Supporting information for

Complexes of Dichlorogermylene with Phosphine/Sulfoxide-Supported Carbone as Ligand.

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Page

Selected spectroscopic data

400.10.fid — UA-083 CD2Cl2 1H

8.14
8.07
7.71
7.59
5.32
3.68
3.60
3.24
3.13
0.82
0.80
0.71
0.69

6.20
9.70
2.20
2.08
2.08
6.37
6.00

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)
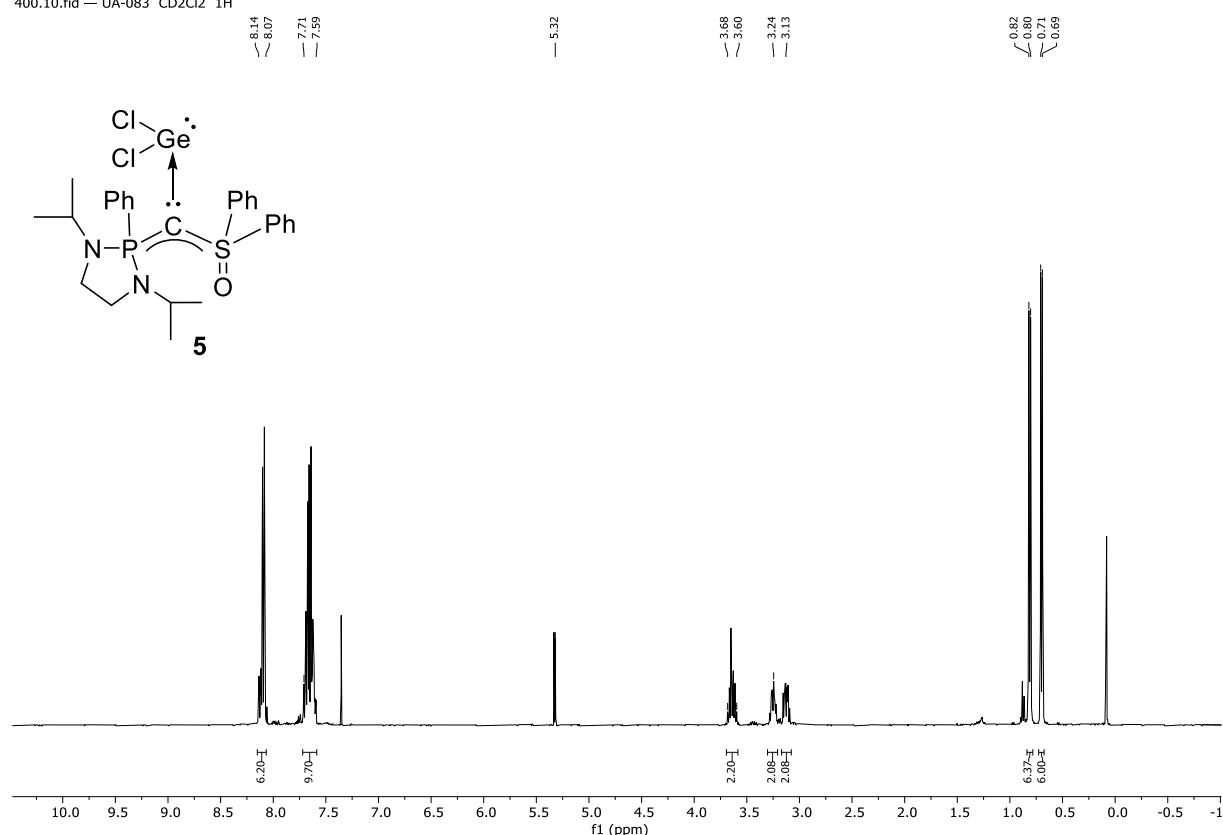
Figure S1: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$)

500.3.fid — UA-083 CD2CL2 13C{1H}

140.74
134.68
134.22
132.91
132.81
130.34
130.15
130.04
129.08
47.35
46.73
46.01
45.98
39.31
39.24
19.95

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
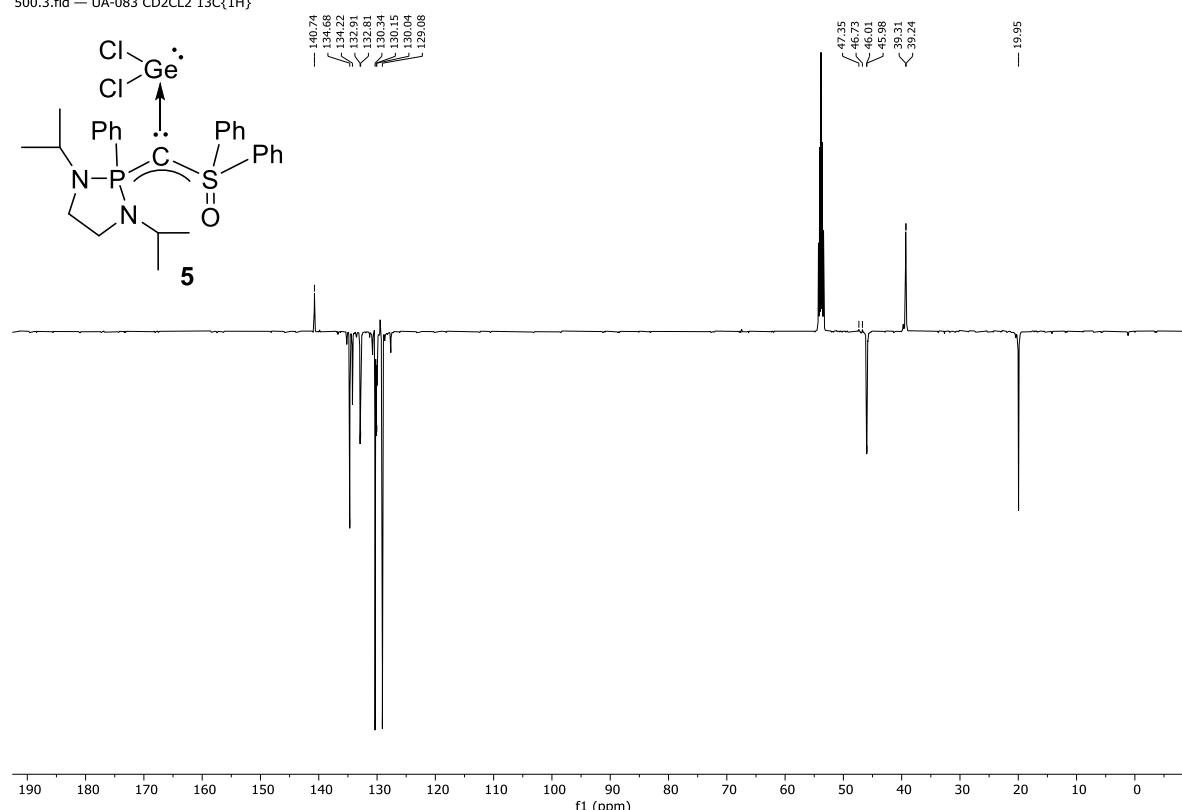
Figure S2: J-mod ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$)

