Small Molecule Capture by P/Al-based Dimeric Lewis Pairs

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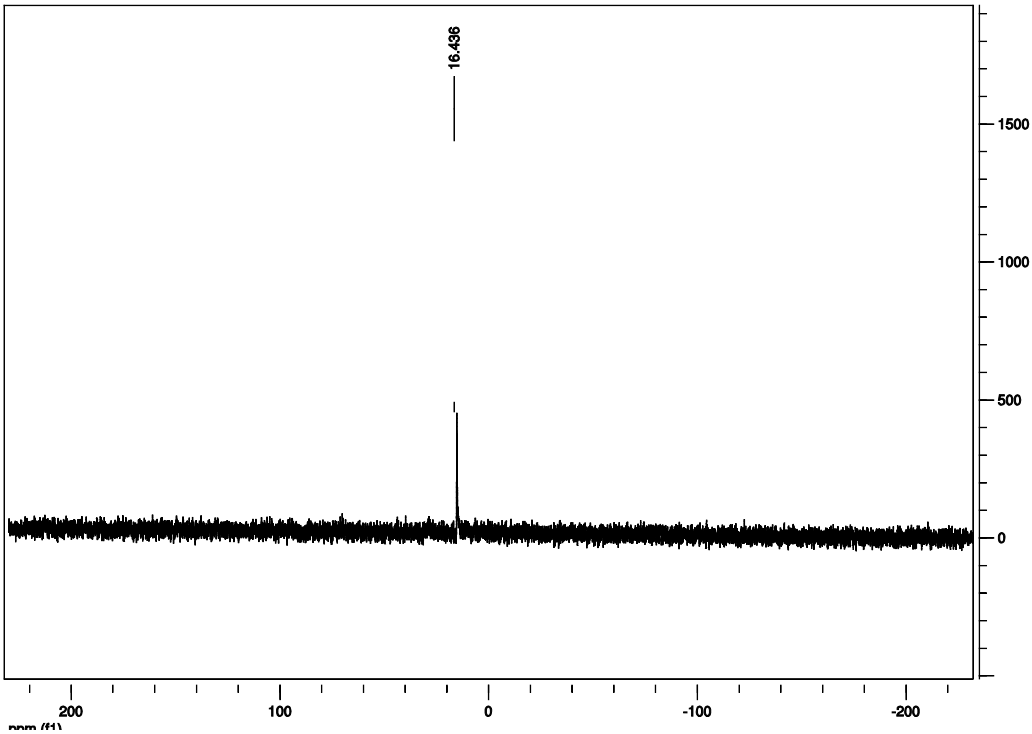
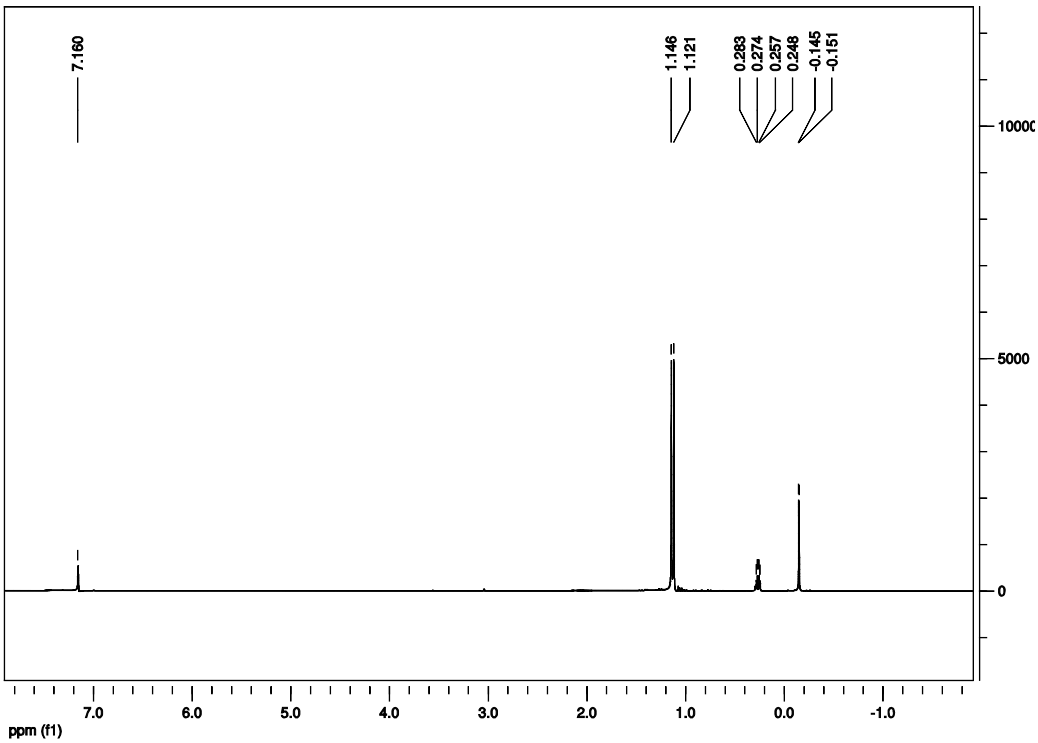
4. COMPUTED STRUCTURES 20

1. Experimental Section

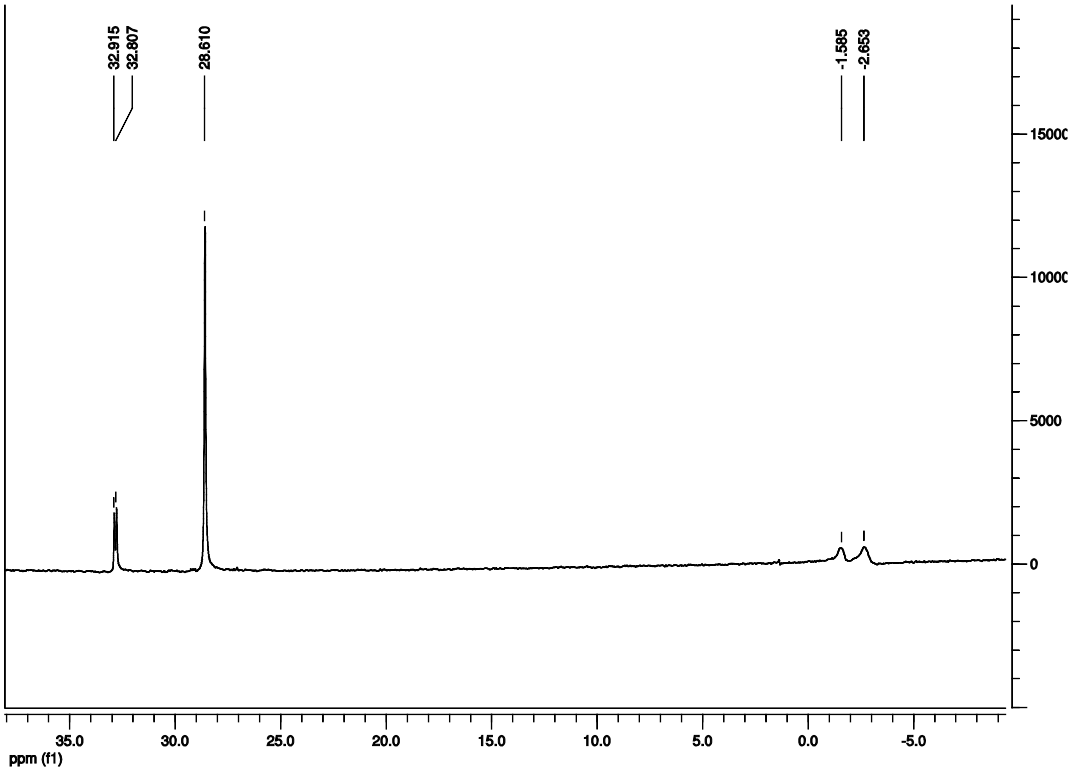
$^{31}P\{^{1}H\}$ NMR of $[1]_2$ in C_6D_6



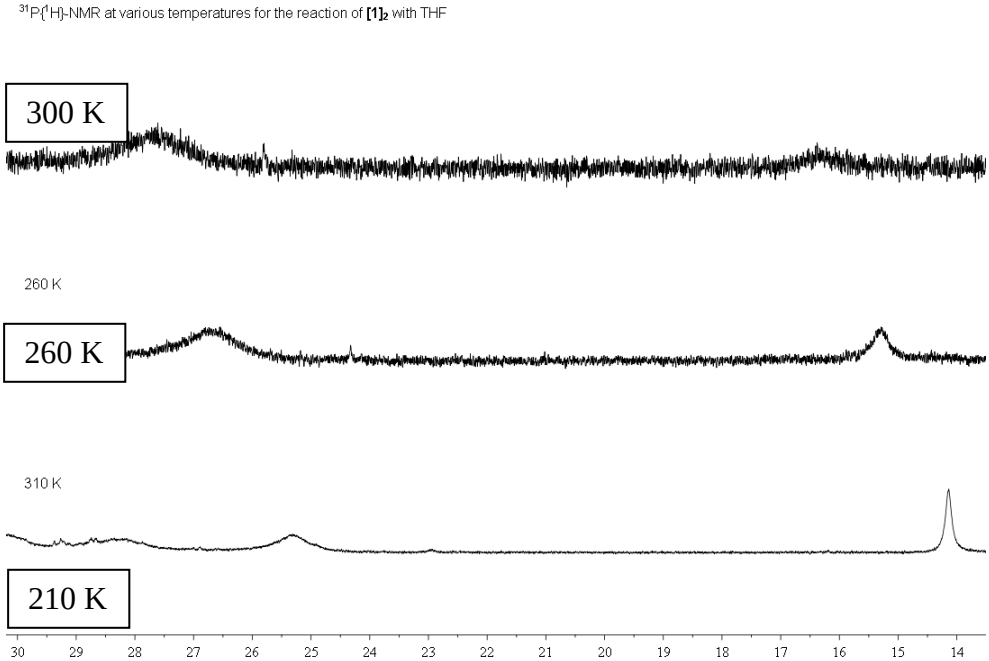
^{1}H NMR of $[1]_2$ in C_6D_6



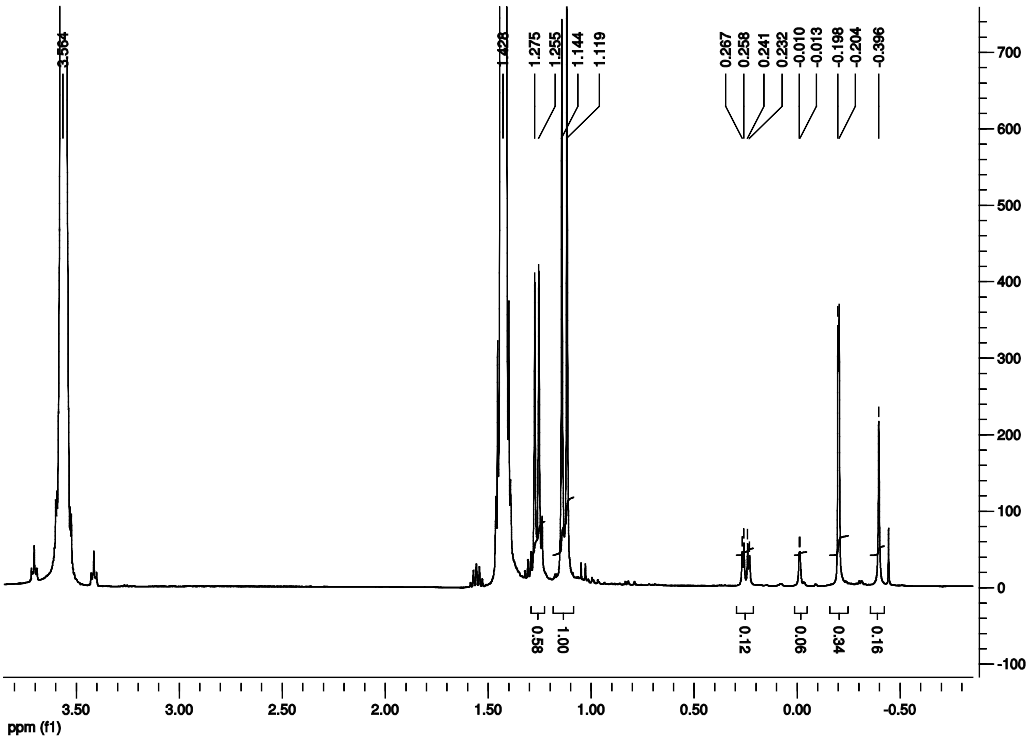
$^{13}C\{^1H\}$ NMR of $[1]_2$ in C_6D_6



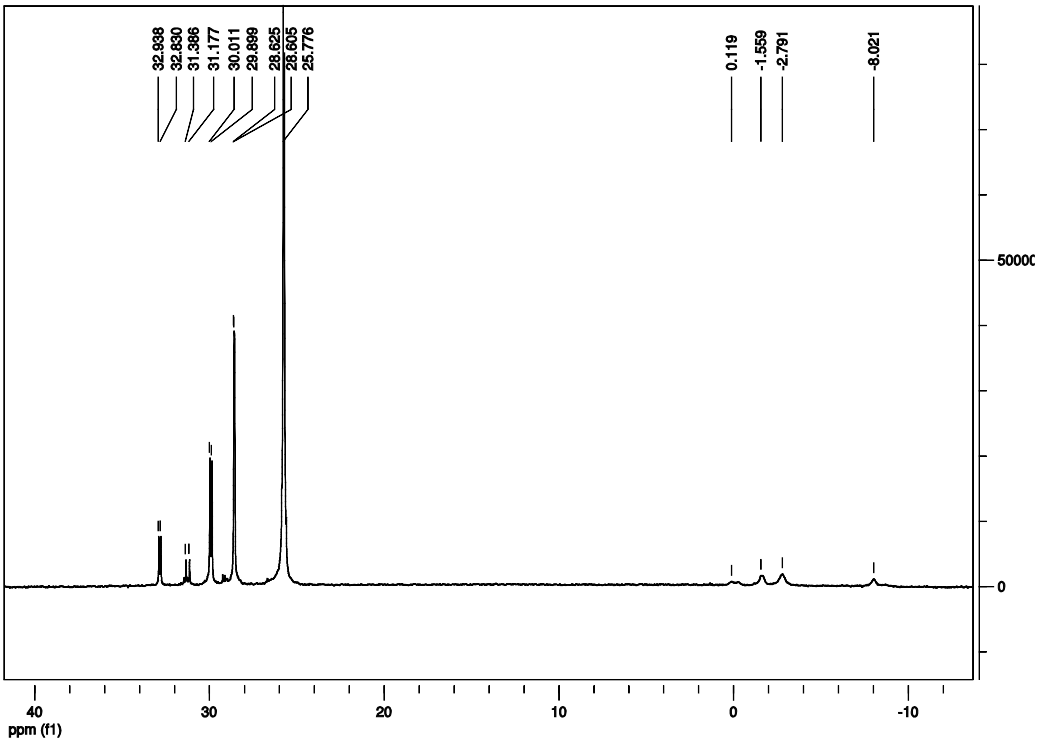
^{31}P NMR of $[1]_2$ and 1-THF in a 3:1 mixture of D-toluene and THF at various temperatures



