H	3.4804	1.6288	1.6288
H	5.8436	1.0936	1.0936
H	7.6698	2.1854	2.1854
H	7.1037	3.7920	3.7920
C	4.6611	4.5420	4.5420
H	1.1384	0.9347	0.9347
H	-0.1531	0.5780	0.5780
H	-0.7392	2.5285	2.5285
H	-0.0243	4.8066	4.8066
C	1.4027	5.5798	5.5798
C	0.5325	4.4438	4.4438
C	1.3771	3.4953	3.4953
C	1.8163	3.8876	3.8876
C	2.5836	3.0518	3.0518
C	2.8869	1.7661	1.7661
C	2.4528	1.3532	1.3532
C	1.7433	2.2134	2.2134
P	1.1867	1.6470	1.6470
C	2.0975	0.0935	0.0935
C	1.2859	-0.8453	-0.8453
C	1.8028	-2.0054	-2.0054
C	3.1673	-2.2676	-2.2676
C	3.9765	-1.3592	-1.3592
C	3.4842	-0.1636	-0.1636
C	4.5042	0.7297	0.7297
P	-1.0287	1.0791	1.0791
C	-1.8555	0.6588	0.6588
C	-2.1528	1.7046	1.7046
C	-2.7558	1.3839	1.3839
C	-3.0838	0.0742	0.0742
C	-2.8238	-0.9513	-0.9513
C	-2.2177	-0.6571	-0.6571
H	-2.0130	-1.4626	-1.4626
C	-1.0954	-0.5113	-0.5113
C	0.0553	-1.2636	-1.2636
C	0.0094	-2.4031	-2.4031
C	-1.2044	-2.8172	-2.8172
C	-2.3556	-2.0758	-2.0758
C	-2.3280	-0.9168	-0.9168
C	-3.5929	-0.1453	-0.1453
H	1.5297	4.8771	4.8771
H	2.9264	3.3971	3.3971
H	3.4531	1.0790	1.0790
H	2.6761	0.3400	0.3400
H	0.2167	-0.6506	-0.6506
H	1.1381	-2.7009	-2.7009
H	3.6009	-3.1726	-3.1726

H	5.0476	-1.5615	-1.5615
C	-1.8401	3.1362	3.1362
H	-2.9717	2.1929	2.1929
H	-3.5567	-0.1445	-0.1445
H	-3.0992	-1.9812	-1.9812
H	1.0036	-0.9589	-0.9589
H	0.9235	-2.9686	-2.9686
H	-1.2597	-3.7153	-3.7153
H	-3.3086	-2.3973	-2.3973
H	4.0380	5.3818	5.3818
H	5.5756	4.9488	4.9488
H	4.0830	4.0399	4.0399
H	0.8943	6.3128	6.3128
H	2.4896	5.7141	5.7141
H	1.1775	5.8185	5.8185
H	-0.1438	3.9076	3.9076
H	1.1559	5.1038	5.1038
H	-0.0808	5.0677	5.0677
H	5.3433	0.8908	0.8908
H	4.9100	0.2580	0.2580
H	4.1076	1.7068	1.7068
H	-2.3598	3.8132	3.8132
H	-0.7616	3.3363	3.3363
H	-2.1285	3.3921	3.3921
H	-3.4269	0.9372	0.9372
H	-4.3817	-0.4642	-0.4642
H	-3.9671	-0.2870	-0.2870