— 50.92
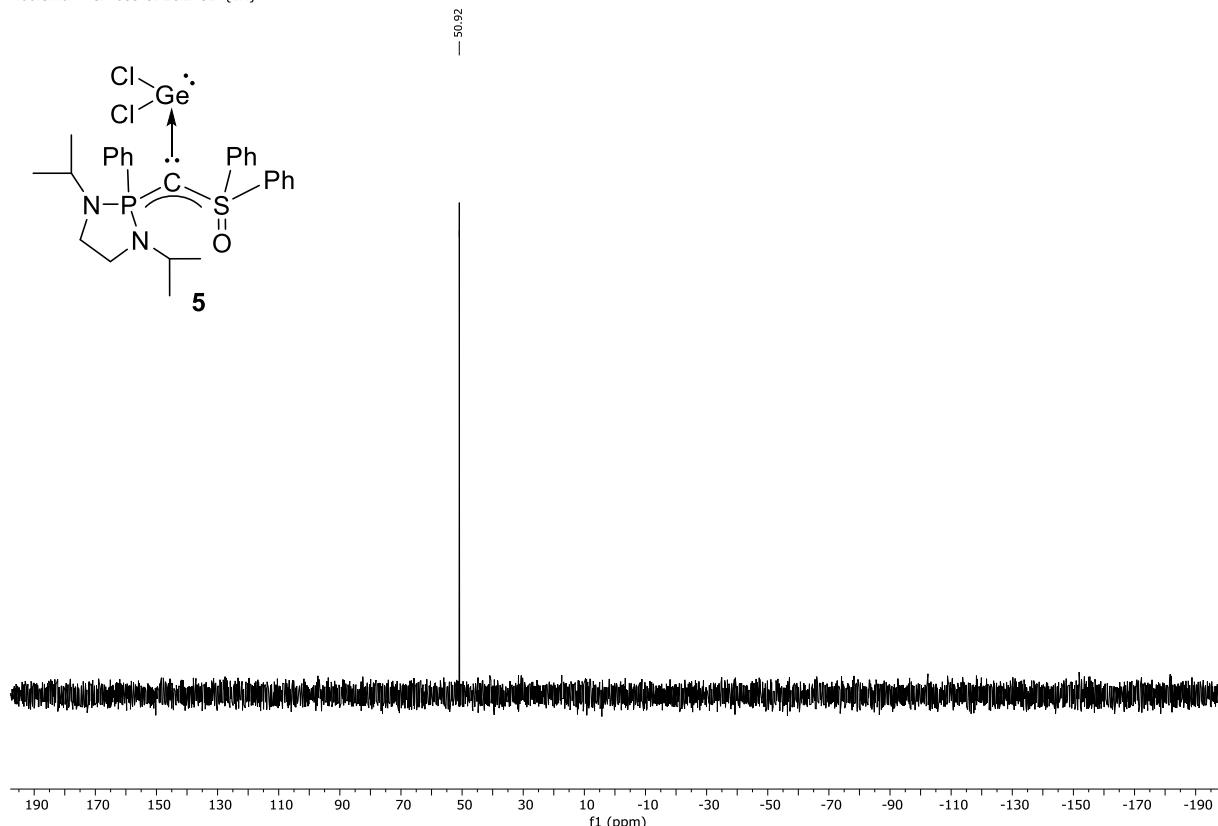
Figure S3: $^{31}P\{1H\}$ NMR (161 MHz, CD$_2$Cl$_2$)

authesserre_u_300a.29.fid — hfa ECOIH — UA-085-BY-GeCl2 in benzene — 31P{

— 49.47
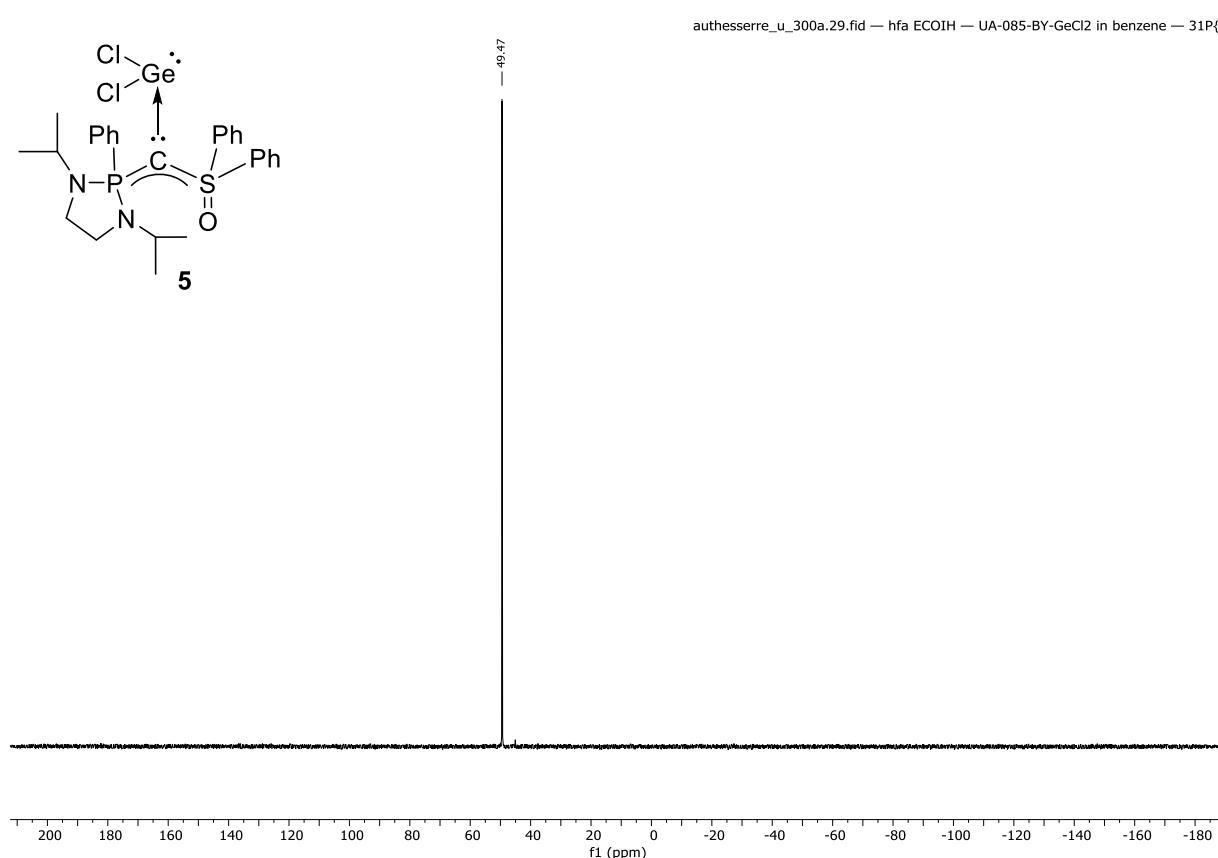
Figure S4: $^{31}P\{1H\}$ NMR (161 MHz, C$_6$D$_6$)
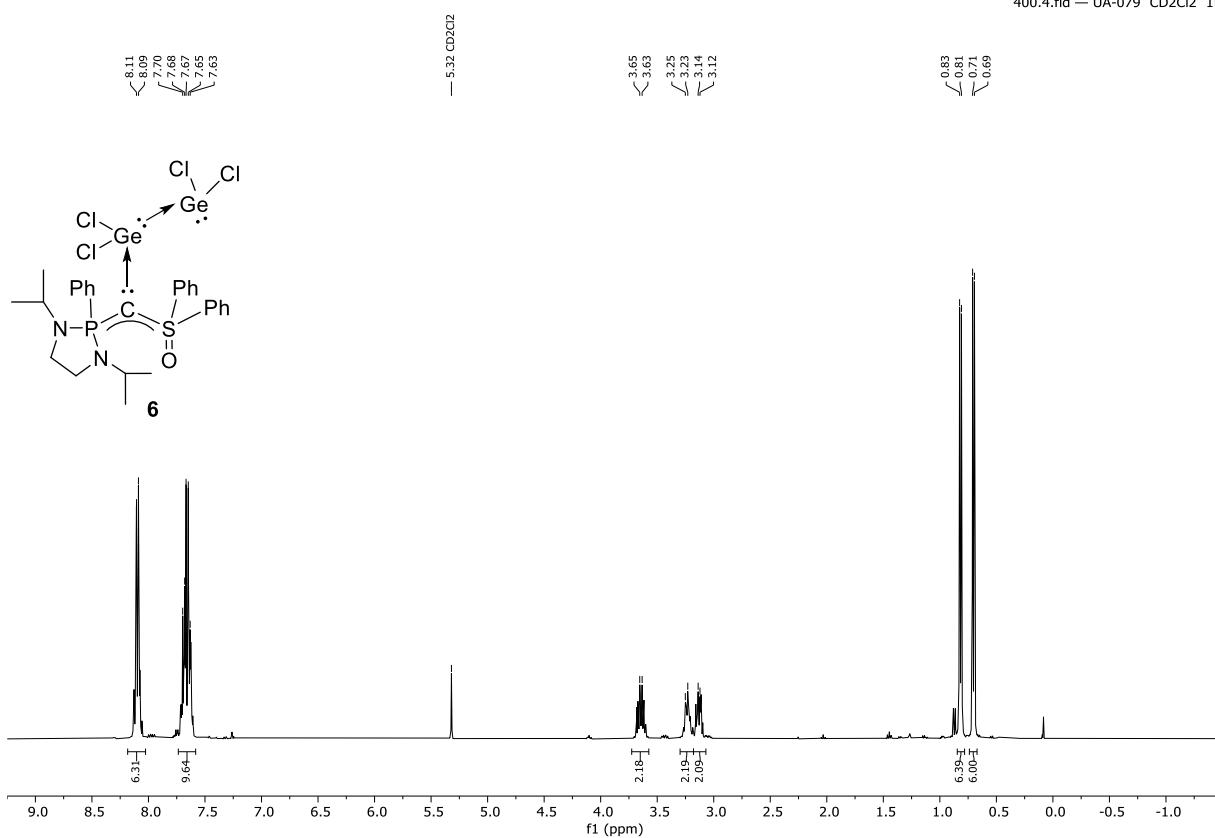
Figure S5: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$)
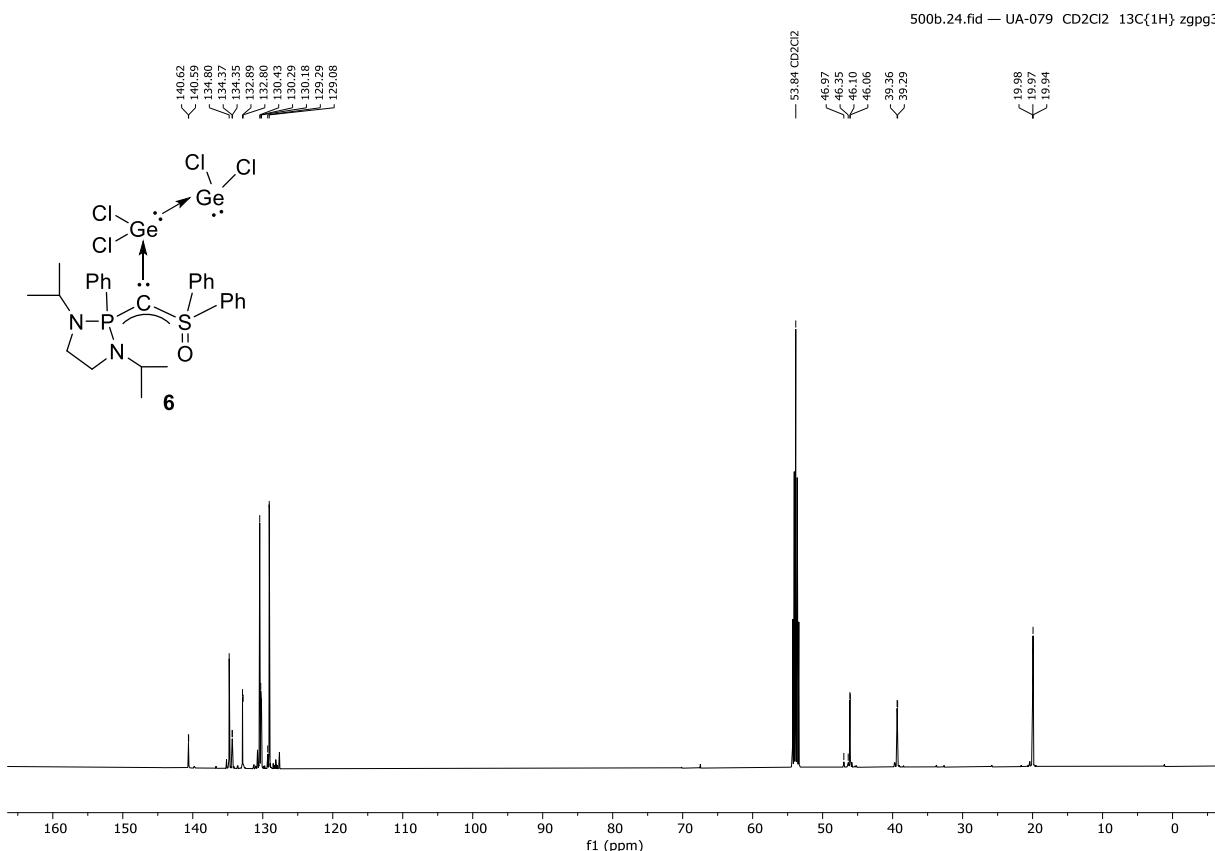
Figure S6: ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$)