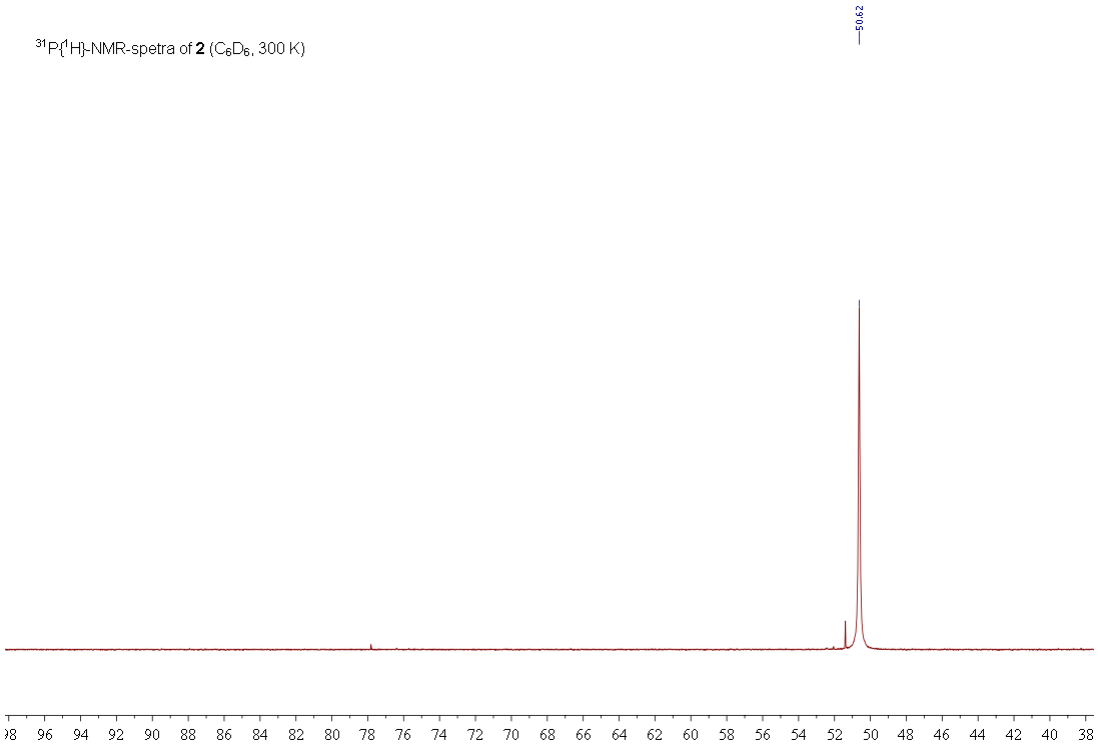
^{1}H NMR of $[1]_2$ and 1-THF in C_6D_6 and THF at ambient temperature



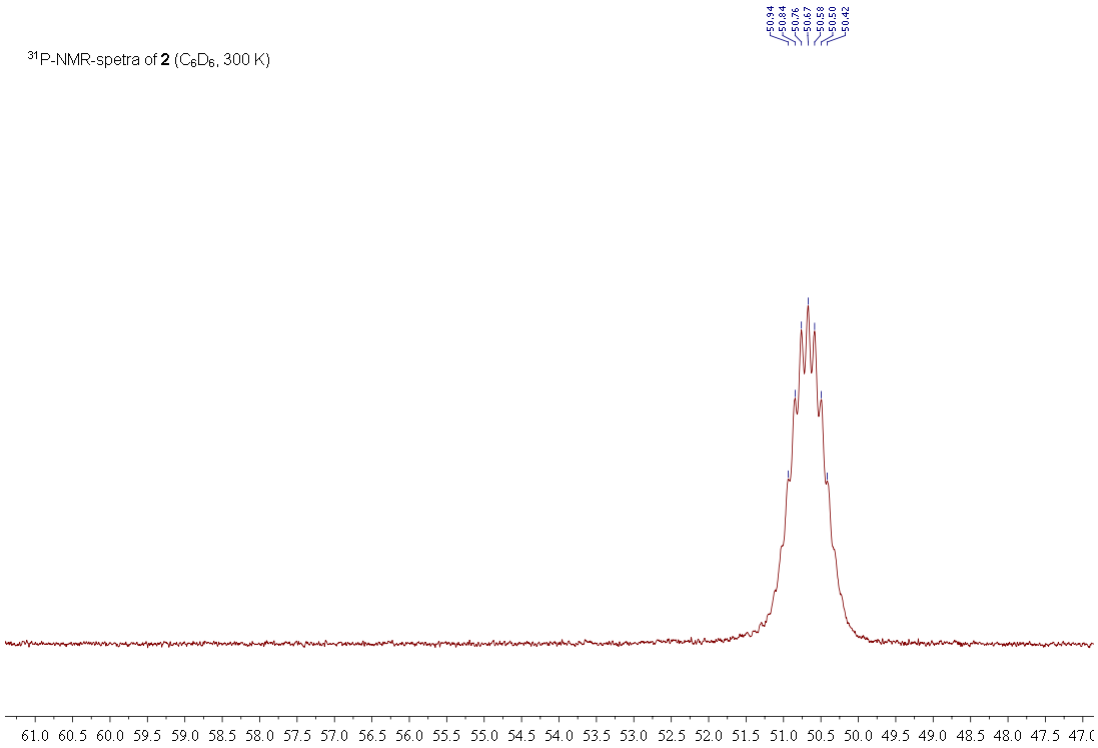
^{13}C NMR of $[1]_2$ and 1-THF in C_6D_6 and THF at ambient temperature