int0-oToloTol

E: -1764.134043

H_{cont}: 0.50977602

G_{cont}: 0.42703577

E_{sp}: -1765.497759

P	-1.2427	-1.0293	-1.0293
P	0.9073	-0.6001	-0.6001
C	-2.0772	-1.2605	-1.2605
C	-1.8777	0.6360	0.6360
C	1.8290	-1.8826	-1.8826
C	-1.4044	-1.3167	-1.3167
C	-2.0931	-1.5040	-1.5040
C	-3.4788	-1.6446	-1.6446
C	-4.1537	-1.6175	-1.6175
C	-3.4807	-1.4350	-1.4350
H	-0.3194	-1.1757	-1.1757
H	-1.5440	-1.5335	-1.5335
H	-4.0358	-1.7906	-1.7906
H	-5.2385	-1.7565	-1.7565
C	-1.8419	1.8048	1.8048
C	-2.4406	0.6942	0.6942
C	-2.9242	1.8845	1.8845
C	-2.8460	3.0477	3.0477
C	-2.3183	2.9960	2.9960
H	-2.4952	-0.2241	-0.2241
H	-3.3574	1.9021	1.9021
H	-3.2094	3.9950	3.9950
H	-2.2692	3.9107	3.9107
C	1.6193	-3.2497	-3.2497
C	2.3925	-4.2005	-4.2005
C	3.3761	-3.8319	-3.8319
C	3.6183	-2.4816	-2.4816
C	2.8527	-1.5193	-1.5193
H	3.0589	-0.4627	-0.4627
H	2.2171	-5.2589	-5.2589
H	3.9652	-4.5974	-4.5974
H	4.4062	-2.1701	-2.1701
C	1.2581	0.9537	0.9537
C	1.0475	1.2014	1.2014
C	1.7551	1.9819	1.9819
C	2.0245	3.2501	3.2501
C	1.7964	3.5035	3.5035
C	1.3177	2.4880	2.4880
H	2.4085	4.0324	4.0324
H	1.9979	4.4925	4.4925
H	1.1322	2.6981	2.6981
C	-1.3656	1.8206	1.8206
H	-0.5283	1.1336	1.1336
H	-1.0446	2.8295	2.8295
H	-2.1728	1.5038	1.5038
C	-4.2641	-1.4307	-1.4307
H	-5.2313	-1.9353	-1.9353
H	-4.4600	-0.4064	-0.4064
H	-3.7126	-1.9422	-1.9422
C	0.6048	-3.7039	-3.7039
H	0.5693	-3.0330	-3.0330
H	-0.4102	-3.7272	-3.7272
H	0.8415	-4.7130	-4.7130
C	0.5808	0.1627	0.1627
H	0.0836	-0.6872	-0.6872
H	-0.1157	0.6059	0.6059
H	1.4322	-0.2519	-0.2519
H	1.9287	1.7693	1.7693

PMe2P

E: -420.7533951

H_{cont}: 0.07959972

G_{cont}: 0.04557994

E_{sp}: -420.9606427

C	3.6598	2.7219	2.7219
P	3.9366	1.3241	1.3241
C	4.6605	0.1102	0.1102
H	2.9719	2.4302	2.4302
H	4.6070	3.0456	3.0456
H	3.2233	3.5810	3.5810
H	4.9030	-0.8290	-0.8290
H	5.5852	0.5034	0.5034
H	3.9551	-0.1162	-0.1162

int2-MeMe

E: -1262.372703

H_{cont}: 0.24503998

G_{cont}: 0.18405438

E_{sp}: -1262.994834

C	3.6505	2.7295	2.7295
P	4.0188	1.3556	1.3556
C	4.6592	0.0987	0.0987
H	2.9817	2.4072	2.4072
H	4.5916	3.0972	3.0972
H	3.1809	3.5699	3.5699
H	4.8636	-0.8486	-0.8486
H	5.6087	0.4539	0.4539
H	3.9472	-0.0920	-0.0920
P	1.7972	0.4991	0.4991
P	-0.3070	-0.3164	-0.3164
C	2.1547	-0.9022	-0.9022
C	1.1206	1.7697	1.7697
C	-0.6277	1.0802	1.0802
C	0.3972	-1.5460	-1.5460
H	0.8659	2.6830	2.6830
H	1.8701	2.0219	2.0219
H	0.2110	1.3902	1.3902
H	2.5690	-1.7494	-1.7494
H	1.2296	-1.2301	-1.2301
H	2.8898	-0.5932	-0.5932
H	-1.4089	0.7850	0.7850
H	0.2774	1.3702	1.3702
H	-0.9984	1.9561	1.9561
H	-0.3844	-1.8552	-1.8552
H	0.7289	-2.4455	-2.4455
H	1.2503	-1.1359	-1.1359