140.57
140.54
135.17
135.14
134.80
134.39
134.35
132.99
132.89
132.77
130.74
130.43
130.36
130.31
130.17
129.12
129.06
128.50
127.61

54.38 CD2Cl2
54.11 CD2Cl2
53.84 CD2Cl2
53.84 CD2Cl2
53.57 CD2Cl2
53.30 CD2Cl2
46.10
46.04
45.82
45.77
39.73
39.65
39.35
39.26

20.43
20.37
20.10
20.06
19.97
19.95
19.92

6

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
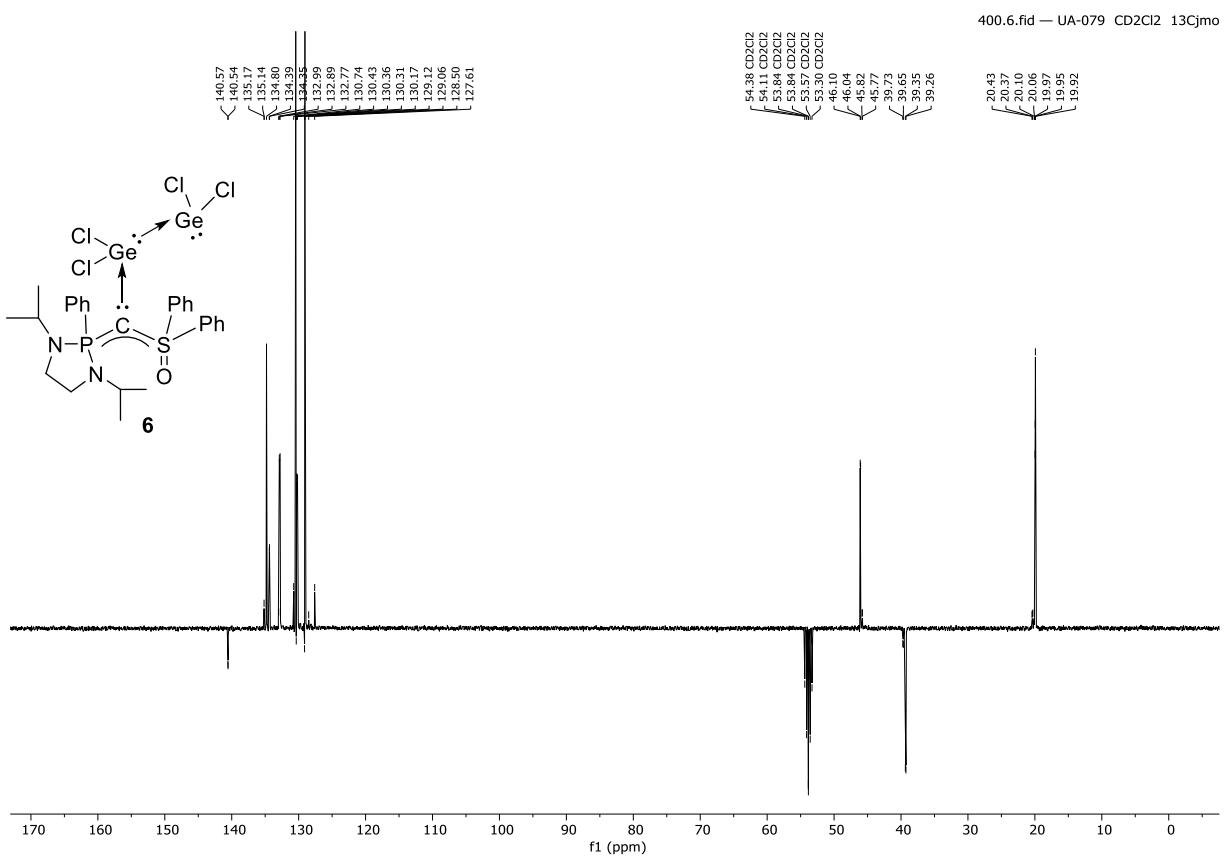
Figure S7: J-Mod^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$)