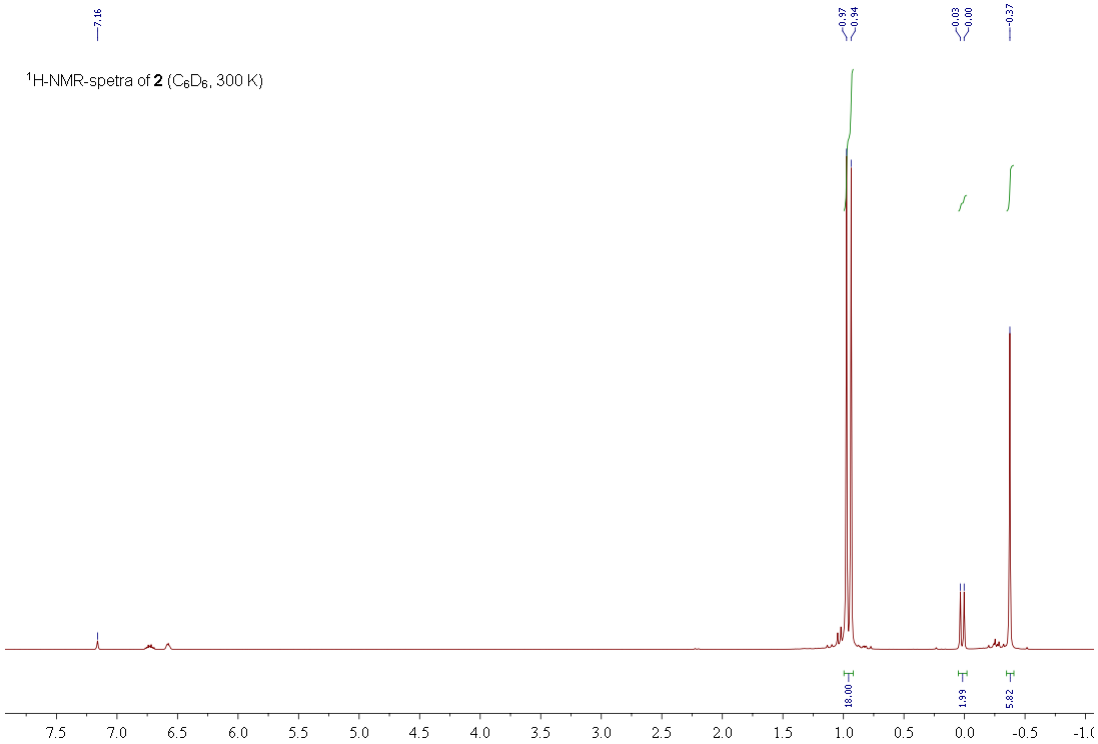
$^{31}P\{^{1}H\}$ NMR of 2 in C_6D_6



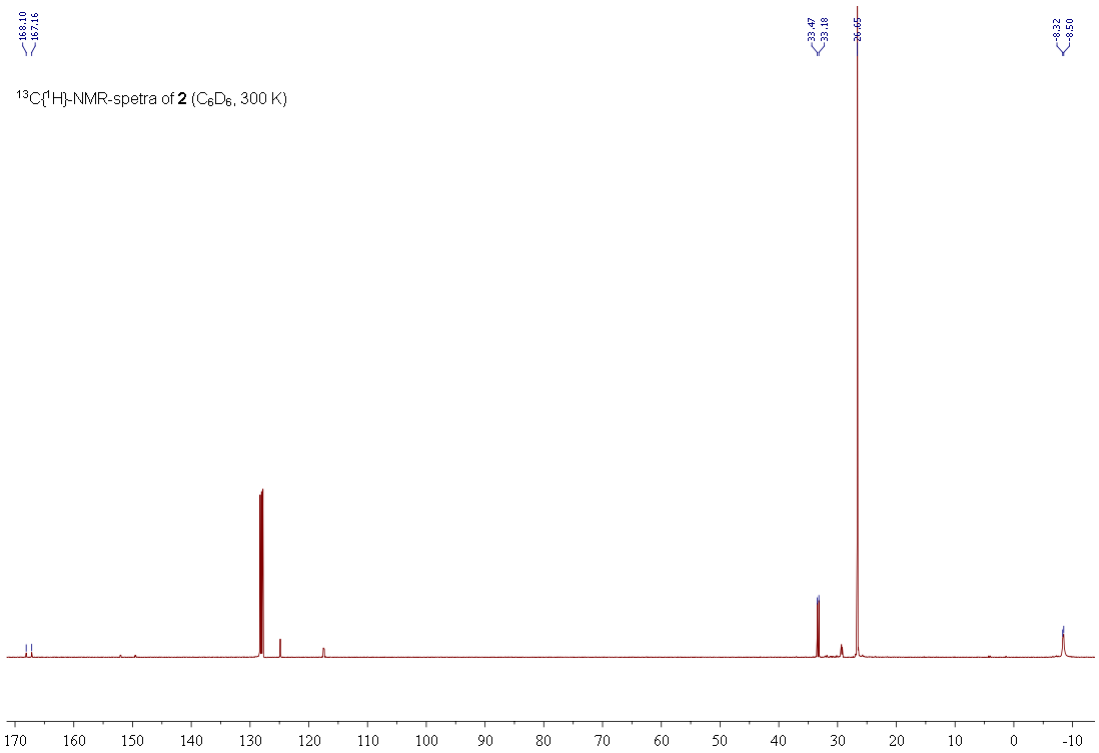
^{31}P NMR of 2 in C_6D_6



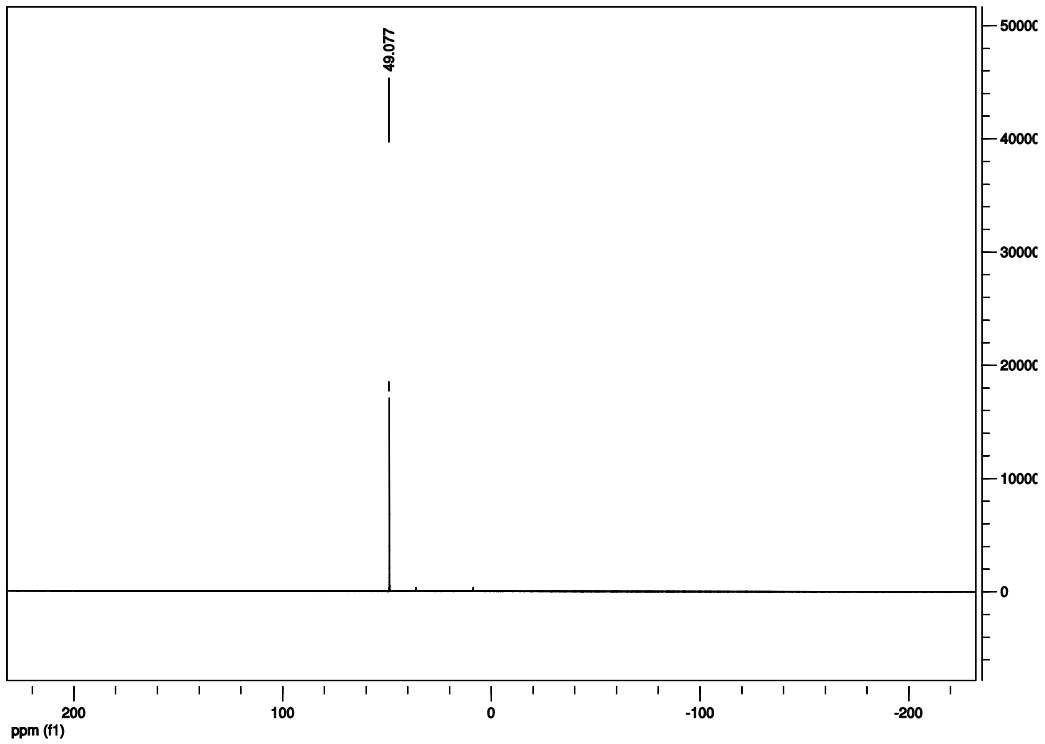
^{1}H NMR of 2 in C_6D_6



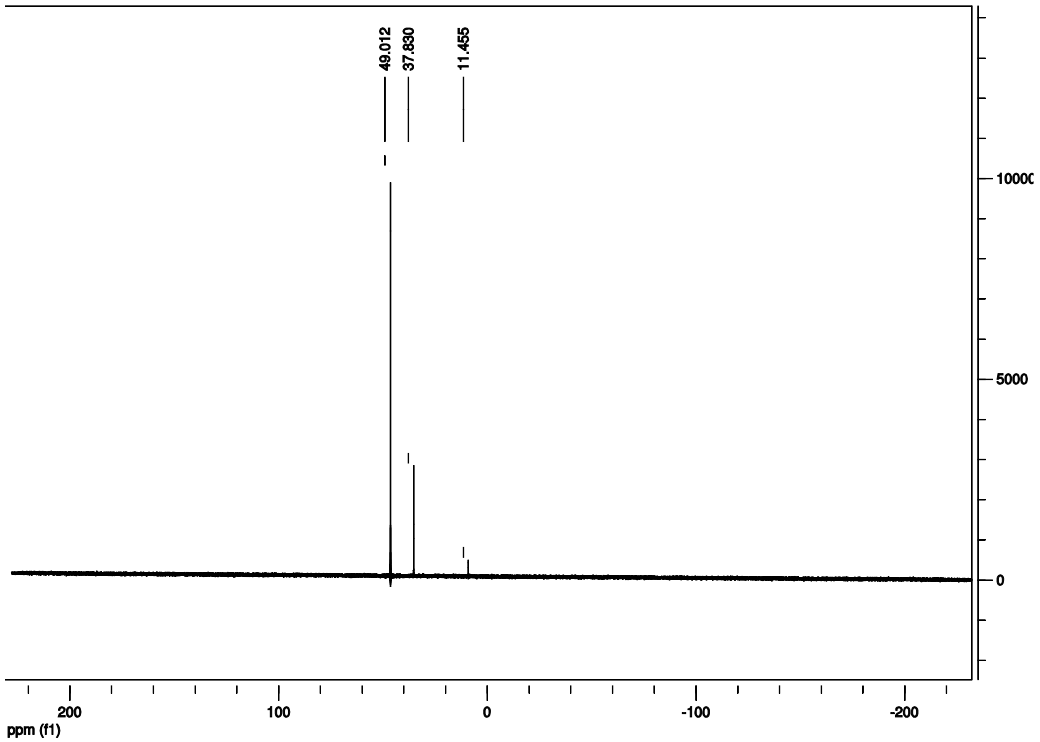
$^{13}C\{^{1}H\}$ NMR of 2 in C_6D_6



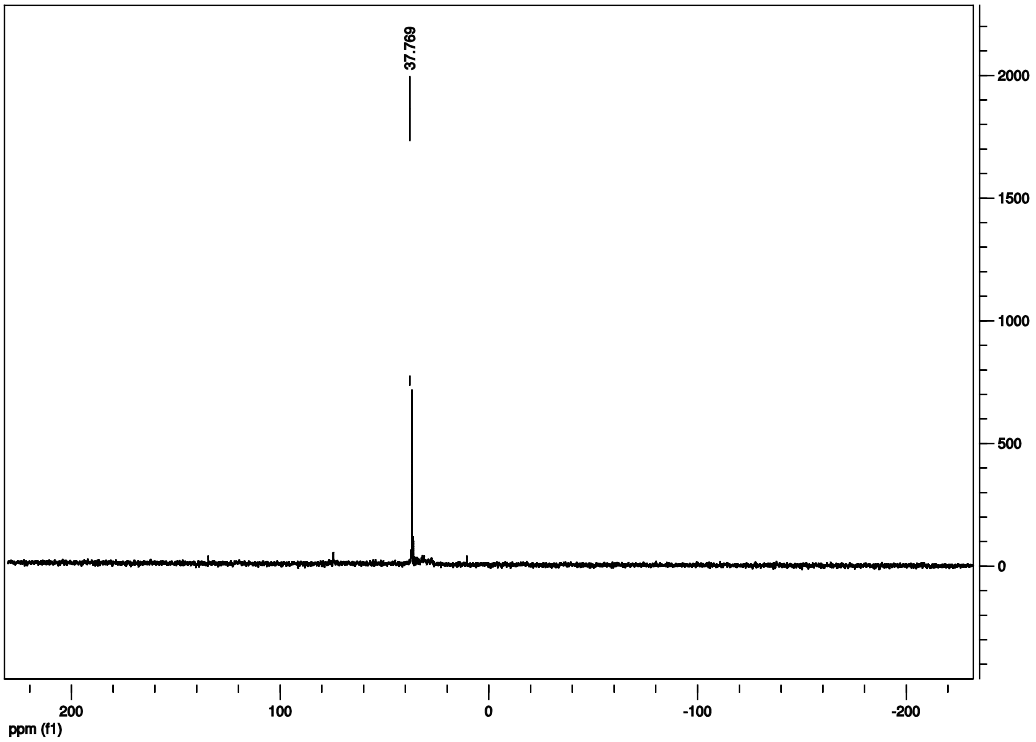
$^{31}P\{^{1}H\}$ NMR of 2 D-toluene



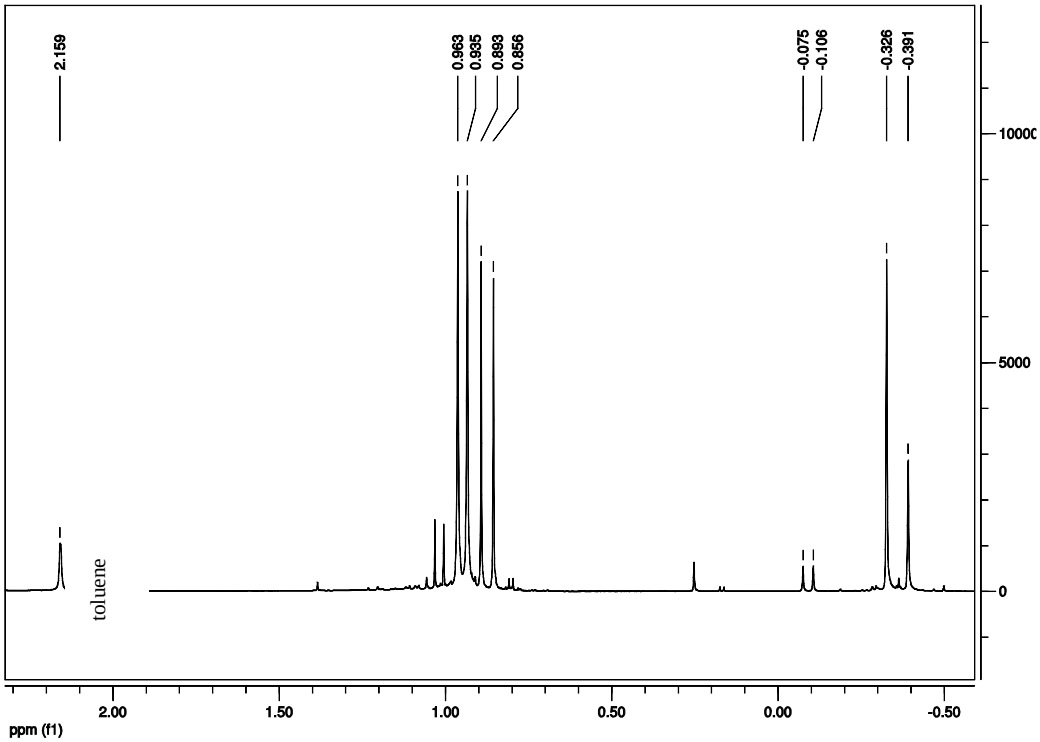
$^{31}P\{^{1}H\}$ NMR of 2 + $[3]_2$ (+ Me*P*t*Bu*$_2$) in D-toluene



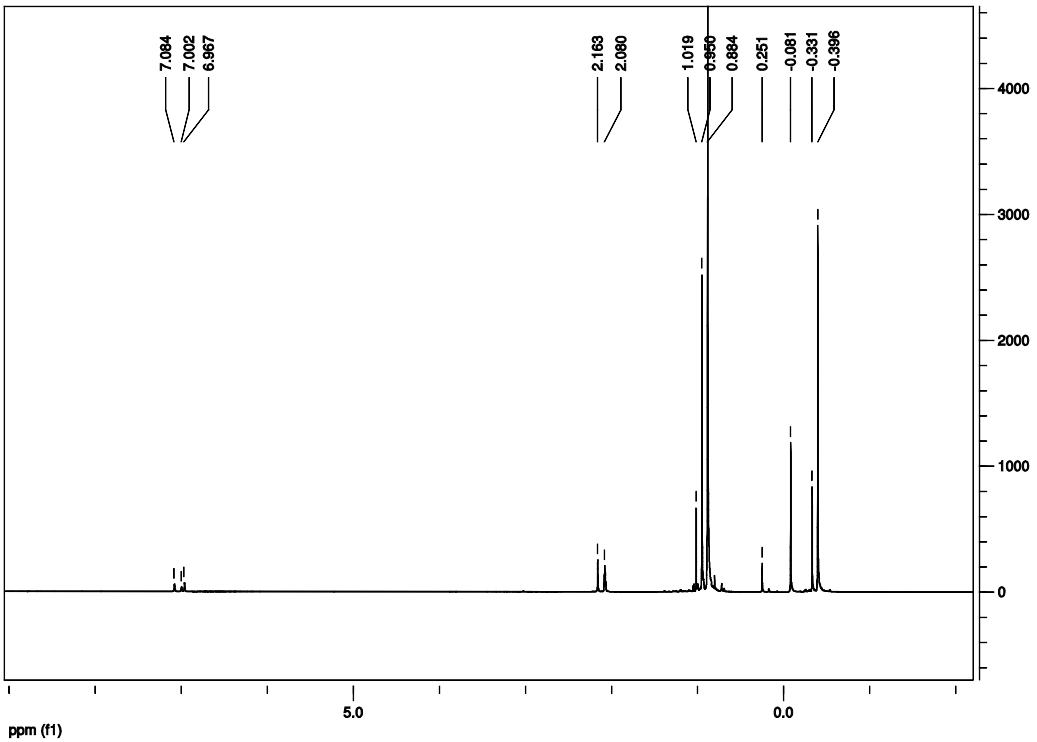
$^{31}P\{^{1}H\}$ NMR of $[3]_2$ in D-toluene



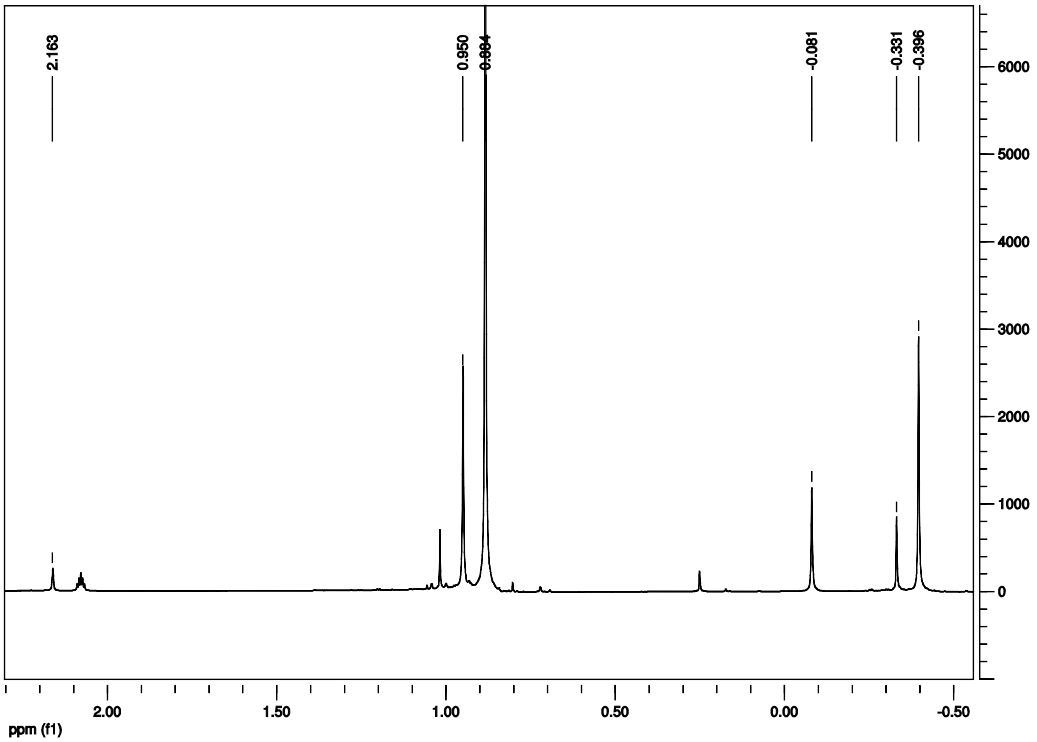
$^{1}H\{^{31}P\}$ NMR of 2 + $[3]_2$ in D-toluene



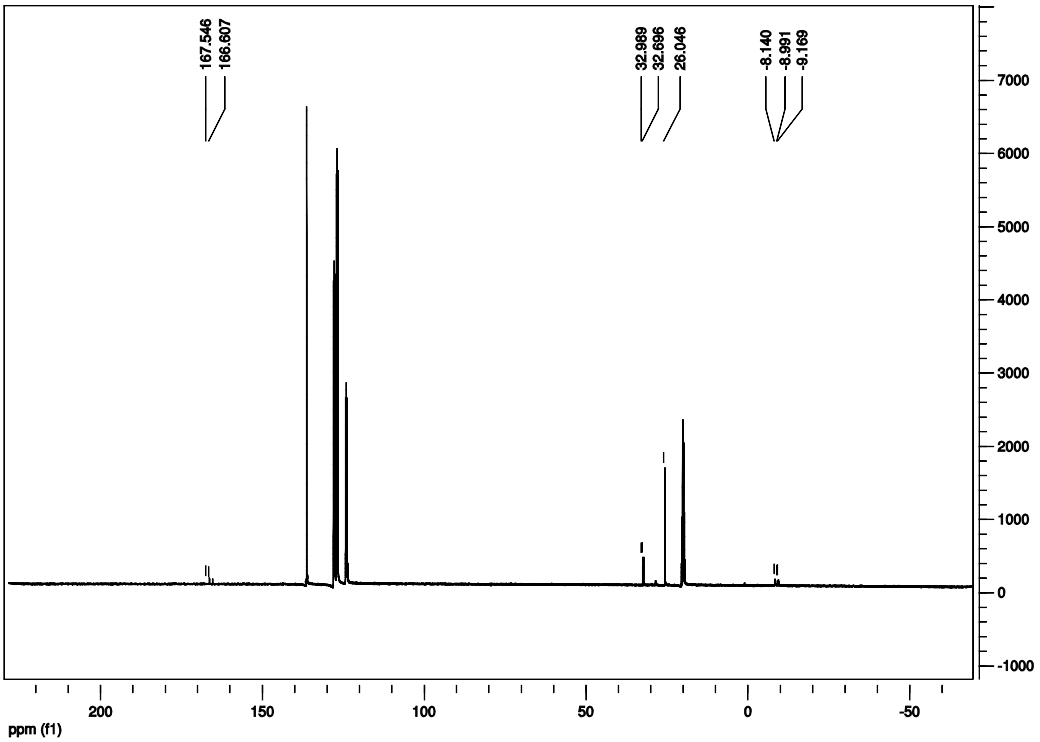
$^{1}H\{^{31}P\}$ NMR of 2 + $[3]_2$ in D-toluene – *full spectrum*



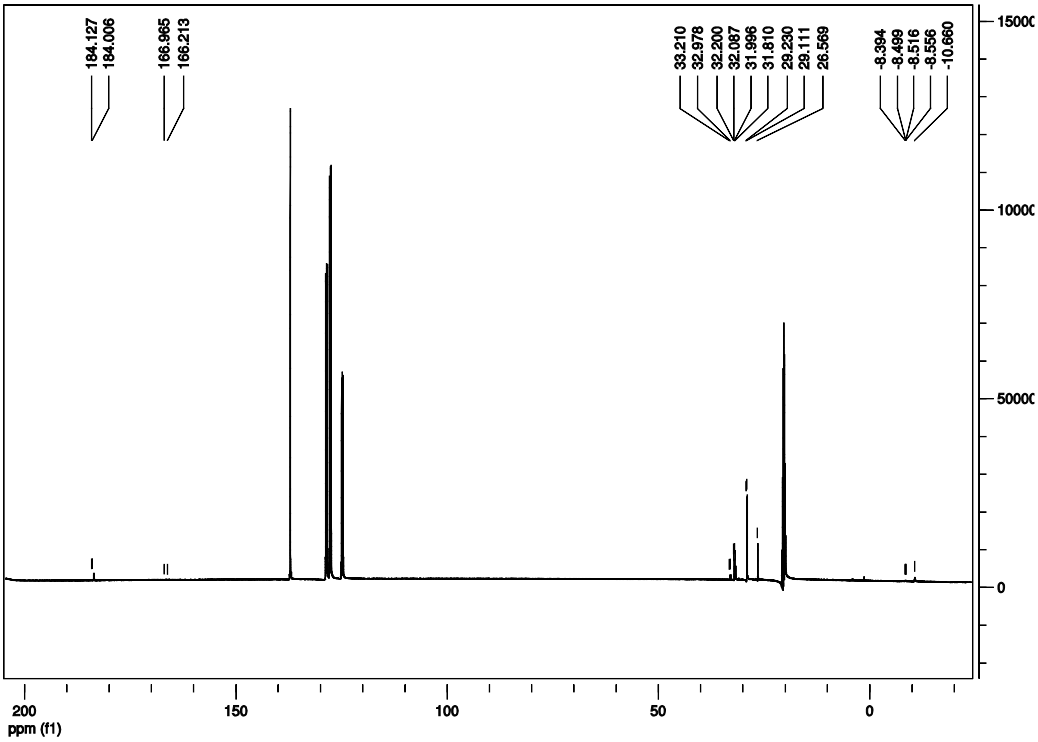
$^{1}H\{^{31}P\}$ NMR of 2 + $[3]_2$ in D-toluene – *enlarged spectrum*



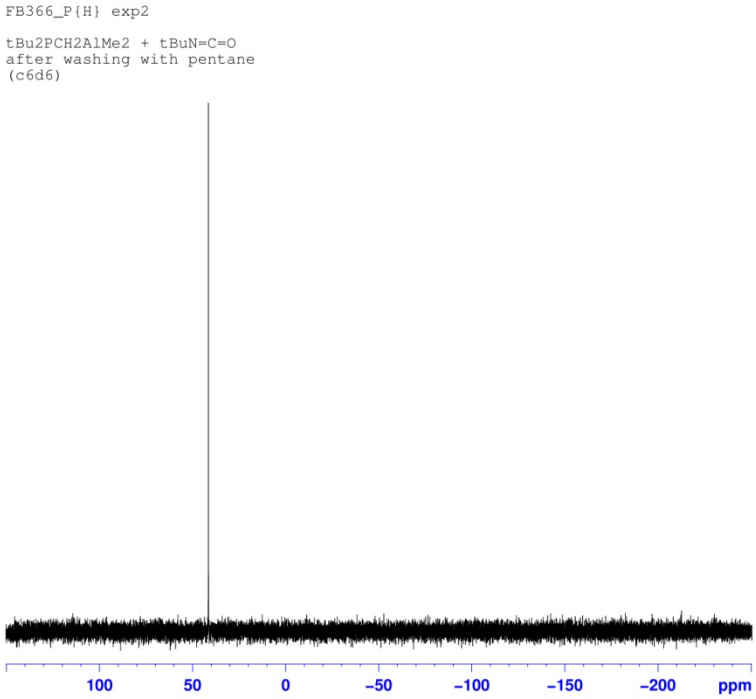
$^{13}C\{^{1}H\}$ NMR of 2 in D-toluene at -50°C