ts2-MeMe

E: -1262.370439

H_{cont}: 0.24404243

G_{cont}: 0.1838426

E_{sp}: -1262.990737

C	3.7777	2.7353	2.7353
P	4.0576	1.3479	1.3479
C	4.7620	0.0943	0.0943
H	3.2040	2.4233	2.4233
H	4.7535	3.1257	3.1257
H	3.2446	3.5570	3.5570
H	4.9520	-0.8481	-0.8481
H	5.7287	0.4633	0.4633
H	4.1016	-0.1042	-0.1042
P	1.9217	0.5526	0.5526
P	-0.4871	-0.4069	-0.4069
C	2.2487	-0.8384	-0.8384
C	1.2441	1.8187	1.8187
C	-0.9315	0.9692	0.9692
C	0.2501	-1.5530	-1.5530
H	1.0973	2.7723	2.7723
H	1.9200	1.9833	1.9833
H	0.2685	1.4760	1.4760
H	2.8079	-1.6365	-1.6365
H	1.2903	-1.2538	-1.2538
H	2.8309	-0.4982	-0.4982
H	-1.6319	0.5991	0.5991
H	-0.0457	1.3714	1.3714
H	-1.4238	1.7894	1.7894
H	-0.5093	-1.8440	-1.8440
H	0.6204	-2.4697	-2.4697
H	1.0853	-1.0733	-1.0733

***o*-^{t}BuPh2P**

E: -1117.442261

H_{cont}: 0.43033184

G_{cont}: 0.36101732

E_{sp}: -1118.372327

C	1.6867	3.5702	3.5702
P	2.5966	3.4151	3.4151
C	4.2536	2.8248	2.8248
C	4.2258	1.9015	1.9015
C	5.3685	1.3063	1.3063
C	6.6014	1.6395	1.6395
C	6.6494	2.5515	2.5515
C	5.5100	3.1660	3.1660
C	0.8662	2.4628	2.4628
C	0.0728	2.3974	2.3974
C	0.0798	3.4742	3.4742
C	0.8538	4.5968	4.5968

C	1.6639	4.6956	4.6956
H	3.2649	1.6464	1.6464
H	5.2936	0.5962	0.5962
H	7.5229	1.1973	1.1973
H	7.6284	2.8157	2.8157
C	5.8107	4.2052	4.2052
H	0.8557	1.6242	1.6242
H	−0.5419	1.5162	1.5162
H	−0.5271	3.4551	3.4551
H	0.8039	5.4355	5.4355
C	2.3788	6.0284	6.0284
C	4.5952	4.8521	4.8521
C	6.6483	5.3383	5.3383
C	6.6096	3.5430	3.5430
C	2.1690	7.0662	7.0662
C	3.8980	5.8784	5.8784
C	1.7799	6.6032	6.6032
H	7.4924	2.9940	2.9940
H	5.9745	2.8418	2.8418
H	6.9530	4.3139	4.3139
H	6.0843	5.8539	5.8539
H	7.5837	4.9709	4.9709
H	6.9063	6.0803	6.0803
H	3.9901	5.4388	5.4388
H	4.9483	5.5451	5.5451
H	3.9405	4.1130	4.1130
H	4.4314	5.7204	5.7204
H	4.1669	5.0530	5.0530
H	4.3035	6.8049	6.8049
H	2.5678	6.7151	6.7151
H	2.7122	7.9854	7.9854
H	1.1121	7.3383	7.3383
H	0.6993	6.7804	6.7804
H	2.2629	7.5606	7.5606
H	1.9223	5.9206	5.9206