51.14
45.00

6

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)
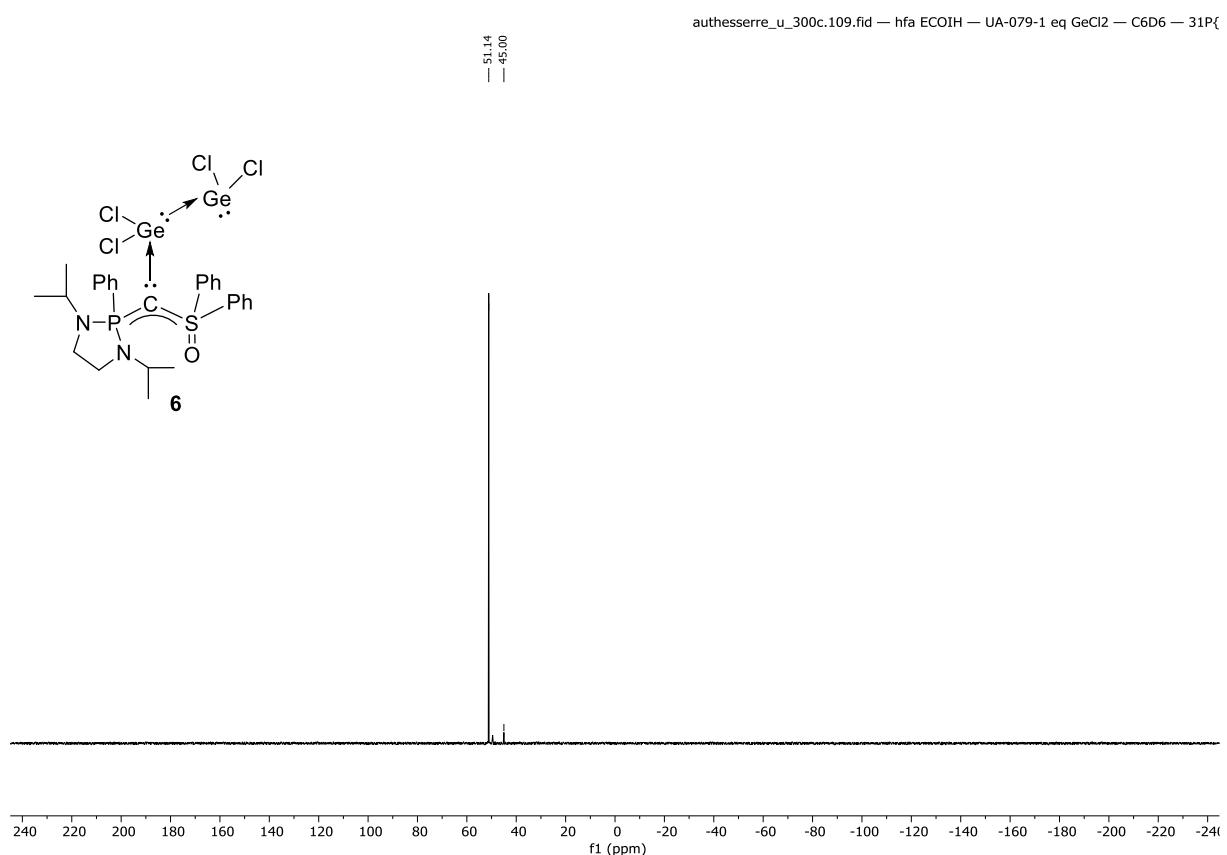
Figure S8: ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$)

51.15
44.76

100.00
3.25

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -24(
f1 (ppm)
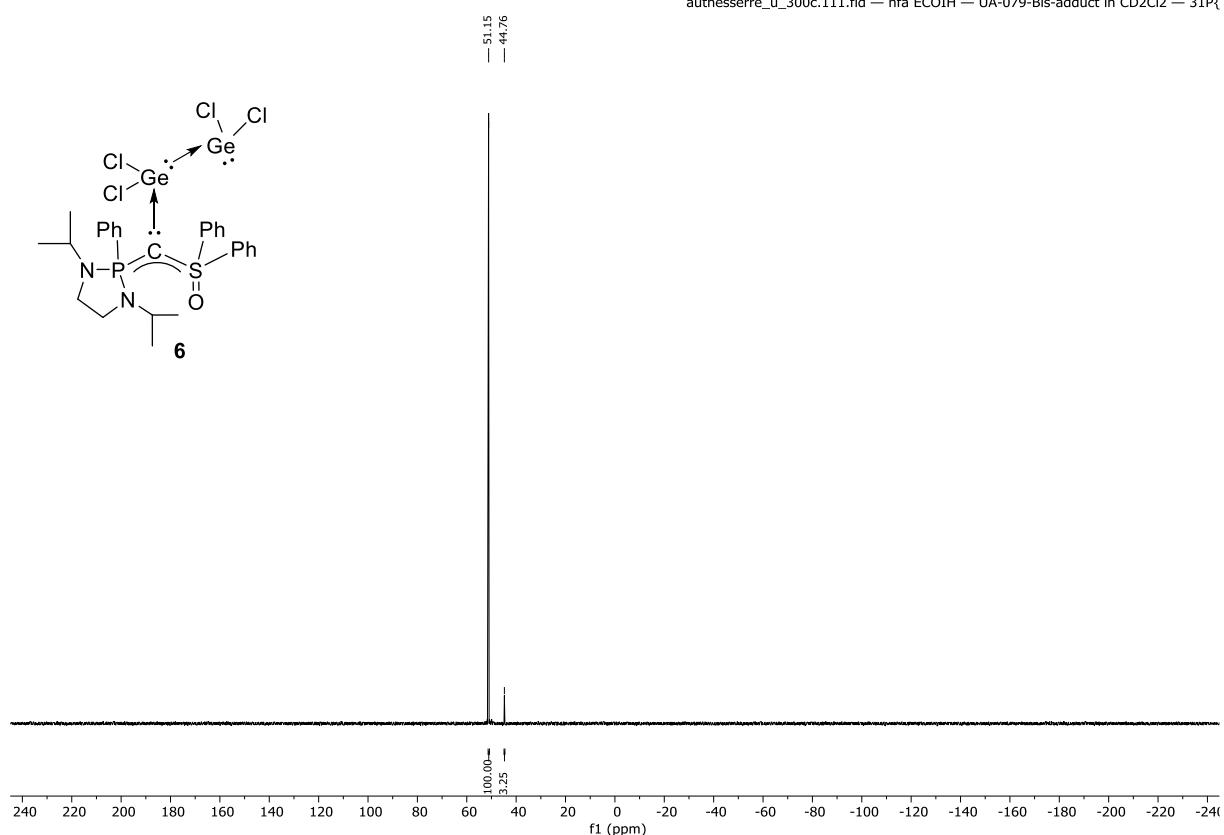
Figure S9: $^{31}P\{^1H\}$ NMR (121 MHz, CD$_2$Cl$_2$)