$^{13}C\{^{1}H\}$ NMR of 2 + $[3]_2$ in D-toluene



$^{31}P\{^{1}H\}$ NMR of 6 in C_6D_6

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NS                    32
DS                     4
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FIDRES          0.990830 Hz
AQ             0.5046772 sec
RG               14596.5
DW                 7.700 usec
DE                 6.00 usec
TE                301.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

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NUC1                  31P
P1                   6.25 usec
PL1                 -1.00 dB
SFO1         161.9674942 MHz

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NUC2                   1H
PCPD2             80.00 usec
PL2                3.00 dB
PL12              18.00 dB
PL13              18.00 dB
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SSB                    0
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PC                  1.40
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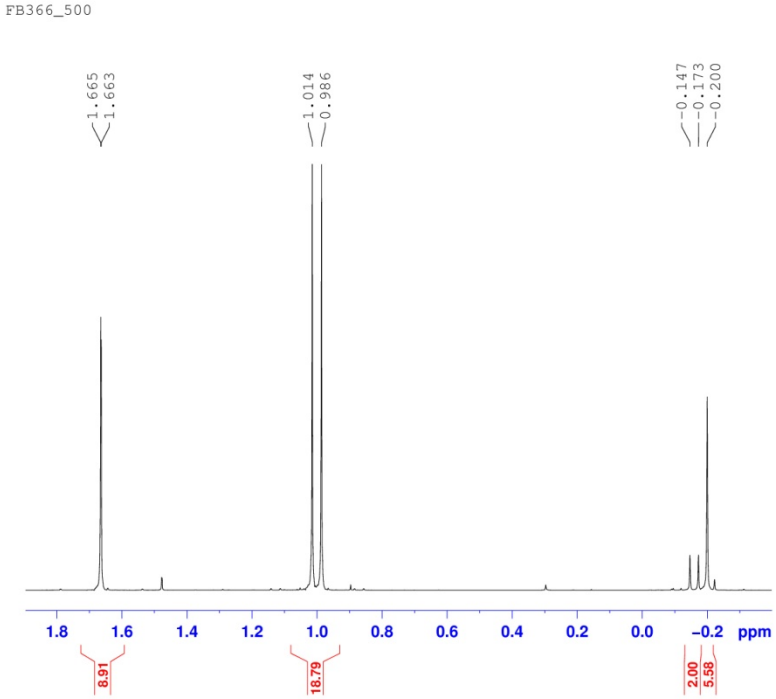
^{1}H NMR of 6 in C_6D_6

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TE                296.0 K
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TD0                   1

======== CHANNEL f1 ========
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P1                  6.70 usec
PL1                 4.00 dB
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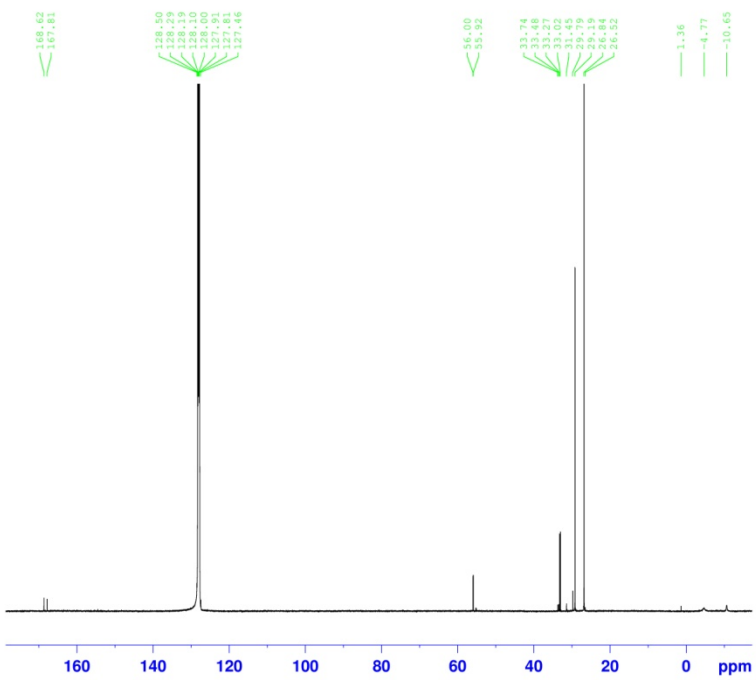
^{13}C NMR of 6 in C_6D_6

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SOLVENT           C6D6
NS                8192
DS                   4
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FIDRES        0.420739 Hz
AQ           1.1884362 sec
RG                2050
DW              18.133 usec
DE                6.50 usec
TE               296.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                11.20 usec
PL1               -2.00 dB
PL1W        88.77790070 W
SFO1        125.7929966 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                4.00 dB
PL12              25.28 dB
PL13              28.00 dB
PL2W         8.72000027 W
PL12W        0.06494062 W
PL13W        0.03471494 W
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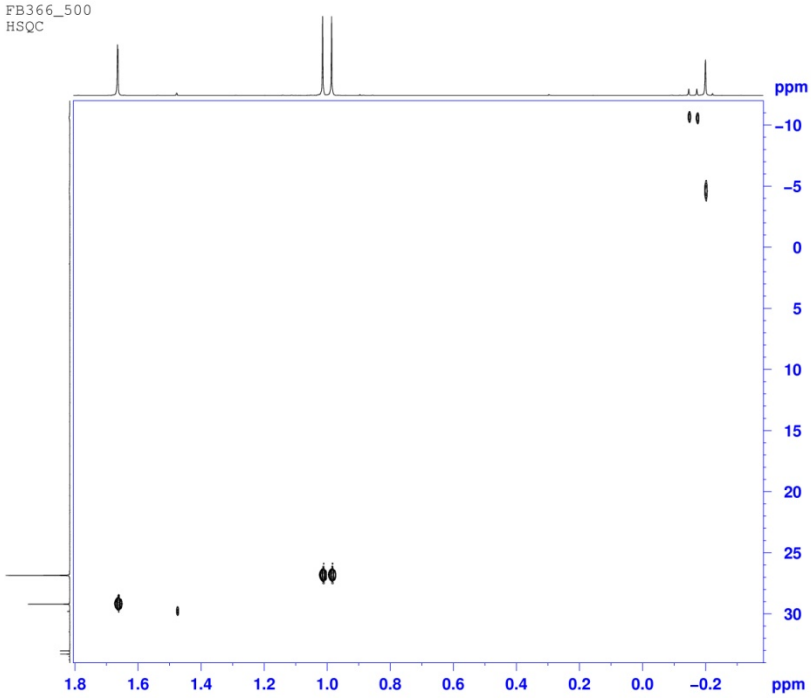
2D NMR (HSQC) of 6 in C_6D_6 (Part 1)

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PROCNO                1
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PULPROG       hsqcetgp
TD                2048
SOLVENT           C6D6
NS                   2
DS                  16
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FIDRES         0.976563 Hz
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RG                2050
DW              250.000 usec
DE                6.50 usec
TE               296.0 K
CNST2       145.0000000
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D1           1.29999995 sec
D4           0.00172414 sec
D11          0.03000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00005680 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                 1H
P1                 6.70 usec
P2                13.40 usec
P28             1000.00 usec
PL1                4.00 dB
PL1W         8.72000027 W
SFO1        500.2303752 MHz

======== CHANNEL f2 ========
CPDPRG2           garp
NUC2                13C
P3                11.20 usec
P4                22.40 usec
PCPD2             70.00 usec
PL2               -2.00 dB
PL12              13.92 dB
PL2W        88.77790070 W
PL12W        2.27145886 W
SFO2        125.7848207 MHz

====== GRADIENT CHANNEL =====
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GPNAM2          SINE.100
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GPZ2              20.10 %
P16             1000.00 usec
ND0                  2  2
TD                 128
SFO1        125.7848 MHz
FIDRES       68.788574 Hz
SW           70.000 ppm
F2MODE    Echo-Antiecho
SI                2048
SF          500.2299933 MHz
WDW               QSINE
SSB                  2
LB                0.00 Hz
GB                   0
PC                4.00
SI                2048
MC2       echo-antiecho
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WDW               QSINE
SSB                  2
LB                0.00 Hz
GB                   0
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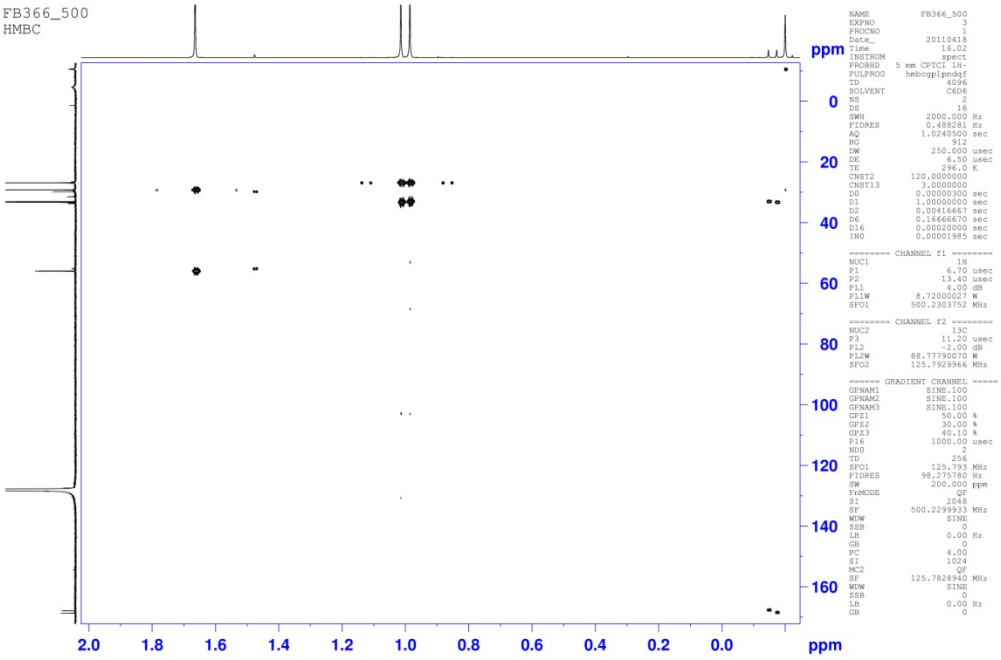
2D NMR (HMBC) of 6 in C_6D_6 (Part 2)



2. X-ray structure determination

Single crystals suitable for X-ray diffraction were obtained as described in the synthetic procedures. The crystallographic data were collected with a Bruker 6 kW APEX Smart and a Bruker 12 kW APEX Smart 6000 diffractometer. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 1.

Table 1. Crystal data, data collection, and structure refinement.

	[1]$_2$	**6**
Empirical formula	$C_{22}H_{52}Al_2P_2$	$C_{16}H_{35}AlNOP$
Crystal system	monoclinic	monoclinic
Space group	*P2(1)/c*	*P2(1)/c*
a/pm	1073.67(6)	1284.25(2)
b/pm	857.49(4)	993.33(1)
c/pm	1553.82(8)	1515.09(2)
α/°	90	90
β/°	108.514(1)	95.085(1)
γ/°	90	90
V (nm^3)	1.3565(1)	1.92517(4)
ρ_{calc} [g cm^{-3}]	1.059	1.088
Z	2	4
μ [cm^{-1}]	0.231(Mo-K$_\alpha$)	1.670(Cu-K$_\alpha$)
T [K]	153	153
Unique reflections	3951	3529
Reflections $I>2\sigma(I)$	3037	3262
Refined parameters	126	192
$R1$ I>2σ(I)[a]	0.0349	0.0365
$wR2$[b] (all data)	0.0926	0.1029
ρ_{fin} (max/min) [eÅ^{-3}]	0.475/-0.286	0.345/-0.336

3. Computational Section

General. The computational study was performed using Gaussian 09 suite of programs (Revision A.02).[1] All DFT calculations were conducted using the dispersion-corrected functional M06-2X and 6-31+G(d,p) basis set.[2] Frequency calculations on the computed structures confirmed the nature of the computed minima and transition states and allowed ZPE corrections on the computed energies. Small negative eigenvalues located on the methyl groups have been neglected. The computed energies reported in this work refer to the molecules in the gas phase. The computed electronic energies (E), zero point energies (ZPE) and Gibbs free energies (G) are given in atomic units. Relative energies (ΔE, ΔE(ZPE) and ΔG) are given in kcal·mol^{-1}.

3.1. Structural analysis of 1

We performed a computational analysis to investigate on the stability of dimer [**1**]$_2$. The energies of the computed structures are reported in Table 1. Thermal corrections to enthalpy, thermal corrections to Gibbs free energy and total entropy of the computed structures are listed in Table 2.

	E	Δ*E*	ZPE	Δ*E*(ZPE)	G	Δ*G*
[**1**]$_2$	-2036,821298	0,0	0,698158	0,0	-2036,187570	0,0
[**1**]$_2$[(a)]	-2036,816385	3,1	0,698676	3,4	-2036,181744	3,7
[**1**]*$_2$	-2036,771353	31,3	0,695934	29,9	-2036,144558	27,0
[**1**]**$_2$	-2036,783616	23,6	0,697684	23,3	-2036,151994	22,3
1	-1018,368068	26,7[(b)]	0,345941	24,8[(b)]	-1018,069449	15,3[(b)]
1*	-1018,368305	26,6[(b)]	0,346773	25,1[(b)]	-1018,068164	14,2[(b)]

Table 1. M06-2X/6-31+G(d,p) energies of the computed structures. (a) Dimer [**1**]$_2$ in the twisted boat conformation. (b) Such relative energies refer to 1 mole of monomer (**1** or **1***), relatively to 0.5 moles of dimer in the chair conformation ([**1**]$_2$).

	Hcorr	Stot	Gcorr
[**1**]$_2$	0,739237	222,064	0,633727
[**1**]$_2$[(a)]	0,739710	221,137	0,634640
[**1**]*$_2$	0,737990	234,028	0,626795
[**1**]**$_2$	0,738972	225,936	0,631622
1	0,367379	144,718	0,298619
1*	0,368054	142,935	0,300142

Table 2. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures. (a) Dimer [**1**]$_2$ in the twisted boat conformation.

3.2. Reaction of [1]$_2$ with CO_2

We performed a computational analysis to investigate on the reaction of **1** (monomeric) with CO_2. We could locate, on the PES (potential energy surface), structures **vdW** and **2** as energy minima, and **TS1** as a transition state connecting **vdW** to **2**. The formation of **1** from 0.5 moles of [**1**]$_2$ is endoergonic (ΔG = 15.3 kcal·mol^{-1}; Table 1). The computed energies for the reaction of **1** with CO_2 are reported in Table 3.

Thermal corrections to enthalpy, thermal corrections to Gibbs free energy and total entropy of the computed structures are listed in Table 4.

	E	Δ*E*	ZPE	Δ*E*(ZPE)	G	Δ*G*
1	-1018.368068	–	0.345941	–	-1018.069449	–
CO_2	-188.516053	–	0.011930	–	-188.524817	–
vdW	-1206.896520	-7.8	0.359351	-6.9	-1206.591653	1.6
TS1	-1206.896302	-7.6	0.358744	-7.1	-1206.589555	3.0
2	-1206.939024	-34.5	0.361508	-32.2	-1206.627119	-20.6

Table 3. M06-2X/6-31+G(d,p) energies of the computed structures.