int0-*o*-^{t}BuPh2P

E: −2234.969569

H_{cont}: 0.86399712

G_{cont}: 0.75550631

E_{sp}: −2236.825381

C	0.7756	4.5186	4.5186
C	1.0554	3.2336	3.2336
C	1.4921	3.3670	3.3670
C	1.7993	2.2804	2.2804
C	1.6674	0.9913	0.9913
C	1.2452	0.8212	0.8212
C	0.9478	1.9055	1.9055
P	0.5313	1.5264	1.5264
C	1.4604	0.0121	0.0121
C	0.6615	−0.6680	−0.6680
C	1.0212	−1.8706	−1.8706
C	2.2171	−2.4658	−2.4658
C	3.0539	−1.7677	−1.7677
C	2.7690	−0.4883	−0.4883
C	3.9863	0.2098	0.2098
P	−1.6008	0.9139	0.9139
C	−2.5503	0.1082	0.1082
C	−2.9858	0.7164	0.7164
C	−3.8384	−0.0418	−0.0418
C	−4.3278	−1.2993	−1.2993
C	−3.9584	−1.8562	−1.8562
C	−3.0779	−1.1575	−1.1575
H	−2.8015	−1.6174	−1.6174
C	−1.3490	−0.4800	−0.4800
C	−0.6340	−1.6106	−1.6106
C	−0.2259	−2.6156	−2.6156
C	−0.5420	−2.5002	−2.5002
C	−1.2983	−1.4179	−1.4179
C	−1.7412	−0.3929	−0.3929
C	−2.6446	0.7156	0.7156
H	1.6067	4.3626	4.3626
H	2.1486	2.4541	2.4541
H	1.9010	0.1206	0.1206
H	1.1751	−0.1889	−0.1889
H	−0.3146	−0.2526	−0.2526
H	0.3514	−2.3489	−2.3489
H	2.5188	−3.4416	−3.4416
H	4.0128	−2.2215	−2.2215
C	−2.6385	2.1407	2.1407
H	−4.1673	0.3791	0.3791
H	−5.0040	−1.8207	−1.8207
H	−4.3463	−2.8241	−2.8241
H	−0.3749	−1.7027	−1.7027
H	0.3469	−3.4629	−3.4629
H	−0.2152	−3.2577	−3.2577
H	−1.5531	−1.3739	−1.3739
C	−0.6405	4.4992	4.4992
C	1.8141	4.6597	4.6597
C	0.8707	5.7842	5.7842
C	5.1637	0.1274	0.1274
C	4.3806	−0.4941	−0.4941
C	3.7974	1.6996	1.6996
C	−3.4007	2.5257	2.5257
C	−1.1498	2.2569	2.2569
C	−3.0468	3.1590	3.1590
C	−1.9465	2.0823	2.0823
C	−3.0278	0.4413	0.4413
C	−3.9510	0.7705	0.7705

H	1.6649	5.6107	5.6107
H	1.7323	3.8466	3.8466
H	2.8331	4.6584	4.6584
H	−0.8093	5.3918	5.3918
H	−1.3952	4.4890	4.4890
H	−0.8124	3.6232	3.6232
H	0.5825	6.6471	6.6471
H	1.8903	5.9697	5.9697
H	0.1874	5.7551	5.7551
H	−0.8591	1.4940	1.4940
H	−0.5036	2.1510	2.1510
H	−0.9385	3.2468	3.2468
H	−3.1179	1.9034	1.9034
H	−3.1488	3.5658	3.5658
H	−4.4925	2.4707	2.4707
H	−4.1421	3.1827	3.1827
H	−2.7015	4.1663	4.1663
H	−2.6282	2.9228	2.9228
H	−1.7521	2.4143	2.4143
H	−0.9875	2.0541	2.0541
H	−2.5876	2.8360	2.8360
H	−3.7765	1.0634	1.0634
H	−4.6330	1.5142	1.5142
H	−4.4588	−0.2060	−0.2060
H	−3.7254	1.2222	1.2222
H	−2.1554	0.4702	0.4702
H	−3.5356	−0.5275	−0.5275
H	4.9104	0.6374	0.6374
H	5.4604	−0.9005	−0.9005
H	6.0416	0.6303	0.6303
H	3.4012	2.2175	2.2175
H	4.7714	2.1513	2.1513
H	3.1393	1.9009	1.9009
H	4.6581	−1.5465	−1.5465
H	3.5578	−0.4666	−0.4666
H	5.2477	0.0119	0.0119