authesserre_u_300c.137.fid
hfa ECOIH
UA-019-75h heating
C6D6

56.29
44.70
29.08

50.53
4.12
45.05

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)
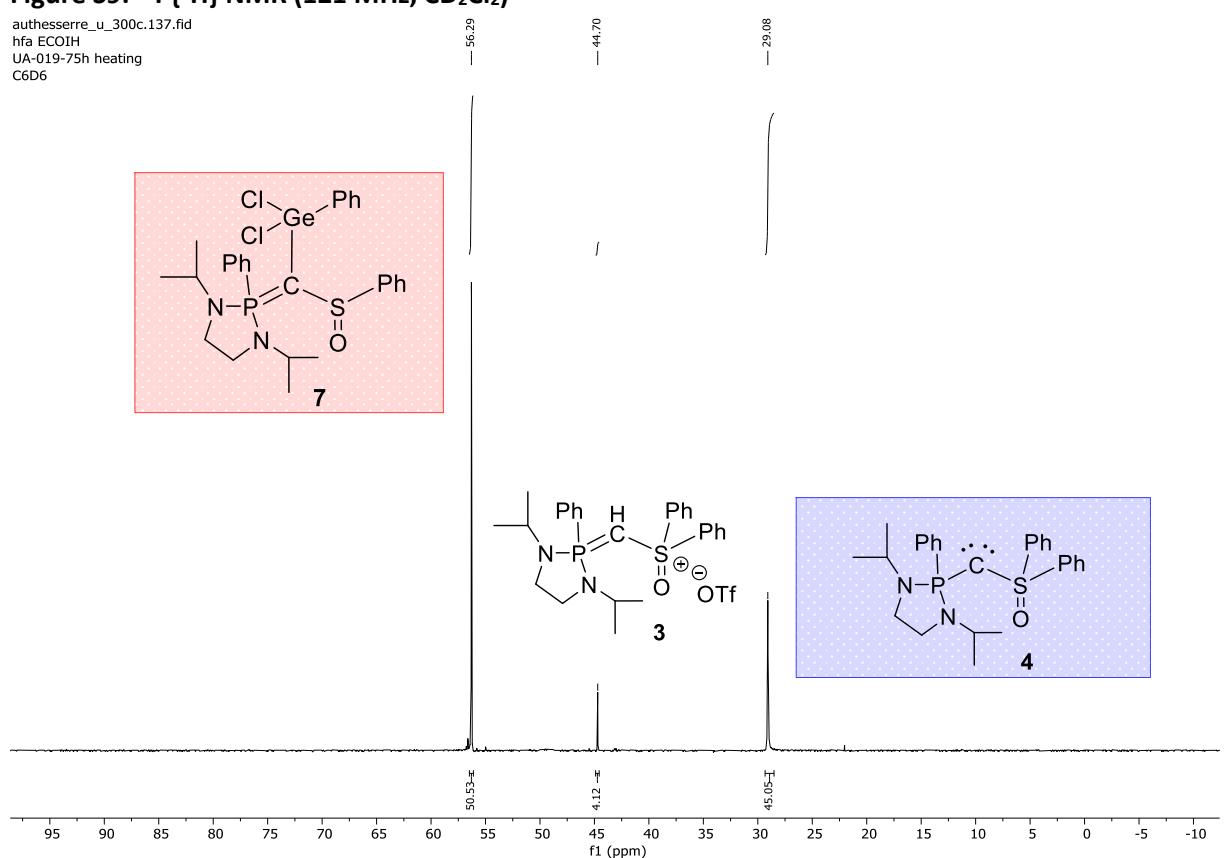
Figure S10: $^{31}P\{^1H\}$ NMR (121 MHz, C$_6$D$_6$)

authesserre_u_300c.136.fid
hfa ECOIH
UA-019-75h heating
C6D6

dioxane
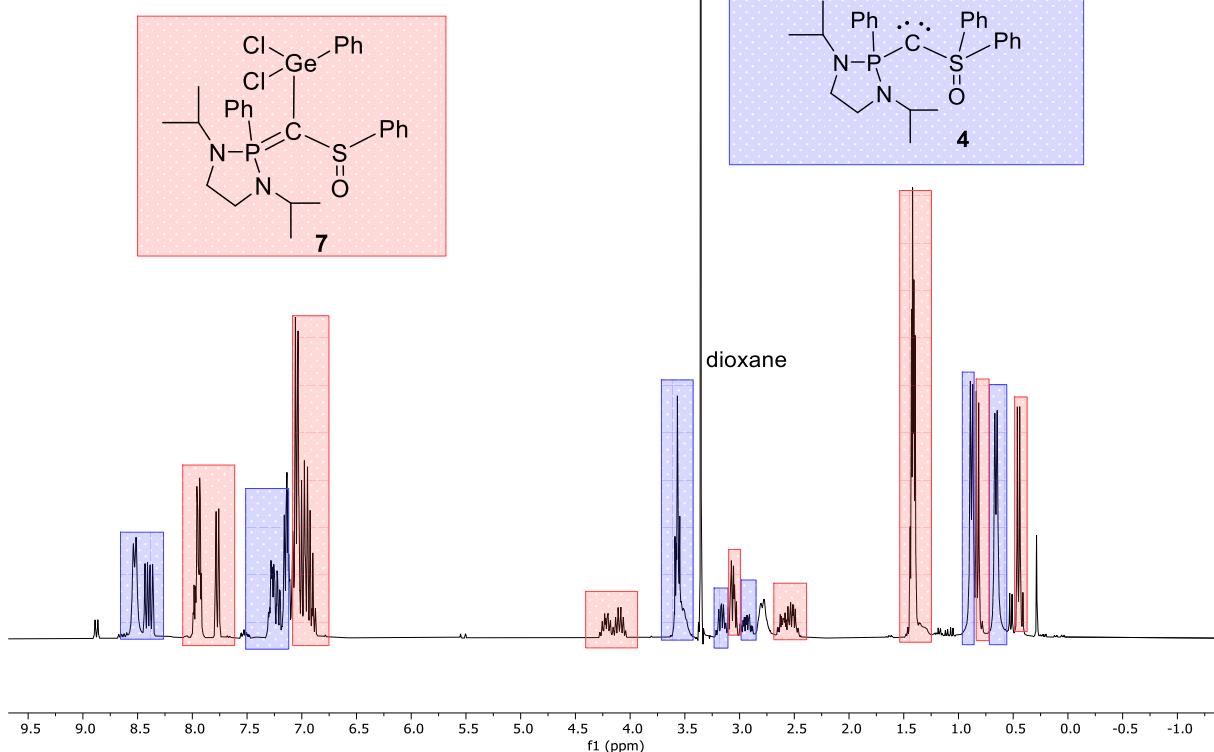
Figure S11: ^{1}H NMR (300 MHz, C$_6$D$_6$)