	Hcorr	Stot	Gcorr
1	0.367379	144.718	0.298619
CO_2	0.015487	51.040	-0.008764
vdW	0.384542	167.690	0.304867
TS1	0.383165	160.833	0.306748
2	0.385244	154.354	0.311905

Table 4. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures.

3.3. Rearrangement of CO_2 adducts

In order to rationalize the unexpected rearrangement of **2** into **3**, which we have observed in select cases, and which was also observed by Fontaine and co-workers for the CO_2-adducts, we resorted again to computational chemistry.

First, we computed the reaction pathway proposed by Fontaine *et al.*[3] for the rearrangement of $Me_2PCH_2AlMe_2$–CO_2 adduct (**2-Me**) into the Al-carboxylate **3Me** (analogous to **3**) at M06-2X/6-31+G(d,p) level of theory. This allowed comparison of our results with the ones obtained by Fontaine *et al.* using the B3LYP functional and 6-31+G(d,p) basis set.[3] The computed reaction pathway is analogous to the one shown for the rearrangement of **2** (into **3**) in Figure 3. The relative SCF energies and Gibbs free energies for the computed structures using the two different functionals are reported in Table 5. We observed deviations in the computed relative energies within ±3 kcal·mol^{-1}. We note that the overall barrier predicted using the M06-2X functional (36.0 kcal·mol^{-1}) is even higher than the one predicted by B3LYP (34.7 kcal·mol^{-1}). We point out that such high reaction barriers contrast with the facile rearrangement observed experimentally. In fact, the complete rearrangement of **2**-Me was observed to occur in 1h at room temperature, while it was complete after only 10 minutes with **2**-Ph, for which a similar barriers were predicted.[3]

	Δ*E* (B3LYP)	Δ*E* (M06-2X)	Δ*G* (B3LYP)	Δ*G* (M06-2X)
2-Me	0.0	0.0	0.0	0.0
TS1-Me	18.7	21.6	16.1	18.2
vdW-Me	18.4	20.4	14.8	16.2
TS2-Me	36.8	38.8	34.7	36.0
3-Me	-12.2	-12.7	-11.1	-12.9
[3-Me]$_2$	-35.6	-38.6	-28.7	-30.7

Table 5. Comparison between the computed relative SCF energies (non ZPE corrected) and Gibbs free energies of the computed structures (in kcal·mol^{-1}), which were optimized at B3LYP/6-31+G(d,p) and M06-2X/6-31+G(d,p) level of theory.

	E	Δ*E*	ZPE	Δ*E*(ZPE)	G	Δ*G*
2-Me	-971.161601	0.0	0.189703	0.0	-971.012362	0.0
TS1-Me	-971.127142	21.6	0.187685	20.4	-970.983316	18.2
vdW-Me	-971.129031	20.4	0.187979	19.4	-970.986560	16.2
TS2-Me	-971.099695	38.8	0.187924	37.7	-970.954962	36.0
3-Me	-971.181908	-12.7	0.189703	-11.7	-971.012362	-12.9
[**3-Me**]$_2$	-1942.446273	-38.6	0.386470	-36.4	-1942.122585	-30.7

Table 6. M06-2X/6-31+G(d,p) energies of the computed structures.

	Hcorr	Stot	Gcorr
2-Me	0.205109	117.588	0.149239
TS1-Me	0.204375	127.437	0.143826
vdW-Me	0.205618	132.904	0.142471
TS2-Me	0.204239	125.241	0.144733
3-Me	0.207680	123.651	0.148929
[**3-Me**]$_2$	0.417843	198.167	0.323687

Table 7. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures.

Next, we computed the analogous reaction pathway for the rearrangement of *t*$Bu_2PCH_2AlMe_2$–CO_2 adduct **2** into **3**, and finally [**3**]$_2$. We note that with *tert*-butyl substituents on phosphorus (instead of Me or Ph) the CO_2 uptake is far more exothermic. Consequently, the reverse reaction, namely the dissociation of CO_2 from **2** to give **vdW** occurs with a significantly higher barrier (23.6 kcal·mol^{-1} for **2** *vs* 16.2 kcal·mol^{-1} for **2-Me**). The overall barrier for such rearrangement is of 45.2 kcal·mol^{-1}, which leads to the conclusion that the rearrangement cannot occur at room temperature *via* this mechanism. This is in agreement with the thermal stability observed for some samples of **2**, which resulted stable towards rearrangement even upon heating. The computed energies are reported in Table 8. Thermal corrections to enthalpy, thermal corrections to Gibbs free energy and total entropy of the computed structures are listed in Table 9.

	E	Δ*E*	ZPE	Δ*E*(ZPE)	G	Δ*G*
2	-1206.939024	0.0	0.361508	0.0	-1206.627119	0.0
TS1	-1206.896302	26.8	0.358744	25.1	-1206.589555	23.6
vdW	-1206.896520	26.7	0.359351	25.3	-1206.591653	22.3
TS2	-1206.864624	46.7	0.359534	45.4	-1206.555072	45.2
3	-1206.957927	-11.9	0.363694	-10.5	-1206.642561	-9.7
[**3**]$_2$	-2413.976699	-31.0	0.730053	-28.7	-2413.319897	-20.6
2·CO_2	-1395.459745	0.0	0.373928	0.0	-1395.143112	0.0
TS3	-1395.412234	26.9	0.374325	0.6	-1395.089963	33.4
7R	-1395.490868	-22.5	0.378216	3.0	-1395.164512	-13.4
TS4	-1395.453595	0.9	0.374636	0.8	-1395.130383	8.0
3-CO_2	-1395.470274	-6.6	0.376366	1.5	-1395.150064	-4.4

Table 8. M06-2X/6-31+G(d,p) energies of the computed structures.

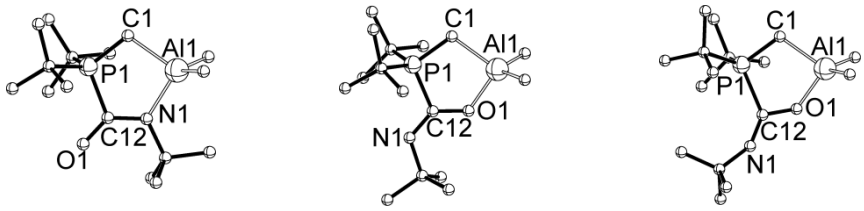
	Hcorr	Stot	Gcorr
2	0.385244	154.354	0.311905
TS1	0.383165	160.833	0.306748
vdW	0.384542	167.690	0.304867
TS2	0.383338	155.294	0.309552
3	0.387032	150.833	0.315366

[**3**]$_2$	0.775863	250.583	0.656803
2·CO$_2$	0.401326	178.251	0.316633
TS3	0.400188	163.990	0.322271
7R	0.404211	163.861	0.326355
TS4	0.398545	158.551	0.323213
3-CO$_2$	0.403179	174.624	0.320210

Table 9. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures.

3.4. Reaction of [1]$_2$ with tBuNCO

To gain a deeper understanding of the exclusive formation of **6** from the reaction of [**1**]$_2$ with *t*BuNCO, we computed the structures of all possible products that could result from P/Al addition to either the C=O or the C=N bond of *t*BuNCO, namely *Z*-**7**$_{\mathbf{C=O}}$, *E*-**7**$_{\mathbf{C=O}}$ and **7** (shown below). Formation of *Z*-**7**$_{\mathbf{C=O}}$ from [**1**]$_2$ is energetically unfavored (ΔG = 20.3 kcal·mol^{-1}), probably as a consequence of steric repulsion between the bulky *tert*-butyl substituent on the nitrogen atom of the isocyanate and the *tert*-butyl substituents on the phosphorus atom, while the formation of products *E*-**7**$_{\mathbf{C=O}}$ (ΔG = -9.0 kcal·mol^{-1}) and **6** (ΔG = -12.6 kcal·mol^{-1}) from [**1**]$_2$ is energetically favored, with **7** being the most stable product.



7 *E*-**7**$_{C=O}$ *Z*-**7**$_{C=O}$

The relative energies reported in Table 10 refer to the reaction of 1 isocyanate molecules with half a molecule of [**1**]$_2$. Thermal corrections to enthalpy, thermal corrections to Gibbs free energy and total entropy of the computed structures are listed in Table 11.

	E	Δ*E*	ZPE	Δ*E*(ZPE$_{corr}$)	G	Δ*G*
½ [**1**]$_2$	-1018.408192	–	0.399338	–	-1018.093785	–
***t*BuNCO**	-325.804863	–	0.135757	–	-325.70	–
7	-1344.248326	-22.1	0.486737	-21.1	-1343.82	-12.6
E-**7**$_{C=O}$	-1344.242265	-18.3	0.485775	-17.9	-1343.81	-9.0
Z-**7**$_{C=O}$	-1344.195588	11.0	0.485573	11.3	-1343.77	20.3

Table 10. M06-2X/6-31+G(d,p) energies of the computed structures.

	Hcorr	Stot	Gcorr
½ [**1**]$_2$	0.369619	111.032	0.316864

***t*BuNCO**	0.145001	92.161	0.101212
7	0.515925	179.129	0.430816
***E*-7$_{C=O}$**	0.514553	176.879	0.430512
***Z*-7$_{C=O}$**	0.515102	178.072	0.430494

Table 11. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures.

3.5. Substrate assisted frustration

We have considered the possibility that the substrate induces frustration by promoting the cleave of the P–Al bond in [**1**]$_2$. To test this hypothesis, we calculated two CO_2-adducts (**4** and **5**) of [**1**]$_2$ at the M06-2X/6-31+G(d,p) level of theory. The computed energies are reported in Tables 12. Thermal corrections to enthalpy, thermal corrections to Gibbs free energy and total entropy of the computed structures are listed in Table 13.

	E	**Δ*E***	**ZPE**	**Δ*E*(ZPE)**	**G**	**Δ*G***
[**1**]$_2$	-2036.821298	–	0.698158	–	-2036.187570	–
CO_2	-188.516053	–	0.011930	–	-188.52	–
4	-2225.341813	-2.8	0.711095	-2.2	-2224.701982	6.5
5	-2225.303509	21.2	0.709663	21.0	-2224.668514	27.5

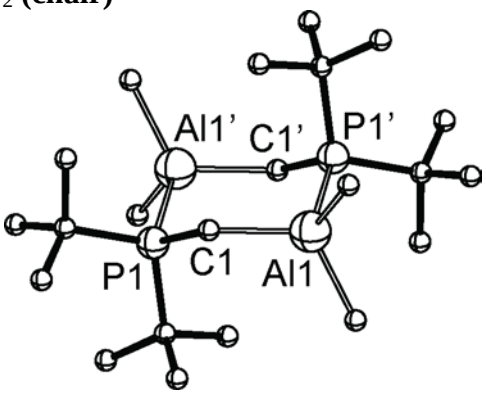
Table 12. M06-2X/6-31+G(d,p) energies of the computed structures.

	Hcorr	**Stot**	**Gcorr**
[**1**]$_2$	0.739237	222.064	0.633727
CO_2	0.015487	51.040	-0.008764
4	0.755616	243.690	0.639831
5	0.755540	253.707	0.634995

Table 13. M06-2X/6-31+G(d,p) thermal corrections to enthalpy (a.u.), thermal corrections to Gibbs free energy (a.u.) and total entropy (cal/mol·K) for the computed structures.

4. Computed Structures

[1]$_2$ (chair)



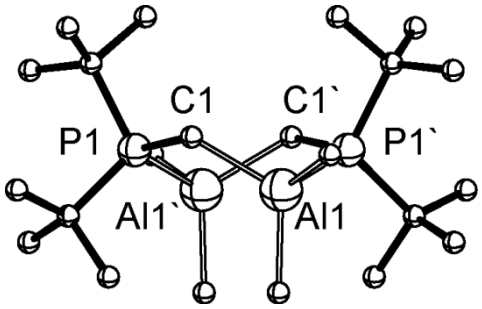
C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.81981, C1-Al1 2.03266, Al1-P1` 2.51356, P1`-C1` 1.81987, C1`-Al1` 2.03276, Al1`-P1 2.51060, P1-C1-Al1 125.253, P1`-C1`-Al1` 125.244.

C	0.959876	0.912055	-1.450824
C	-0.960345	-0.907302	1.452755
H	1.544280	1.679402	-1.978956
H	-0.757148	-0.116057	2.183336
H	-1.545434	-1.670452	1.986261
H	0.759025	0.124816	-2.186257
P	2.003652	0.150098	-0.169466
P	-2.003942	-0.149112	0.169109
Al	-0.897471	1.680242	-1.147066
Al	0.895696	-1.679224	1.151141
C	1.872985	-1.801509	2.884401
H	1.480690	-2.678341	3.418628
H	2.944791	-1.990578	2.739479
H	1.781397	-0.951237	3.568886
C	1.034541	-3.446863	0.238463
H	2.076791	-3.789987	0.215047
H	0.502118	-4.165084	0.880041
H	0.629901	-3.571191	-0.770255
C	-2.469636	-1.574360	-0.982867
C	-3.533594	0.530288	1.053202
C	-1.037454	3.446760	-0.232258
H	-0.510256	4.166520	-0.876429
H	-2.080491	3.787150	-0.203430
H	-0.628168	3.572116	0.774463
C	-1.874273	1.804420	-2.880640
H	-2.946942	1.989132	-2.736611
H	-1.484504	2.684011	-3.412154
H	-1.778695	0.956231	-3.567228
C	2.474504	1.574342	0.981803
C	3.530316	-0.532403	-1.056336
C	3.003893	-1.425040	-2.194826
H	3.845944	-1.979851	-2.624835
H	2.270801	-2.157623	-1.838421
H	2.550729	-0.835596	-2.996210
C	4.345362	-1.420932	-0.103893
H	3.731161	-2.223370	0.315778
H	5.163580	-1.888328	-0.665330
H	4.788671	-0.863872	0.722910
C	4.425146	0.550691	-1.666635
H	4.934886	1.146513	-0.904957
H	5.198101	0.071661	-2.280648
H	3.859269	1.225903	-2.317420
C	3.725523	1.251963	1.808749
H	4.637515	1.252061	1.206240
H	3.841767	2.025255	2.577843
H	3.635098	0.287217	2.318107
C	2.675457	2.890388	0.218687
H	2.986422	3.664710	0.930823
H	3.446908	2.817956	-0.552557
H	1.745104	3.226139	-0.247728
C	1.305389	1.753784	1.965161
H	1.254811	0.926202	2.676613
H	1.455168	2.681176	2.531876
H	0.343633	1.835671	1.453041
C	-4.427701	-0.554545	1.661561
H	-3.861894	-1.229402	2.312775
H	-5.202159	-0.076904	2.274757
H	-4.935579	-1.150615	0.898859
C	-3.010778	1.423307	2.193048
H	-2.557909	0.834155	2.994833
H	-2.278307	2.157277	1.838271
H	-3.854562	1.976423	2.621838
C	-4.348534	1.417577	0.099536
H	-5.169197	1.882544	0.659425
H	-3.735367	2.221793	-0.318210
H	-4.788512	0.859979	-0.728698
C	-3.719885	-1.254942	-1.812074
H	-3.833283	-2.028844	-2.580994
H	-4.632928	-1.256570	-1.211176
H	-3.630534	-0.290261	-2.321740

C	-2.669122	-2.890301	-0.219261
H	-3.443576	-2.819377	0.549106
H	-2.975105	-3.666388	-0.931640
H	-1.739418	-3.222490	0.250897
C	-1.298402	-1.751356	-1.964182
H	-1.444280	-2.679933	-2.529964
H	-1.249497	-0.924469	-2.676587
H	-0.337000	-1.829345	-1.450736

[**1**]$_2$ **(twisted boat)**



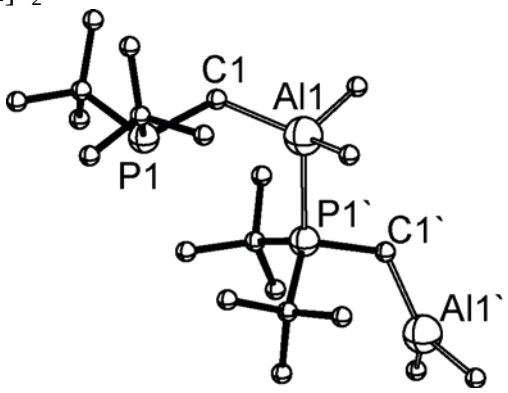
C₁

Selected bond lengths [Å] and angles [°]: P1-C1 1.82945, C1-Al1 2.03864, Al1-P1` 2.51881, P1`-C1` 1.82944, C1`-Al1` 2.03863, Al1-P1 2.51880, P1-C1-Al1 123.553, P1`-C1`-Al1` 123.555.