ts2-*o*-^{t}BuPh2P*o*-^{t}BuPh2P

E: −3352.42102

H_{cont}: 1.29667454

G_{cont}: 1.14367999

E_{sp}: −3355.199606

C	1.3821	4.2698	4.2698
P	2.7044	3.6104	3.6104
C	3.9170	2.9328	2.9328
C	3.3845	2.1069	2.1069
C	4.1312	1.6040	1.6040
C	5.4787	1.9409	1.9409
C	6.0329	2.7235	2.7235
C	5.3152	3.2159	3.2159
C	0.5494	3.3379	3.3379
C	−0.4407	3.6878	3.6878
C	−0.6405	5.0308	5.0308
C	0.1433	5.9815	5.9815
C	1.1576	5.6548	5.6548
H	2.3330	1.8380	1.8380
H	3.6573	0.9619	0.9619
H	6.1033	1.5841	1.5841
H	7.0943	2.9641	2.9641
C	6.1962	3.9972	3.9972
H	0.6604	2.2841	2.2841
H	−1.0547	2.9111	2.9111
H	−1.4100	5.3520	5.3520
H	−0.0471	7.0293	7.0293
C	1.9620	6.8067	6.8067
C	1.6331	3.7021	3.7021
C	1.8850	2.1857	2.1857
C	2.3108	1.6110	1.6110
C	2.5049	0.2497	0.2497
C	2.2749	−0.6104	−0.6104
C	1.9232	−0.0662	−0.0662
C	1.7458	1.3117	1.3117
P	1.2164	1.6974	1.6974
C	1.7783	0.2737	0.2737
C	0.7402	0.0687	0.0687
C	0.7828	−0.8756	−0.8756
C	1.8980	−1.7015	−1.7015
C	2.9331	−1.5095	−1.5095
C	2.9590	−0.5162	−0.5162
C	4.2995	−0.4827	−0.4827
P	−1.2264	1.0111	1.0111
C	−2.3113	0.8360	0.8360
C	−2.9470	1.9598	1.9598
C	−3.6646	1.7121	1.7121
C	−3.8630	0.4364	0.4364
C	−3.3510	−0.6615	−0.6615
C	−2.5785	−0.4489	−0.4489
H	−2.1759	−1.3169	−1.3169
C	−1.0288	−0.7180	−0.7180
C	−0.3426	−1.6612	−1.6612
C	0.0756	−2.8901	−2.8901
C	−0.1922	−3.1997	−3.1997
C	−0.9198	−2.3041	−2.3041
C	−1.3706	−1.0659	−1.0659
C	−2.2290	−0.1813	−0.1813
H	2.4842	2.2662	2.2662
H	2.8268	−0.1324	−0.1324
H	2.3892	−1.6915	−1.6915
H	1.8040	−0.7419	−0.7419

H	-0.1764	0.6524	0.6524
H	-0.0649	-0.9818	-0.9818
H	1.9706	-2.4898	-2.4898
H	3.7993	-2.1643	-2.1643
C	-3.0463	3.3673	3.3673
H	-4.1317	2.5475	2.5475
H	-4.4479	0.3070	0.3070
H	-3.5472	-1.6778	-1.6778
H	-0.0787	-1.4043	-1.4043
H	0.6256	-3.5814	-3.5814
H	0.1535	-4.1410	-4.1410
H	-1.1450	-2.5922	-2.5922
C	5.5139	4.4481	4.4481
C	6.7821	5.2413	5.2413
C	7.3642	3.0922	3.0922
C	1.4761	8.1934	8.1934
C	3.4272	6.6959	6.6959
C	1.8401	6.7632	6.7632
C	0.5547	4.1104	4.1104
C	2.9459	4.4318	4.4318
C	1.1313	4.1389	4.1389
C	5.4743	-0.4781	-0.4781
C	4.4076	-1.7618	-1.7618
C	4.5389	0.7448	0.7448
C	-3.8379	4.3432	4.3432
C	-1.6843	4.0194	4.0194
C	-3.8029	3.2282	3.2282
C	-1.4726	1.0996	1.0996
C	-2.5882	-0.8928	-0.8928
C	-3.5490	0.1455	0.1455
H	7.9828	2.7470	2.7470
H	6.9927	2.2058	2.2058
H	8.0185	3.6503	3.6503
H	5.9914	5.9140	5.9140
H	7.4099	4.9732	4.9732
H	7.4133	5.8036	5.8036
H	4.7032	5.1651	5.1651
H	6.2642	4.9336	4.9336
H	5.0999	3.5972	3.5972
H	3.5317	6.8925	6.8925
H	3.8298	5.6938	5.6938
H	4.0473	7.4236	7.4236
H	1.5791	8.3476	8.3476
H	2.0927	8.9566	8.9566
H	0.4296	8.3805	8.3805
H	0.7907	6.8888	6.8888
H	2.4285	7.5773	7.5773
H	2.2076	5.8170	5.8170
H	2.8181	5.5218	5.5218
H	3.2725	4.2233	4.2233
H	3.7448	4.1149	4.1149
H	0.2838	5.1683	5.1683
H	-0.3527	3.5053	3.5053
H	0.8900	4.0073	4.0073
H	0.7827	5.1812	5.1812
H	1.9144	4.1042	4.1042
H	0.2873	3.5183	3.5183
H	-1.2636	4.4104	4.4104
H	-0.9548	3.3203	3.3203
H	-1.7872	4.8592	4.8592
H	-3.3576	4.4896	4.4896
H	-3.8584	5.3221	5.3221
H	-4.8813	4.0306	4.0306
H	-4.7556	2.6944	2.6944
H	-4.0225	4.2253	4.2253
H	-3.2052	2.6793	2.6793
H	-1.2821	1.7369	1.7369
H	-0.5007	0.8500	0.8500
H	-2.0572	1.6829	1.6829
H	-3.3819	0.6660	0.6660
H	-4.1785	0.7949	0.7949
H	-4.1105	-0.7751	-0.7751
H	-3.2535	-0.2427	-0.2427
H	-1.7021	-1.0967	-1.0967
H	-3.1201	-1.8412	-1.8412
H	5.4579	0.4289	0.4289
H	5.4944	-1.3469	-1.3469
H	6.4187	-0.4896	-0.4896
H	4.3776	1.6680	1.6680
H	5.5889	0.7428	0.7428
H	3.9259	0.7795	0.7795
H	4.3456	-2.6635	-2.6635
H	3.6169	-1.8234	-1.8234
H	5.3752	-1.7837	-1.7837