RMN.48.fid
UA-150 C6D6 31P{1H}

1.00

0.07
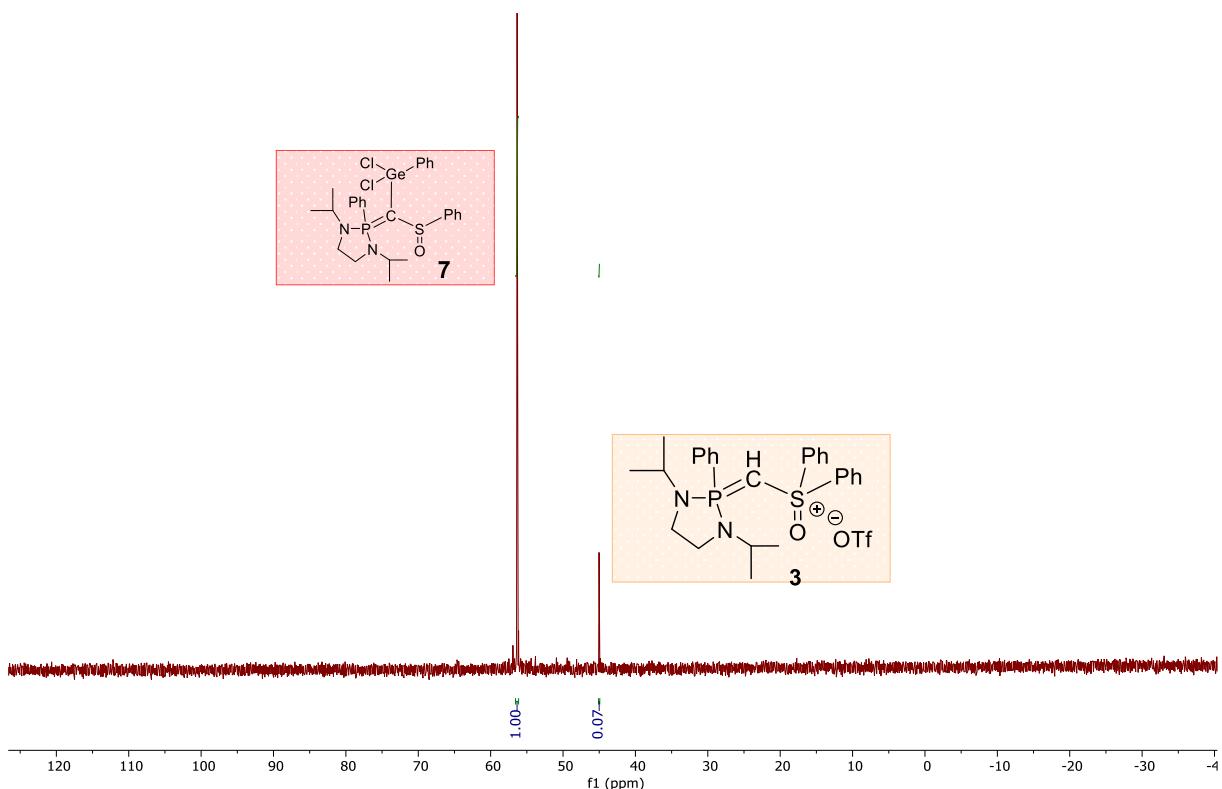
Figure S12: ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$) Migration reaction using 10 mol% of **4**, that get reprotonated into **3** at the end of the heating.
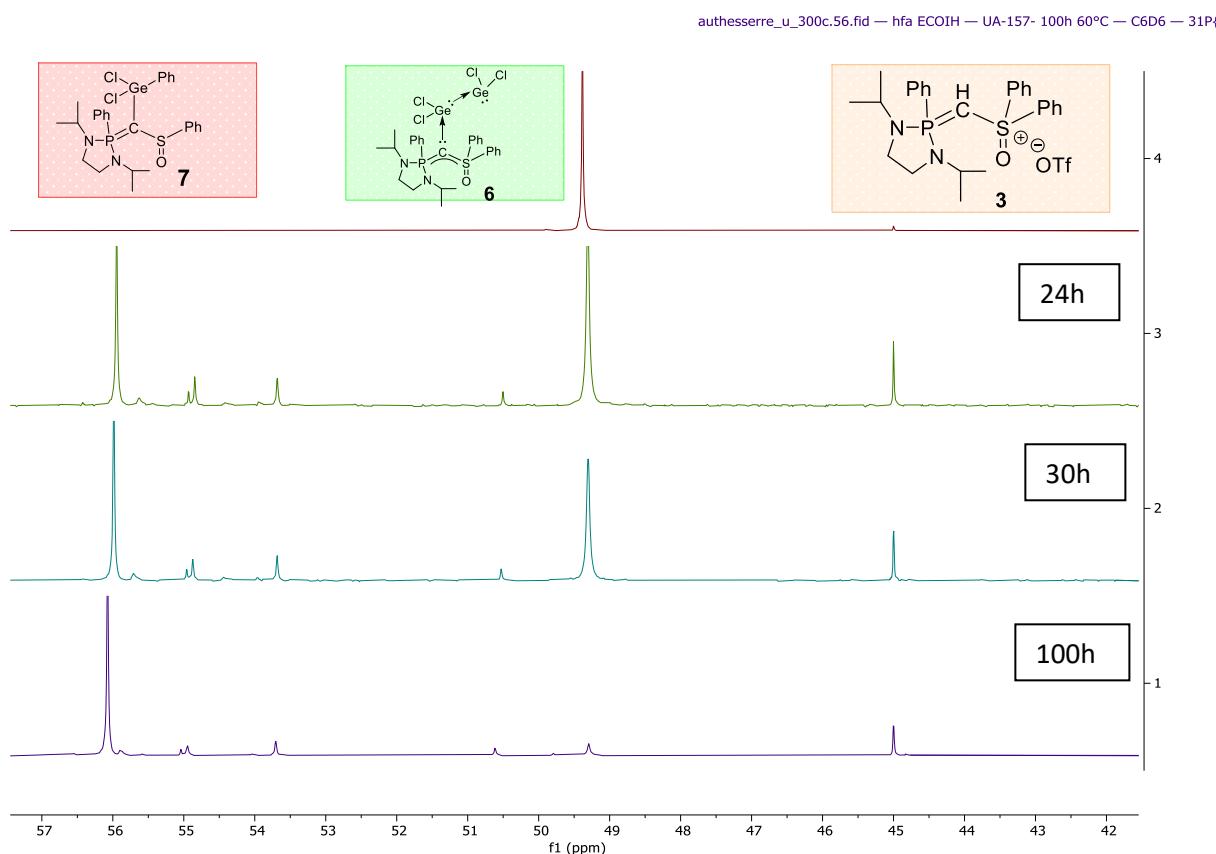
**Figure S13: Monitoring ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$)** Migration reaction using 15 mol% of Et$_3$N.
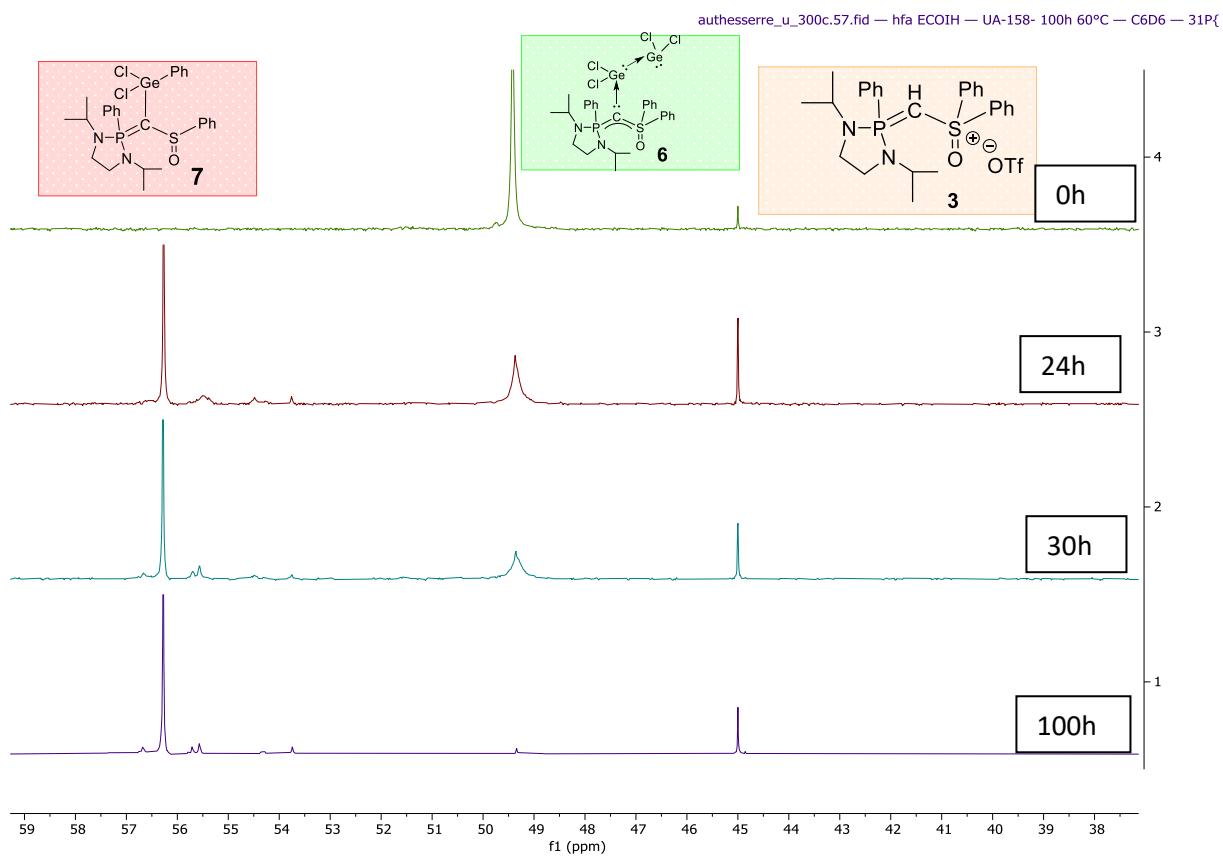

Figure S14: Monitoring ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$) Migration reaction using 15 mol% of DMAP.