C	-0.965891	0.401333	1.586576
H	-1.558993	0.356308	2.512019
H	-0.625974	1.444550	1.514158
C	0.965846	0.400856	-1.586718
H	0.625899	1.444082	-1.514673
H	1.558940	0.355499	-2.512153
P	2.070070	0.148890	-0.150018
Al	0.772976	-0.625593	1.865445
Al	-0.772968	-0.626284	-1.865249
P	-2.070076	0.148938	0.149934
C	1.717939	0.055915	3.479883
H	1.170872	-0.294624	4.366232
H	2.728422	-0.366874	3.559576
H	1.810075	1.143335	3.578774
C	0.720522	-2.614958	1.893371
H	1.713714	-3.040877	2.078531
H	0.100350	-2.912894	2.750636
H	0.306070	-3.121167	1.017642
C	2.913820	1.826071	0.138500
C	3.353043	-1.129689	-0.677081
C	-0.720566	-2.615671	-1.892399
H	-1.713782	-3.041577	-2.077456
H	-0.100345	-2.914011	-2.749485
H	-0.306236	-3.121540	-1.016420
C	-1.718029	0.054573	-3.479906
H	-1.171720	-0.297323	-4.366183
H	-2.728960	-0.367300	-3.558780
H	-1.809129	1.141991	-3.579741
C	-3.353194	-1.129327	0.677396
C	-2.913648	1.826116	-0.139099
C	-2.575350	-2.308084	1.279498
H	-2.066568	-2.029374	2.206251
H	-3.280754	-3.115809	1.508713
H	-1.830176	-2.701079	0.583357
C	-4.352421	-0.624545	1.724454
H	-4.935571	-1.478994	2.089130
H	-3.857232	-0.170172	2.588979
H	-5.059716	0.096569	1.306747
C	-4.119927	-1.639992	-0.553498
H	-4.790077	-2.449604	-0.239453
H	-4.732568	-0.866816	-1.020343
H	-3.443495	-2.043637	-1.311381
C	-4.099196	1.689906	-1.102316
H	-4.953928	1.197046	-0.631634
H	-4.426939	2.691238	-1.407053
H	-3.826405	1.137481	-2.007653
C	-3.365364	2.514245	1.155970
H	-3.744790	3.513175	0.906812
H	-4.165936	1.976683	1.665055
H	-2.537285	2.641162	1.859563
C	-1.860327	2.728755	-0.801178
H	-2.301225	3.715054	-0.989277
H	-0.996057	2.879566	-0.147676
H	-1.514916	2.326004	-1.757020
C	2.575105	-2.308658	-1.278635
H	2.066332	-2.030323	-2.205510
H	3.280452	-3.116530	-1.507506
H	1.829931	-2.701331	-0.582316
C	4.119823	-1.639896	0.553976
H	4.789895	-2.449691	0.240243
H	4.732554	-0.866571	1.020458
H	3.443409	-2.043170	1.312073
C	4.352226	-0.625376	-1.724406
H	5.059538	0.095929	-1.307044

H	4.935373	-1.479988	-2.088712
H	3.857020	-0.171400	-2.589127
C	4.099142	1.690019	1.102017
H	4.953887	1.196866	0.631683
H	4.426979	2.691414	1.406449
H	3.826067	1.137947	2.007486
C	3.365962	2.513691	-1.156682
H	3.745007	3.512837	-0.907816
H	4.166940	1.976093	-1.665096
H	2.538202	2.640075	-1.860749
C	1.860502	2.729141	0.800010
H	2.301634	3.715325	0.988187
H	0.996606	2.880178	0.146070
H	1.514501	2.326683	1.755764

[**1**]*****$_2$



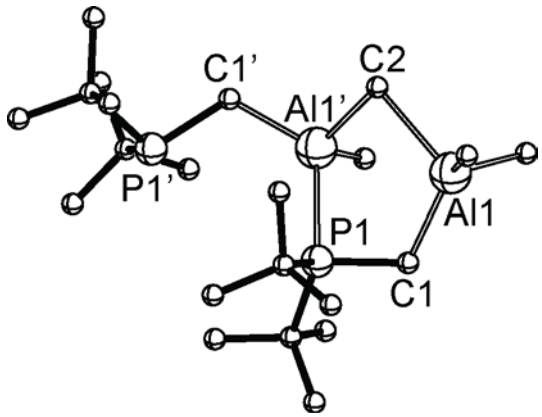
C$_1$

Selected bond lengths [Å] and angles [°]: P1-C1 1.85090, C1-Al1 2.01147, Al1-P1` 2.56072, P1`-C1` 1.84675, C1`-Al1` 1.98609, P1-C1-Al1 127.158, P1`-C1`-Al1` 124.658.

Al	-0.215883	-0.862800	1.686497
C	-1.993789	-0.021618	1.265240
H	-1.823870	1.025424	1.559114
H	-2.694398	-0.403524	2.027814
P	-2.822080	0.073527	-0.387247
P	1.613935	0.079629	0.163050
C	3.204314	-0.130411	1.077963
Al	4.999892	-0.160294	0.229685
C	-3.863578	-1.517233	-0.438564
C	-4.006067	1.556041	-0.144869
C	-4.379570	-1.718437	-1.871763
H	-4.895180	-2.685028	-1.943816
H	-5.086263	-0.943461	-2.177012
H	-3.550840	-1.720139	-2.587955
C	-5.032588	-1.603130	0.547037
H	-5.835390	-0.904066	0.298332
H	-5.459438	-2.614799	0.517523
H	-4.712263	-1.410878	1.576658
C	-2.898925	-2.669783	-0.130198
H	-2.005569	-2.631646	-0.764347
H	-2.573167	-2.661405	0.913057
H	-3.401428	-3.626916	-0.320031
C	-5.080757	1.561220	-1.237836
H	-5.837347	0.788053	-1.076844
H	-5.598850	2.529416	-1.239888
H	-4.642512	1.414197	-2.231871
C	-4.668355	1.681001	1.231678
H	-5.267914	2.600938	1.261752
H	-5.335454	0.846539	1.455420
H	-3.926966	1.745959	2.033480
C	-3.124566	2.798928	-0.360950
H	-2.298727	2.850813	0.359437
H	-2.696515	2.812682	-1.368977
H	-3.728663	3.706729	-0.232548
C	0.442769	-0.157761	3.432648
H	1.520739	-0.304033	3.580597
H	0.227424	0.903727	3.600548
H	-0.055096	-0.711755	4.240217
C	0.059811	-2.830895	1.564454
H	-0.168763	-3.304689	0.604409
H	1.087619	-3.103392	1.839723
H	-0.591882	-3.306008	2.311343
C	5.853555	-1.884780	-0.157461
H	6.927246	-1.836737	0.055678
H	5.432134	-2.721861	0.408880
H	5.758172	-2.137973	-1.221503
C	6.059027	1.460427	-0.093556
H	5.820268	2.296760	0.570204
H	7.125875	1.235522	0.014386
H	5.918664	1.819152	-1.121781
H	3.097173	-1.077321	1.626408
H	3.189288	0.651289	1.850924
C	1.475979	1.939984	-0.115177
C	2.801562	2.618428	-0.471888
H	3.533213	2.519399	0.334252
H	3.246667	2.231579	-1.391912
H	2.620846	3.690155	-0.621140

C	0.980679	2.536186	1.213435
H	0.932601	3.627257	1.115289
H	-0.018206	2.174465	1.469977
H	1.646912	2.302838	2.050772
C	0.425539	2.225199	-1.195280
H	-0.488264	1.639690	-1.041954
H	0.156501	3.288085	-1.161400
H	0.803180	2.014120	-2.200220
C	1.841491	-0.839823	-1.468074
C	2.838373	-0.190638	-2.433630
H	3.010049	-0.862752	-3.282838
H	2.476557	0.761790	-2.827494
H	3.823379	-0.003368	-1.980901
C	2.338314	-2.249457	-1.107550
H	1.648070	-2.759915	-0.431930
H	2.411240	-2.842176	-2.027132
H	3.327598	-2.243034	-0.643308
C	0.476382	-0.987489	-2.158256
H	0.569595	-1.694556	-2.991502
H	-0.277946	-1.371796	-1.464437
H	0.092344	-0.046207	-2.555273

[**1**]**$_2$



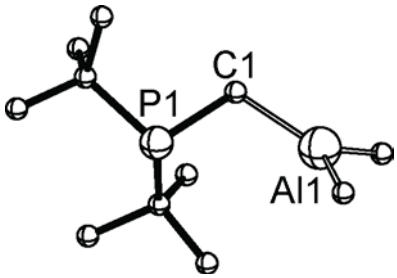
C_1

Selected bond lengths [Å] and angles [°]: P1`-C1` 1.85187, C1`-Al1` 1.99769, Al1`-P1 2.47483, P1-C1 1.18372, C1-Al1 2.02328, Al1-C2 2.29150, Al1`-C2 2.10723, P1`-C1`-Al1` 117.868, P1-C1-Al1 114.862, Al1`-C2-Al1 92.602.

Al	-0.524836	-0.883883	-1.162171
C	1.312246	-1.430494	-0.599058
H	1.820164	-1.983154	-1.404479
H	1.133948	-2.169704	0.195948
P	2.409428	-0.138391	0.146664
P	-1.539239	0.882739	0.243118
C	-3.232057	0.439302	-0.233635
Al	-3.559065	-1.544047	-0.463986
C	3.606475	-1.160804	1.222089
C	3.356994	0.521723	-1.364811
C	4.798576	-0.289699	1.636320
H	5.373045	-0.800334	2.419609
H	5.479314	-0.100412	0.801468
H	4.467914	0.675621	2.037286
C	4.104727	-2.481456	0.625166
H	4.784820	-2.333312	-0.215029
H	4.650372	-3.043377	1.394885
H	3.274510	-3.108775	0.285903
C	2.802843	-1.490428	2.493013
H	2.410840	-0.585148	2.969900
H	1.959974	-2.157948	2.281258
H	3.450675	-2.005256	3.213572
C	4.028163	1.848075	-0.975326
H	4.786716	1.720698	-0.199085
H	4.520609	2.282932	-1.854632
H	3.290952	2.569678	-0.607998
C	4.398101	-0.419089	-1.978544
H	4.767068	0.010558	-2.919404
H	5.262253	-0.558119	-1.323170
H	3.975248	-1.403293	-2.207388
C	2.304413	0.825118	-2.441440
H	1.889466	-0.091040	-2.870394
H	1.474287	1.425857	-2.048346
H	2.767316	1.398112	-3.254889
C	-1.005992	-0.418599	-3.025043
H	-2.030534	-0.035395	-3.105723
H	-0.345514	0.315767	-3.496341
H	-0.967983	-1.328645	-3.639046
C	-1.568786	-2.654977	-0.699758
H	-1.267862	-3.048108	0.275812
H	-2.445540	-3.240197	-1.013746
H	-0.840699	-3.055782	-1.425157
C	-4.478359	-1.913773	-2.174641
H	-4.743228	-2.973014	-2.282316
H	-5.415950	-1.346801	-2.240816
H	-3.878338	-1.638119	-3.050403
C	-4.256176	-2.502847	1.121981
H	-5.238600	-2.087005	1.385008

H	-4.423901	-3.561535	0.886267
H	-3.649108	-2.469688	2.033087
H	-3.386655	0.819963	-1.250162
H	-3.987083	0.904895	0.409097
C	-1.276331	2.705288	-0.195374
C	-2.293535	3.602273	0.517956
H	-3.322607	3.290819	0.309541
H	-2.145051	3.612706	1.601444
H	-2.176904	4.632516	0.159475
C	-1.492460	2.822034	-1.714214
H	-1.355770	3.870048	-2.004311
H	-0.769488	2.222115	-2.274693
H	-2.497621	2.523463	-2.022567
C	0.158036	3.172911	0.104473
H	0.899940	2.409064	-0.149760
H	0.370906	4.070082	-0.489134
H	0.303365	3.432542	1.153422
C	-1.429275	0.598480	2.111283
C	-2.778730	0.836954	2.800749
H	-2.647612	0.707984	3.881937
H	-3.163899	1.846509	2.627803
H	-3.531845	0.116315	2.468276
C	-1.019131	-0.866402	2.317961
H	-0.029394	-1.059199	1.891812
H	-0.968516	-1.075924	3.393639
H	-1.738735	-1.560568	1.879796
C	-0.350392	1.474990	2.759369
H	-0.216622	1.139520	3.795181
H	0.612604	1.379997	2.245961
H	-0.639441	2.528481	2.793813

1

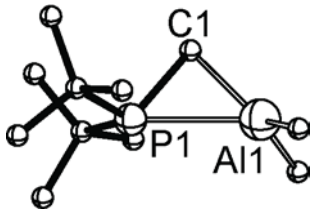


C₁

Selected bond lengths [Å] and angles [°]: P1-C1 1.85050, Al1-C1 1.97002, P1-Al1 3.18762, P1-C1-Al1 113.058.

C	-0.748408	0.959309	-0.027655
H	-0.364364	-0.067706	-0.102376
H	-0.391291	1.382035	0.921203
P	-2.591100	0.806839	-0.102358
Al	0.012981	1.887233	-1.589779
C	1.059025	3.533752	-1.349977
H	1.930232	3.560431	-2.013667
H	0.454127	4.416727	-1.593679
H	1.412180	3.661358	-0.321244
C	-0.202824	1.073295	-3.359008
H	-0.302249	1.826331	-4.148391
H	0.669621	0.459935	-3.617605
H	-1.081233	0.420479	-3.395907
C	-3.023494	0.012480	1.575246
C	-3.105836	2.640126	-0.065051
C	-2.259432	3.565574	0.817220
H	-2.624114	4.596963	0.720935
H	-2.308835	3.295066	1.873948
H	-1.205434	3.565415	0.518974
C	-4.583094	2.761651	0.332067
H	-4.932266	3.784245	0.141050
H	-5.213268	2.077108	-0.246786
H	-4.738484	2.558047	1.394940
C	-2.993022	3.126496	-1.520772
H	-1.957305	3.152327	-1.891804
H	-3.571856	2.501628	-2.206845
H	-3.351350	4.160542	-1.597352
C	-2.738852	0.849993	2.823358
H	-3.409474	1.710097	2.905383
H	-2.887133	0.234340	3.720644
H	-1.705425	1.212786	2.841735
C	-2.177333	-1.269707	1.649472
H	-2.529501	-1.888215	2.484121
H	-2.261528	-1.864204	0.731894
H	-1.120141	-1.047517	1.820993
C	-4.500501	-0.410103	1.552074
H	-5.181933	0.443091	1.522125
H	-4.712719	-1.043726	0.684736
H	-4.731050	-0.985342	2.458012

1*

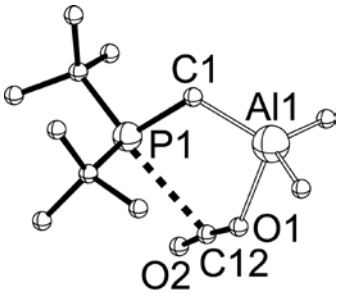


C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.86274, Al1-C1 1.98195, P1-Al1 2.59678, P1-C1-Al1 84.913.