int2-ClPh

E: -2067.058000

H_{cont}: 0.395030038

G_{cont}: 0.32008269

E_{sp}: -2068.420236

P	-0.6476	-1.6005	-1.6005
P	1.3128	-1.1551	-1.1551
C	1.1098	0.6051	0.6051
C	0.7449	0.8710	0.8710
C	0.4998	2.1755	2.1755
C	0.6283	3.2361	3.2361
C	0.9973	2.9834	2.9834
C	1.2281	1.6805	1.6805
C	2.3585	-1.1085	-1.1085

C	3.4988	-0.2898	-0.2898
C	4.3626	-0.3118	-0.3118
C	4.1131	-1.1601	-1.1601
C	2.9980	-1.9968	-1.9968
C	2.1318	-1.9788	-1.9788
C	-1.1309	0.0073	0.0073
C	-0.6365	0.3580	0.3580
C	-0.9096	1.6165	1.6165
C	-1.7014	2.5173	2.5173
C	-2.2024	2.1654	2.1654
C	-1.9101	0.9178	0.9178
C	-1.8550	-1.9528	-1.9528
C	-3.2121	-2.0245	-2.0245
C	-4.1749	-2.2690	-2.2690
C	-3.7992	-2.4612	-2.4612
C	-2.4510	-2.4284	-2.4284
C	-1.4803	-2.1796	-2.1796
H	0.6545	0.0459	0.0459
H	0.2071	2.3662	2.3662
H	0.4365	4.2588	4.2588
H	1.0965	3.8086	3.8086
H	1.4908	1.4928	1.4928
H	3.7142	0.3768	0.3768
H	5.2419	0.3369	0.3369
H	4.7875	-1.1682	-1.1682
H	2.7833	-2.6690	-2.6690
H	1.2551	-2.6322	-2.6322
H	-0.0517	-0.3656	-0.3656
H	-0.5126	1.8892	1.8892
H	-1.9386	3.4944	3.4944
H	-2.8189	2.8705	2.8705
H	-2.2859	0.6530	0.6530
H	-3.5031	-1.8954	-1.8954
H	-5.2281	-2.3171	-2.3171
H	-4.5588	-2.6503	-2.6503
H	-2.1465	-2.6022	-2.6022
H	-0.4245	-2.1641	-2.1641
Cl	-1.5035	-2.8931	-2.8931