X-ray analysis

The data of the structures for **5**, **6** and **7** were collected at 193 K on a Bruker-AXS APEX II CCD Quazar diffractometer (**7**) equipped with a 30 W air-cooled microfocus source or on a Brucker-AXS D8-Venture diffractometer (**5** and **6**) equipped with a CMOS Area detector with MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [44]. The structures were solved using an intrinsic phasing method (ShelXT) [45] and refined using the least–squares method on F^2 (ShelXL-2014) [46]. All non-H atoms were treated anisotropically. All H atoms attached to C atoms were fixed geometrically and treated as riding on their parent atoms with C-H = 0.95 Å (aromatic), 0.98 Å (CH_3), 0.99 Å (CH_2) or 1.0 Å (CH) with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$ or $U_{iso}(H) = 1.5U_{eq}(CH_3)$. Supplementary crystallographic data for CCDC-2068304 (**5**), CCDC-2068305 (**6**), CCDC-2068306 (**7**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

The details of data collection and crystal structures refinement are summarized in Table 1.

Table S1. Crystallographic data for the compounds **5**, **6** and **7**

| Compound	5	6	7
Chemical formula	$C_{27}H_{33}Cl_2GeN_2OPS$	$C_{27}H_{33}Cl_4Ge_2N_2OPS$	$C_{27}H_{33}Cl_2Ge\ N_2OPS$
M_r	608.07	751.56	608.07
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a [Å]	10.3934(6)	11.2219(5)	9.0496(12)
b [Å]	15.3160(9)	18.1701(7)	14.5792(16)
c [Å]	18.0563(11)	15.7026(6)	22.036(3)
α [°]	90	90	90
β [°]	90	93.4488(15)	90.653(4)
γ [°]	90	90	90
V [Å^3]	2874.3(3)	3196.0(2)	2907.2(6)
Z	4	4	4
ρ [g cm^{-3}]	1.405	1.562	1.389
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.403	2.355	1.387
Reflections collected	113982	125271	72609
Independent reflections	7146 R(int)=0.0627	9769 R(int)=0.0497	5915 R(int)=0.1491
Data/ restraints/ parameters	7146/0/320	9769/0/347	5915/0/320
Crystal size [mm^3]	0.460x0.200x0.160	0.380×0.200×0.120	0.100×0.060×0.020
GOOF on F^2	1.070	1.029	1.030
R (I > 2σ(I))	0.0291	0.0306	0.0456
wR2 (all data)	0.0561	0.0741	0.0916
Largest difference peak and hole, [e Å^{-3}]	0.337 and -0.267	0.666 and -0.613	0.343 and -0.453
CCDC number	2068304	2068305	2068306
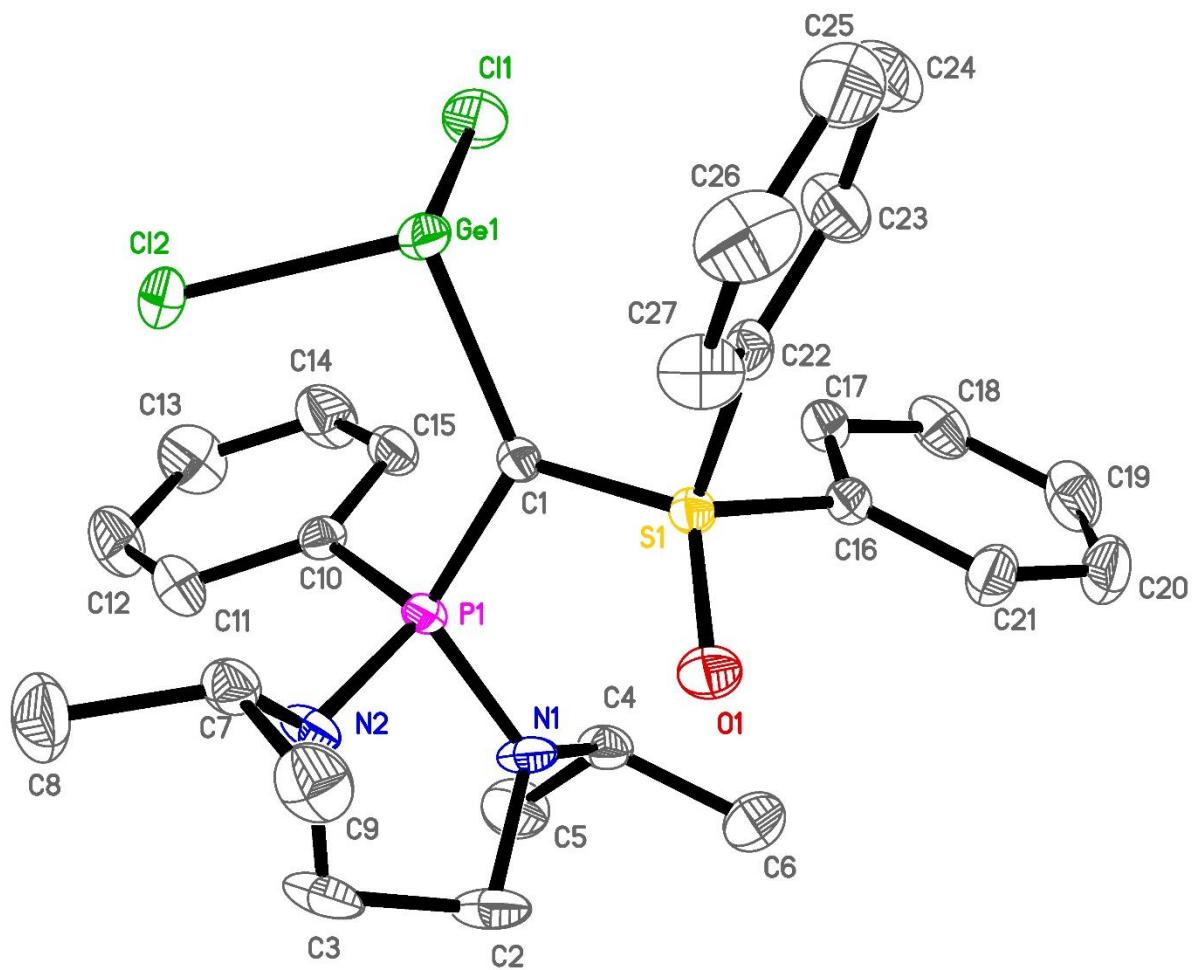
Figure S15: Molecular view of **5**. Thermal ellipsoids set at 50 % probability. H atoms are omitted for clarity. Selected bond lengths [Å]:

C1-Ge1 2.071(2), C1-P1 1.725(2), C1-S1 1.650(2), P1-C10 1.802(3), S1-O1 1.457(2), Ge1-Cl2 2.299(1), Ge1-Cl1 2.331(1), P1-N1 1.649(2), P1-N2 1.648(2), S1-C22 1.780(3), S1-C16 1.784(3). P1-C1-S1 113.73(14), P1-C1-Ge1 128.12(13), Ge1-C1-S1 115.65(13), C1-Ge1-Cl2 96.82(7), Cl2-Ge1-Cl1 95.37(3), Cl1-Ge1-C1 98.81(7).
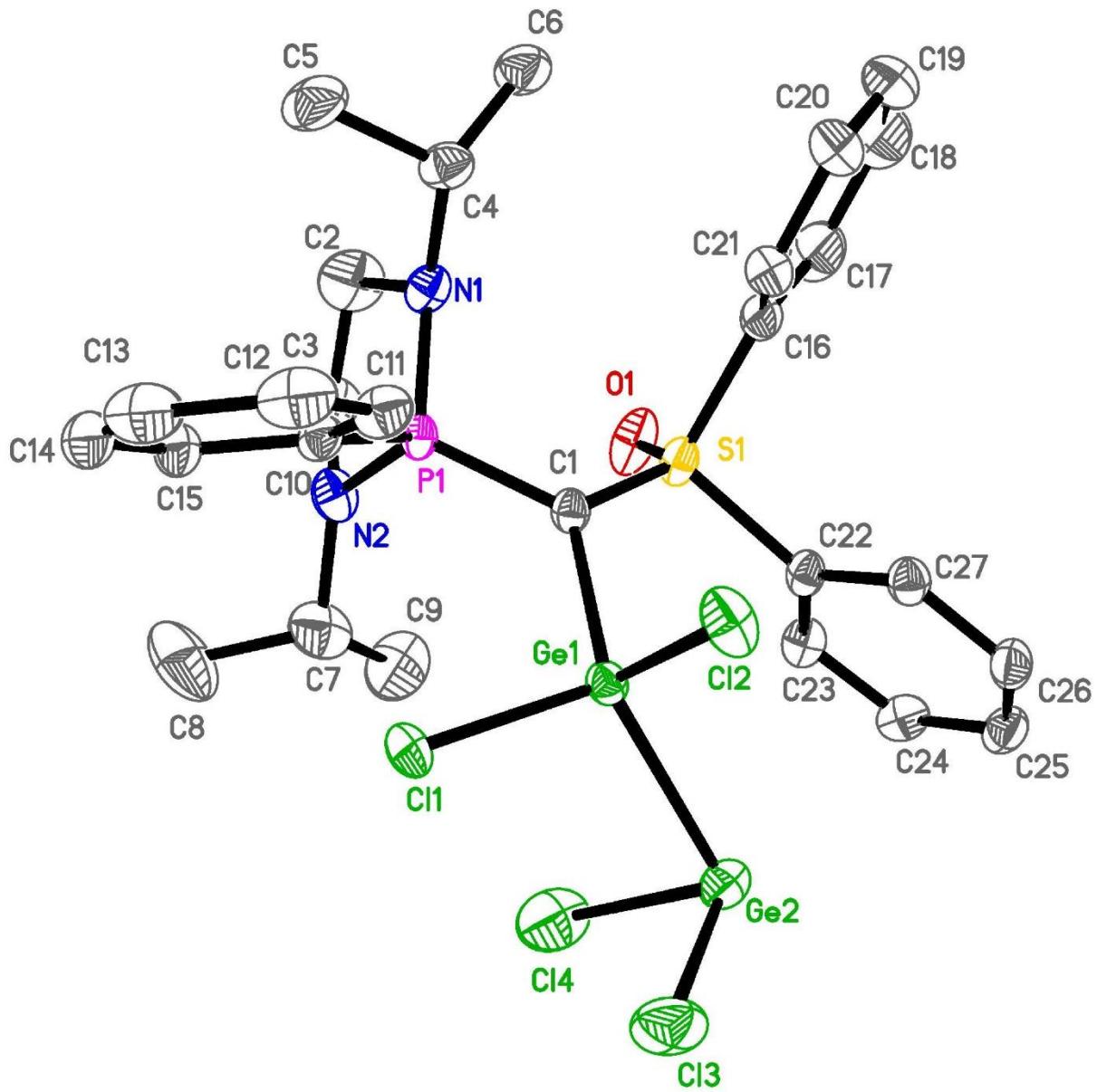
Figure S16: Molecular view of **6**. Thermal ellipsoids set at 50 % probability. H are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-Ge1 1.980(2), C1-P1 1.748(2), C1-S1 1.665(2), Ge1-Ge2 2.582(1), Ge1-Cl1 2.185(1), Ge1-Cl2 2.245(1), Ge2-Cl4 2.267(1), Ge2-Cl3 2.275(1), P1-C10 1.792(2), S1-O1 1.455(1), S1-C22 1.778(2), S1-C16 1.782(2), P1-C1-S1 112.40(10), P1-C1-Ge1 127.01(9), Ge1-C1-S1 117.30(9), C1-Ge1-Cl1 105.44(5), Cl1-Ge1-Cl2 101.33(2), Cl2-Ge1-Ge2 107.25(2), Cl1-Ge1-Ge2 109.25(2), Ge1-Ge2-Cl4 92.09(2), Cl4-Ge2-Cl3 98.84(3), Ge1-Ge2-Cl3 89.41(2).
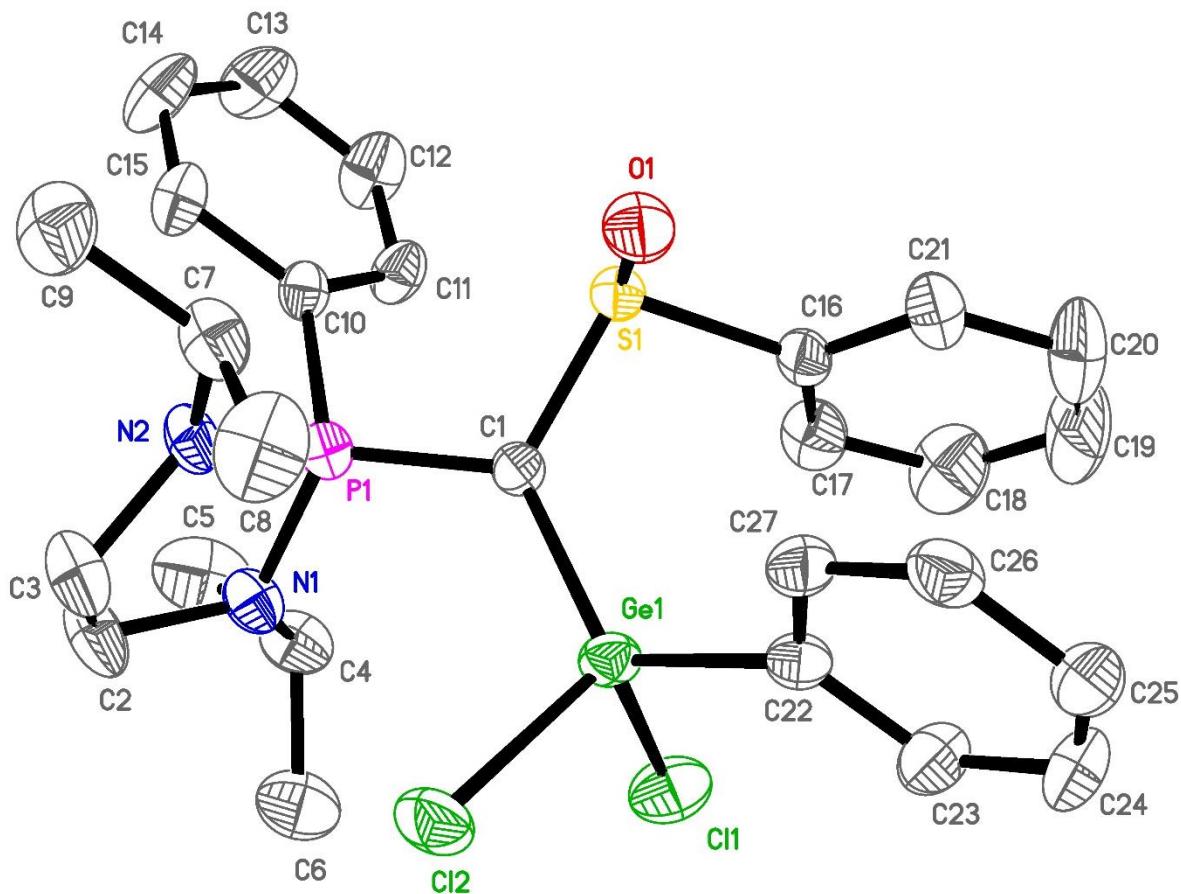
Figure S17: Molecular view of **7**. Thermal ellipsoids set at 50 % probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.707(3), C1-S1 1.744(3), C1-Ge1 1.891(3), Ge1-C22 1.927(3), Ge1-C22 1.927(3), Ge1-Cl2 2.172(1), Ge1-Cl1 2.173(1), P1-C10 1.805(3), S1-O1 1.499(2), S1-C16 1.800(4), P1-C1-S1 114.48(18), S1-C1-Ge1 120.89(17), Ge1-C1-P1 122.37(19), C1-Ge1-C22 119.52(14), C1-Ge1-Cl2 111.27(10), C22-Ge1-Cl2 104.77(10), C1-Ge1-Cl1 111.72(10), C22-Ge1-Cl1 106.65(11), Cl2-Ge1-Cl1 101.15(4), N1-P1-N2 94.89(15), N1-P1-C1 113.16(16), N2-P1-C1, 120.48(15), N1-P1-C10 111.60(15), N2-P1-C10 108.20(16), C1-P1-C10 107.98(16), O1-S1-C1 112.64(15), O1-S1-C16 105.28(16), C1-S1-C16 100.04(16), C4-N1-C2 119.6(3), C4-N1-P1 122.2(2), C2-N1-P1 111.5(2), C3-N2-C7 120.0(3), C3-N2-P1 113.4(2), C7-N2-P1 122.5(2).