C	-0.156507	2.470709	0.008617
H	-0.357890	2.936305	0.978089
H	-0.651647	3.046006	-0.776000
P	-0.638066	0.671786	0.050855
Al	1.701510	1.788892	-0.096472
C	2.681519	1.590037	1.599779
H	2.895483	0.535704	1.810255
H	3.649334	2.102910	1.544879
H	2.143397	1.994503	2.463025
C	2.639253	1.493298	-1.802100
H	3.659876	1.889186	-1.740218
H	2.730965	0.424275	-2.028006
H	2.146819	1.971519	-2.654539
C	-1.613754	0.369349	-1.538099
C	-1.711588	0.478884	1.598836
C	-0.747408	0.900346	-2.691849
H	0.245771	0.439423	-2.694334
H	-1.234875	0.650354	-3.641968
H	-0.622059	1.986103	-2.658174
C	-2.982198	1.054507	-1.576954
H	-3.400018	0.976822	-2.588841
H	-3.691598	0.578205	-0.894048
H	-2.914023	2.117542	-1.321485
C	-1.774423	-1.144182	-1.745395
H	-2.239597	-1.326870	-2.722064
H	-0.802420	-1.647410	-1.732383
H	-2.408237	-1.606737	-0.986135
C	-2.780805	1.562265	1.773390
H	-2.353856	2.568096	1.730303
H	-3.566766	1.494599	1.019287
H	-3.253128	1.443205	2.756799
C	-0.719818	0.569872	2.770900
H	-1.262391	0.444015	3.715724
H	0.049944	-0.206055	2.708387
H	-0.217608	1.542183	2.804253
C	-2.370715	-0.905077	1.622544
H	-2.801890	-1.081903	2.615656
H	-3.184849	-0.978449	0.895623
H	-1.648588	-1.704171	1.421867

vdW



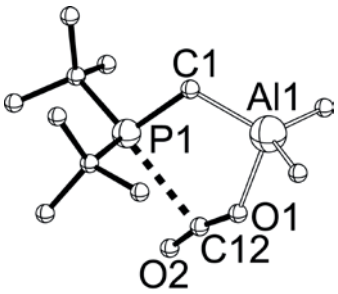
C_1

Selected bond lengths [Å] and angles [°]: P1-C12 3.07270, C12-O1 1.17731, C12-O2 1.15416, Al1-O1 2.26887, P1-C1 1.85002, Al1-C1 1.99200, P1-C12-O1 83.486, C12-O1-Al1 134.509, O2-C12-O1 172.837.

O	1.650470	0.799693	-0.569222
C	2.591098	1.279998	-0.049043
C	-0.813775	2.671314	0.430265
H	-1.048453	2.594656	1.501321
H	-1.668892	3.174047	-0.042253
O	3.586214	1.635107	0.415433
P	0.723597	3.693430	0.310486
Al	-0.573713	0.772511	-0.121974
C	-1.154949	0.139306	-1.890304
H	-1.327938	-0.942099	-1.898538
H	-2.084943	0.624011	-2.210858
H	-0.405134	0.355595	-2.660576
C	-0.326422	-0.461665	1.390551
H	-1.282395	-0.700741	1.872693
H	0.124295	-1.412857	1.086162
H	0.313340	-0.023034	2.167676
C	0.529009	4.532778	-1.380255
C	0.520453	4.977008	1.696097
C	-0.572846	5.592312	-1.468016
H	-0.696559	5.905106	-2.512998

H	-1.537748	5.208610	-1.119720
H	-0.326184	6.484441	-0.886168
C	1.876340	5.152721	-1.779825
H	2.674742	4.402960	-1.764960
H	1.807087	5.555092	-2.798407
H	2.172641	5.971434	-1.120002
C	0.210807	3.417249	-2.389155
H	-0.787879	2.997484	-2.238139
H	0.250799	3.827275	-3.405866
H	0.937722	2.597738	-2.336403
C	-0.895500	5.529816	1.888599
H	-0.912073	6.176622	2.775496
H	-1.231953	6.127003	1.038957
H	-1.623571	4.729673	2.051068
C	0.925577	4.218058	2.972549
H	0.845134	4.886027	3.839194
H	0.277170	3.354819	3.160569
H	1.958190	3.859388	2.910387
C	1.510145	6.130698	1.497295
H	2.522107	5.761794	1.294296
H	1.212107	6.791276	0.677661
H	1.551205	6.738119	2.410141

TS1

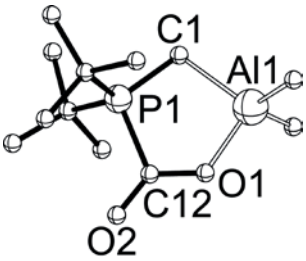


C_1

Selected bond lengths [Å] and angles [°]: P1-C12 2.88333, C12-O1 1.18360, C12-O2 1.15653, Al1-O1 2.16704, P1-C1 1.84359, Al1-C1 1.99953, P1-C12-O1 87.910, C12-O1-Al1 138.029, O2-C12-O1 166.935.

O	1.605899	0.821170	-0.367386
C	2.521948	1.462283	0.020849
C	-0.809117	2.661807	0.437456
H	-1.039612	2.600091	1.509972
H	-1.671514	3.147025	-0.039291
O	3.554360	1.871475	0.343710
P	0.712798	3.691476	0.287796
Al	-0.543104	0.753405	-0.096721
C	-1.046410	0.127769	-1.893538
H	-1.195707	-0.957195	-1.913806
H	-1.978173	0.591725	-2.239340
H	-0.280367	0.365037	-2.641154
C	-0.491439	-0.487552	1.429807
H	-1.501487	-0.703814	1.799768
H	-0.034857	-1.449258	1.170367
H	0.070644	-0.071147	2.275507
C	0.509900	4.531478	-1.397100
C	0.565018	4.964608	1.684995
C	-0.590330	5.594131	-1.470848
H	-0.727918	5.904223	-2.514736
H	-1.551354	5.215100	-1.107120
H	-0.331424	6.487219	-0.895429
C	1.854971	5.147345	-1.811424
H	2.652598	4.396797	-1.805228
H	1.774165	5.547691	-2.829777
H	2.160071	5.967251	-1.157436
C	0.179502	3.413840	-2.399669
H	-0.817513	2.994806	-2.238265
H	0.212035	3.820833	-3.417765
H	0.904949	2.592424	-2.351384
C	-0.842520	5.528957	1.907182
H	-0.835672	6.173376	2.795781
H	-1.189192	6.131601	1.065388
H	-1.574380	4.734624	2.080631
C	0.990049	4.194552	2.947973
H	0.931842	4.857967	3.819748
H	0.338423	3.335629	3.143644
H	2.018946	3.829281	2.863862
C	1.559275	6.110813	1.467637
H	2.564430	5.735531	1.244088
H	1.247501	6.773894	0.655237
H	1.622090	6.716507	2.380238

2

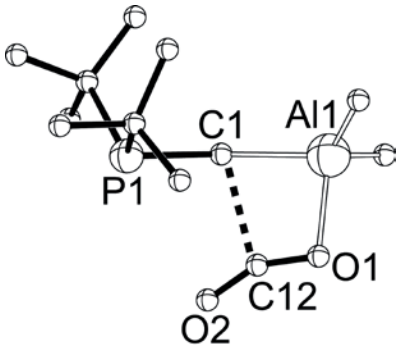


C_1

Selected bond lengths [Å] and angles [°]: P1-C12 1.90243, C12-O1 1.28138, C12-O2 1.21498, Al1-O1 1.88039, P1-C1 1.77526, Al1-C1 2.08461, P1-C12-O1 111.977, C12-O1-Al1 124.004, O2-C12-O1 129.318.

O	1.509373	1.295208	0.006161
C	1.877674	2.514414	0.146951
C	-1.031417	2.662407	0.252519
H	-1.456423	2.721202	1.259157
H	-1.799555	2.954775	-0.467306
O	2.997404	2.972168	0.260283
P	0.397815	3.709929	0.145060
Al	-0.284367	0.731021	0.013195
C	-0.718763	-0.085345	-1.729423
H	-0.288703	-1.091026	-1.805402
H	-1.803223	-0.197113	-1.855765
H	-0.350268	0.484599	-2.590014
C	-0.581806	-0.287374	1.675225
H	-1.642832	-0.523227	1.824717
H	-0.040952	-1.240674	1.669472
H	-0.244712	0.263833	2.562648
C	0.473706	4.563763	-1.511519
C	0.605223	4.783036	1.655880
C	-0.570553	5.685639	-1.569690
H	-0.620930	6.064811	-2.596578
H	-1.571147	5.337907	-1.291439
H	-0.296145	6.523759	-0.921852
C	1.872564	5.126166	-1.808582
H	2.644507	4.355186	-1.757729
H	1.858284	5.535768	-2.825032
H	2.152710	5.932716	-1.129999
C	0.152350	3.484605	-2.561033
H	-0.857123	3.078751	-2.456028
H	0.232805	3.939284	-3.554298
H	0.862816	2.652323	-2.515916
C	-0.705031	5.522642	1.962103
H	-0.568570	6.094949	2.886497
H	-0.979589	6.227763	1.173332
H	-1.540204	4.833885	2.114866
C	0.927259	3.814730	2.809861
H	0.945813	4.385741	3.744624
H	0.171960	3.028552	2.918570
H	1.906202	3.345566	2.678576
C	1.754006	5.786234	1.496914
H	2.676285	5.296517	1.172258
H	1.496769	6.583380	0.792671
H	1.936109	6.256306	2.470277

TS2



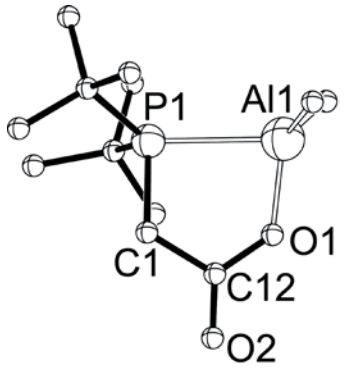
C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.86455, C1-Al1 2.08483, Al1-O1 1.95587, C12-O1 1.22113, C12-O2 1.15979, C12-C1 2.27763, O1-C12-O2 153.322, P1-C1-Al1 146.128.

Al	2.676786	-0.789477	0.834728
C	3.128379	0.929079	1.653292
C	3.165626	-2.484995	1.680339
C	0.772125	-1.044302	0.026129
P	-0.608607	-0.268200	-0.957626
C	2.392690	-1.115805	-1.572723
O	3.421784	-0.847109	-0.972779
O	1.793233	-1.417926	-2.518494
H	2.591888	1.055471	2.602045
H	4.197424	0.931747	1.899313
H	2.930412	1.816944	1.046802
H	2.999402	-3.343544	1.019801

H	4.221988	-2.496469	1.971898
H	2.582730	-2.662050	2.592003
H	0.600948	-2.127821	-0.017450
H	0.571433	-0.783140	1.088988
C	-2.107229	-0.782999	0.109975
C	-0.283941	1.590082	-0.744692
C	-2.441410	-2.207207	-0.368957
H	-1.605006	-2.898171	-0.216483
H	-3.297047	-2.594378	0.198772
H	-2.699591	-2.218630	-1.432100
C	-3.309609	0.113668	-0.210350
H	-4.224453	-0.358099	0.169880
H	-3.225261	1.093595	0.268496
H	-3.433441	0.261074	-1.289151
C	-1.904820	-0.823180	1.629797
H	-2.863811	-1.048629	2.113973
H	-1.205660	-1.611538	1.925747
H	-1.545951	0.126517	2.036080
C	-1.312451	2.379058	-1.572972
H	-2.315008	2.347453	-1.144714
H	-1.007301	3.432207	-1.615673
H	-1.366692	2.001438	-2.599659
C	1.084592	1.842738	-1.401916
H	1.112592	1.451167	-2.425609
H	1.269831	2.922797	-1.451417
H	1.907594	1.404241	-0.833788
C	-0.267769	2.113600	0.692568
H	-1.266589	2.087624	1.138524
H	0.412170	1.540285	1.331973
H	0.073612	3.157285	0.707016

3



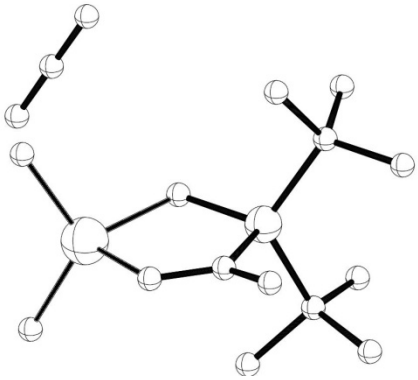
C_1

Selected bond lengths [Å] and angles [°]: P1-Al1 2.53167, P1-C1 2.53167, C1-C12 1.54252, C12-O1 1.31223, O1-Al1 1.80816, C12-O2 1.21009, O1-C12-O2 124.756, O1-C12-C1 115.320.

C	0.021389	0.059090	1.138168
P	1.582472	0.930877	1.598841
Al	0.580481	1.570160	3.834172
O	-0.976030	1.299046	2.954851
C	-1.203578	0.726989	1.796001
O	-2.281267	0.684870	1.247252
C	2.939486	-0.350864	1.373672
C	4.312620	0.333021	1.380335
C	2.856479	-1.282834	2.593811
C	2.771653	-1.186561	0.097764
C	1.708972	2.365800	0.391029
C	2.737190	3.374072	0.927971
C	0.326707	3.044625	0.371982
C	2.071565	1.951014	-1.038561
H	2.005196	2.832444	-1.687394
H	1.382228	1.198140	-1.434927
H	2.836200	-0.584905	-0.810753
H	1.818922	-1.724361	0.087620
H	-0.145770	-0.023604	0.061412
H	0.082787	-0.958154	1.544798
C	0.961947	0.170825	5.159563
C	0.920336	3.457630	4.258747
H	1.994549	0.205377	5.526344
H	0.311676	0.320695	6.030409
H	0.389843	3.724827	5.180816
H	0.586259	4.158910	3.486705
H	1.985121	3.645929	4.443582
H	0.770137	-0.842377	4.790798
H	3.571891	-1.935400	0.058675
H	3.092123	1.565764	-1.112681
H	-0.440633	2.416413	-0.090424
H	0.402624	3.964196	-0.219421
H	-0.016433	3.320961	1.373900
H	2.474552	3.709426	1.936127
H	4.481113	0.929749	0.479958

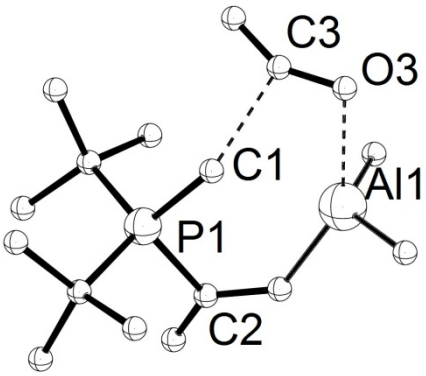
H	3.751859	2.968863	0.950682
H	5.091973	-0.436984	1.415819
H	3.040589	-0.744376	3.527382
H	3.615963	-2.066694	2.492632
H	1.883123	-1.777588	2.676229
H	4.440950	0.978050	2.256478
H	2.746740	4.252935	0.272641

2·CO_2



O	1.047024	2.030340	-0.260719
C	0.992516	2.931603	-1.169941
C	-1.459566	1.407466	-1.570137
H	-2.359197	1.854184	-1.135954
H	-1.762748	0.638038	-2.284086
O	1.736282	3.871794	-1.367508
P	-0.480220	2.669063	-2.345255
Al	-0.284367	0.731021	0.013195
C	0.485910	-1.062850	-0.270657
H	1.105031	-1.359606	0.584179
H	-0.301062	-1.821731	-0.366995
H	1.117884	-1.137683	-1.162986
C	-1.187366	1.153138	1.714475
H	-2.075342	0.528035	1.870985
H	-0.527995	0.991653	2.574992
H	-1.516425	2.199457	1.758267
C	-1.347338	4.267291	-2.423833
H	-2.279160	4.142766	-2.934813
H	-1.529576	4.623368	-1.431412
H	-0.743066	4.975355	-2.951469
C	0.259121	2.058131	-3.892038
H	-0.499840	1.606451	-4.496078
H	0.699089	2.875498	-4.424241
H	1.012782	1.333269	-3.665167
C	-2.980890	0.453666	-0.463716
O	-2.385517	0.110168	0.590376
O	-3.576262	0.797164	-1.517809