Cl

E: -459.8385799

H_{cont}: 0.005193105

G_{cont}: -0.012209447

E_{sp}: -459.9974297

Cl	0.0000	0.0000	0.0000

ts2-ClPh

E: -2067.051076

H_{cont}: 0.394704217

G_{cont}: 0.318826497

E_{sp}: -2068.41369

P	-0.9838	-1.8369	-1.8369
P	1.4184	-1.1733	-1.1733
C	0.9828	0.5285	0.5285
C	0.2368	0.6770	0.6770
C	-0.2227	1.9245	1.9245
C	0.0701	3.0588	3.0588
C	0.8084	2.9277	2.9277
C	1.2470	1.6781	1.6781
C	2.4946	-1.0235	-1.0235
C	3.6015	-0.1556	-0.1556
C	4.4774	-0.1488	-0.1488
C	4.2749	-1.0146	-1.0146
C	3.1966	-1.9005	-1.9005
C	2.3211	-1.9103	-1.9103
C	-1.1780	-0.1055	-0.1055
C	-0.5345	0.2019	0.2019
C	-0.5740	1.4953	1.4953
C	-1.2702	2.4927	2.4927
C	-1.9079	2.1939	2.1939
C	-1.8545	0.9038	0.9038
C	-1.9628	-1.9727	-1.9727
C	-3.2973	-1.5543	-1.5543
C	-3.9852	-1.6797	-1.6797
C	-3.3634	-2.2525	-2.2525
C	-2.0549	-2.7201	-2.7201
C	-1.3588	-2.5817	-2.5817
H	-0.0044	-0.2059	-0.2059
H	-0.8108	2.0152	2.0152
H	-0.2896	4.0388	4.0388
H	1.0271	3.8064	3.8064
H	1.7714	1.5864	1.5864
H	3.7909	0.5118	0.5118
H	5.3322	0.5326	0.5326
H	4.9598	-1.0010	-1.0010
H	3.0276	-2.5879	-2.5879
H	1.4725	-2.5995	-2.5995
H	0.0023	-0.5799	-0.5799
H	-0.0597	1.7248	1.7248
H	-1.3090	3.5069	3.5069
H	-2.4397	2.9745	2.9745
H	-2.3213	0.6958	0.6958
H	-3.8011	-1.1453	-1.1453
H	-5.0180	-1.3305	-1.3305
H	-3.9090	-2.3506	-2.3506
H	-1.5710	-3.1988	-3.1988

H -0.3310 -2.9415 -2.9415
Cl -2.4094 -2.7012 -2.7012

Ph2PCl

E: -1263.496189
H_{cont}: 0.198724686
G_{cont}: 0.146661146
E_{sp}: -1264.26106

Cl 0.0061 -3.3034 -3.3034
P 0.1309 -1.5549 -1.5549
C -1.3584 -0.6495 -0.6495
C -2.0469 0.0880 0.0880
C -3.1111 0.9130 0.9130
C -3.5010 0.9866 0.9866
C -2.8329 0.2292 0.2292
C -1.7653 -0.5849 -0.5849
C 1.4101 -0.6620 -0.6620
C 1.2607 0.6965 0.6965
C 2.2739 1.3842 1.3842
C 3.4485 0.7282 0.7282
C 3.6092 -0.6224 -0.6224
C 2.6016 -1.3116 -1.3116
H -1.7366 0.0244 0.0244
H -3.6391 1.4924 1.4924
H -4.3357 1.6283 1.6283
H -3.1506 0.2807 0.2807
H -1.2317 -1.1724 -1.1724
H 0.3420 1.2211 1.2211
H 2.1338 2.4388 2.4388
H 4.2385 1.2676 1.2676
H 4.5248 -1.1462 -1.1462
H 2.7292 -2.3718 -2.3718

ts4-ototolotol

E: -881.9736116
H_{cont}: 0.24641078
G_{cont}: 0.19250582
E_{sp}: -881.9736107

C -1.6215 -1.2177 -1.2177
C -2.2298 -0.2827 -0.2827
C -3.4652 0.3470 0.3470
C -3.9277 1.2885 1.2885
C -3.1850 1.5900 1.5900
C -1.9843 0.9239 0.9239
C -1.5060 -0.0123 -0.0123
P -0.0740 -1.1209 -1.1209
C 1.2666 -0.2137 -0.2137
C 2.4742 -0.8926 -0.8926
C 2.6378 -2.3462 -2.3462
C 3.5096 -0.1870 -0.1870
C 3.3748 1.1589 1.1589
C 2.1826 1.8229 1.8229
C 1.1392 1.1383 1.1383
H -2.2605 -1.9196 -1.9196
H -0.6175 -1.8622 -1.8622
H -0.7323 -0.8740 -0.8740
H -4.0504 0.1152 0.1152
H -4.8798 1.7934 1.7934
H -3.5570 2.3260 2.3260
H -1.4244 1.1256 1.1256
H 1.9244 -2.9694 -2.9694
H 3.6499 -2.6976 -2.6976
H 2.4504 -2.5432 -2.5432
H 4.4422 -0.7096 -0.7096
H 4.2014 1.6857 1.6857
H 2.0580 2.8742 2.8742
H 0.2045 1.6596 1.6596

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