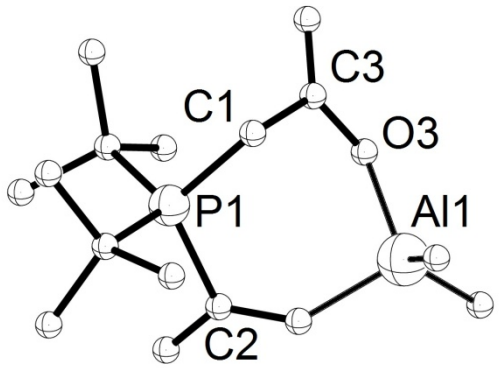
TS3



O	1.712613	-1.286367	-1.182255
C	0.638099	-1.727561	-1.421765
C	-0.342095	0.367625	1.754469
H	-0.906551	1.188335	2.208663
H	-0.480645	-0.494330	2.412387
O	-0.189092	-2.400624	-1.887104
P	-0.957149	-0.071303	0.053345
Al	3.070267	-0.095901	-0.129622
C	3.929502	-1.462497	0.962636
H	4.470845	-2.196980	0.356102
H	4.651072	-1.014214	1.654442
H	3.202157	-2.006716	1.576091
C	3.854093	0.914566	-1.600201
H	4.491137	1.722214	-1.221931
H	4.478634	0.287200	-2.245369
H	3.087196	1.379559	-2.229706
C	-1.298150	1.612953	-0.756959
C	-2.598779	-0.936793	0.455022
C	1.146984	0.701931	1.828105
O	1.737382	0.774505	0.650883
O	1.698315	0.877560	2.890168
C	-1.765727	2.692652	0.229294
H	-0.937501	3.040886	0.859384
H	-2.134475	3.558739	-0.340369
H	-2.579362	2.348800	0.879175
C	-2.354181	1.438885	-1.858600
H	-3.354905	1.302593	-1.443514

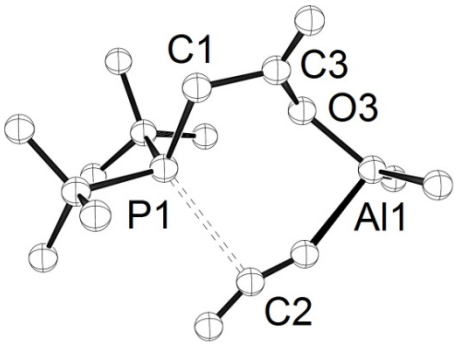
H	-2.371058	2.343216	-2.476738
H	-2.129479	0.589924	-2.513195
C	0.000366	2.090921	-1.430713
H	0.776900	2.336693	-0.706855
H	0.399894	1.328662	-2.108938
H	-0.220884	2.984937	-2.025185
C	-3.591802	-0.093120	1.264003
H	-4.051083	0.687147	0.651165
H	-4.396973	-0.736960	1.637991
H	-3.121172	0.379931	2.131823
C	-2.228157	-2.190471	1.272900
H	-3.127528	-2.799424	1.408992
H	-1.484028	-2.804105	0.752736
H	-1.848349	-1.950968	2.268696
C	-3.271579	-1.434085	-0.844234
H	-3.934288	-0.683790	-1.277981
H	-2.539973	-1.729468	-1.602171
H	-3.881002	-2.316258	-0.618057

6



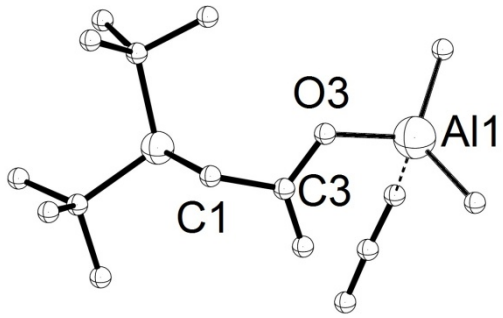
O	-1.425702	-0.993137	1.157192
C	-0.225794	-0.673816	1.417187
C	-0.169740	0.273094	-1.520909
H	0.493282	0.500352	-2.360846
H	-0.736978	-0.637304	-1.742695
O	0.395838	-0.748609	2.456376
P	0.845497	-0.078843	-0.042883
Al	-2.869079	-0.357467	0.140614
C	-3.096610	-1.643323	-1.348383
H	-4.014500	-2.229208	-1.212710
H	-3.191521	-1.140593	-2.320905
H	-2.279309	-2.373190	-1.437078
C	-4.310362	0.091652	1.378855
H	-5.175945	0.518427	0.857344
H	-4.664447	-0.787335	1.931242
H	-3.981904	0.831087	2.119349
C	1.715635	1.480060	0.491409
C	1.927462	-1.541263	-0.478440
C	-1.150730	1.443569	-1.306058
O	-2.121421	1.196223	-0.483336
O	-0.944120	2.503439	-1.861612
C	2.561342	-2.164762	0.775425
H	1.808205	-2.555050	1.463356
H	3.192357	-2.998469	0.445742
H	3.190951	-1.465569	1.327770
C	3.020645	-1.122558	-1.471232
H	3.544749	-2.025740	-1.805425
H	2.613481	-0.631150	-2.361517
H	3.762247	-0.461076	-1.014124
C	1.011761	-2.592673	-1.133095
H	0.669210	-2.287972	-2.126388
H	1.587961	-3.517107	-1.252375
H	0.136356	-2.825418	-0.515384
C	2.887713	1.162602	1.430184
H	3.701325	0.641473	0.916667
H	3.289038	2.115773	1.793608
H	2.567018	0.575950	2.295612
C	0.691812	2.344787	1.253615
H	-0.183508	2.605559	0.653282
H	0.364214	1.859140	2.177264
H	1.191948	3.282001	1.524246
C	2.211975	2.243041	-0.748443
H	2.736822	3.139953	-0.399321
H	2.921586	1.660089	-1.344042
H	1.385538	2.569302	-1.387070

TS3



O	1.712613	-1.286367	-1.182255
C	0.638099	-1.727561	-1.421765
C	-0.342095	0.367625	1.754469
H	-0.906551	1.188335	2.208663
H	-0.480645	-0.494330	2.412387
O	-0.189092	-2.400624	-1.887104
P	-0.957149	-0.071303	0.053345
Al	3.070267	-0.095901	-0.129622
C	3.929502	-1.462497	0.962636
H	4.470845	-2.196980	0.356102
H	4.651072	-1.014214	1.654442
H	3.202157	-2.006716	1.576091
C	3.854093	0.914566	-1.600201
H	4.491137	1.722214	-1.221931
H	4.478634	0.287200	-2.245369
H	3.087196	1.379559	-2.229706
C	-1.298150	1.612953	-0.756959
C	-2.598779	-0.936793	0.455022
C	1.146984	0.701931	1.828105
O	1.737382	0.774505	0.650883
O	1.698315	0.877560	2.890168
C	-1.765727	2.692652	0.229294
H	-0.937501	3.040886	0.859384
H	-2.134475	3.558739	-0.340369
H	-2.579362	2.348800	0.879175
C	-2.354181	1.438885	-1.858600
H	-3.354905	1.302593	-1.443514
H	-2.371058	2.343216	-2.476738
H	-2.129479	0.589924	-2.513195
C	0.000366	2.090921	-1.430713
H	0.776900	2.336693	-0.706855
H	0.399894	1.328662	-2.108938
H	-0.220884	2.984937	-2.025185
C	-3.591802	-0.093120	1.264003
H	-4.051083	0.687147	0.651165
H	-4.396973	-0.736960	1.637991
H	-3.121172	0.379931	2.131823
C	-2.228157	-2.190471	1.272900
H	-3.127528	-2.799424	1.408992
H	-1.484028	-2.804105	0.752736
H	-1.848349	-1.950968	2.268696
C	-3.271579	-1.434085	-0.844234
H	-3.934288	-0.683790	-1.277981
H	-2.539973	-1.729468	-1.602171
H	-3.881002	-2.316258	-0.618057

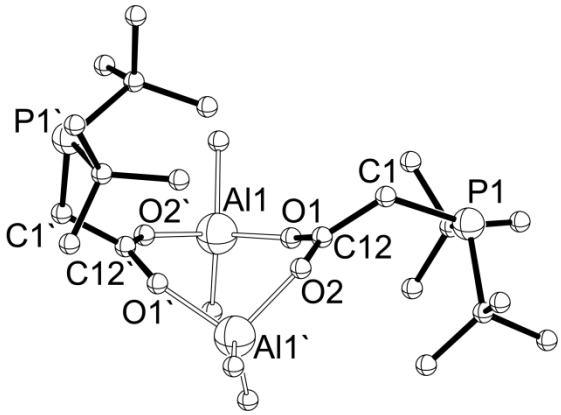
2·CO_2



O	3.147361	-0.683356	-1.233260
C	2.757952	-1.798250	-1.266111
C	-0.536475	-0.194740	1.297353
H	-0.692010	0.676849	1.937861
H	-0.847179	-1.097710	1.822231
O	2.451499	-2.893879	-1.424435
P	-1.518396	-0.065855	-0.313649
Al	3.318763	0.770888	0.282515
C	4.545009	-0.133054	1.499507
H	5.506377	-0.350324	1.020227
H	4.762148	0.483681	2.379100
H	4.122947	-1.077323	1.859521
C	3.717833	2.319002	-0.829677
H	3.741160	3.242392	-0.240151
H	4.691551	2.228104	-1.323294
H	2.959402	2.453512	-1.608551
C	-2.124154	1.730206	-0.275214
C	-2.944259	-1.254078	0.090609
C	0.913433	-0.360164	0.941569
O	1.580539	0.753468	0.753696
O	1.408397	-1.472654	0.774073
C	-0.863006	2.604150	-0.164883
H	-0.370866	2.516193	0.806933
H	-0.122491	2.345340	-0.929393
H	-1.147600	3.654036	-0.307091
C	-3.093256	2.104567	0.848241
H	-3.249886	3.190988	0.846774
H	-4.071280	1.633994	0.712975
H	-2.710179	1.828414	1.836889
C	-2.772932	2.032531	-1.636161

H	-3.022516	3.099625	-1.687675
H	-2.087528	1.805134	-2.458871
H	-3.695421	1.469842	-1.796044
C	-3.550312	-1.180877	1.498170
H	-4.041256	-0.226179	1.692562
H	-4.308716	-1.967877	1.599056
H	-2.809705	-1.349102	2.285035
C	-2.329638	-2.651512	-0.110172
H	-3.086964	-3.416890	0.099858
H	-1.980371	-2.786279	-1.138441
H	-1.478025	-2.831118	0.555535
C	-4.063605	-1.066432	-0.942089
H	-4.639956	-0.154942	-0.755466
H	-3.672000	-1.028429	-1.964848
H	-4.759516	-1.912366	-0.880131

[**3**]$_2$



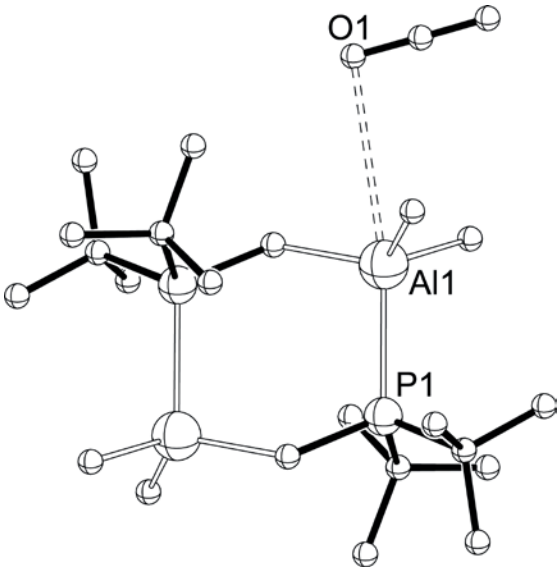
C_1

Selected bond lengths [Å] and angles [°]: Al1-O1 1.85124, O2-C12 1.26481, C12-O2 1.26902, O2-Al1’ 1.87241, Al1’-O1` 1.85495, O1`-C12` 10.26583, C12`-O2` 1.26414, O2`-Al1 1.85726, O2`-Al1-O1 102.405, O1`-Al1`-O2 98.704, O1-C12-O2 122.821, O2`-C12`-O1` 124.196.

Al	0.280675	-1.929861	1.633791
C	1.105091	-1.922962	3.407727
C	0.137283	-3.585939	0.588010
O	-1.462453	-1.298294	1.743582
O	1.080562	-0.696103	0.509025
C	-2.236883	-0.314047	1.571646
C	1.067053	0.253326	-0.326529
O	0.420728	1.328582	-0.135488
O	-1.851273	0.888859	1.490121
Al	-0.331388	1.951871	1.461928
C	0.890823	1.594148	2.956636
C	-0.988589	3.756768	1.093724
C	1.825512	0.107193	-1.605513
C	-3.696783	-0.588852	1.436195
P	3.717508	0.139727	-1.653502
P	-4.487655	-0.516939	-0.282364
C	4.273593	-1.363169	-0.634566
C	4.178254	1.748676	-0.766710
C	-4.426792	1.309330	-0.807204
C	-3.327043	-1.560845	-1.362924
H	0.952596	-2.896267	3.889359
H	2.187700	-1.753845	3.368653
H	0.684014	-1.158240	4.068080
H	-0.127781	-3.409681	-0.461989
H	1.076991	-4.151144	0.595767
H	-0.632656	-4.245603	1.007384
H	1.585707	0.765482	2.779217
H	1.495739	2.488027	3.154855
H	0.350901	1.366400	3.883802
H	-0.162492	4.462915	0.947924
H	-1.618119	3.802793	0.198002
H	-1.586733	4.137319	1.930888
H	1.561575	-0.861104	-2.042170
H	1.496727	0.890382	-2.291281
H	-3.908698	-1.589074	1.817113
H	-4.253850	0.139286	2.030184
C	5.712062	1.786453	-0.676042
H	6.185005	1.546281	-1.634984
H	6.029923	2.795256	-0.386139
H	6.090710	1.093029	0.081232
C	3.586542	2.027035	0.620410
H	2.507476	2.182597	0.573437
H	3.792104	1.240152	1.346898
H	4.021580	2.956852	1.010319
C	3.719016	2.870989	-1.714645
H	4.050948	3.837687	-1.316544
H	4.140359	2.752351	-2.717913
H	2.627229	2.909929	-1.795179
C	5.706450	-1.677261	-1.106138
H	6.409419	-0.873896	-0.870173

H	6.059354	-2.584928	-0.601323
H	5.740096	-1.850601	-2.186217
C	3.381996	-2.542977	-1.055130
H	3.314738	-2.631366	-2.146557
H	3.819523	-3.474574	-0.675992
H	2.373169	-2.459374	-0.643712
C	4.270088	-1.246586	0.893060
H	3.291323	-0.961878	1.285690
H	4.533662	-2.221746	1.323951
H	5.012644	-0.524830	1.246172
C	-1.869510	-1.121253	-1.574786
H	-1.784084	-0.240037	-2.210613
H	-1.348617	-0.919639	-0.636962
H	-1.330600	-1.940860	-2.068819
C	-4.003169	-1.670064	-2.738854
H	-3.456869	-2.394311	-3.355809
H	-5.040990	-2.008801	-2.653497
H	-3.994186	-0.712804	-3.270948
C	-3.319738	-2.951687	-0.702680
H	-4.335109	-3.305705	-0.492350
H	-2.843385	-3.671202	-1.380021
H	-2.743841	-2.951666	0.228293
C	-4.712092	2.174884	0.430191
H	-4.936470	3.197174	0.102251
H	-5.583356	1.812279	0.989526
H	-3.847485	2.219809	1.097956
C	-5.606428	1.478598	-1.783650
H	-5.500196	0.850122	-2.673615
H	-6.557608	1.225472	-1.305478
H	-5.654025	2.522653	-2.116945
C	-3.153021	1.818276	-1.488559
H	-3.237141	2.903955	-1.628936
H	-2.252982	1.627813	-0.898437
H	-3.025244	1.374675	-2.480657

4



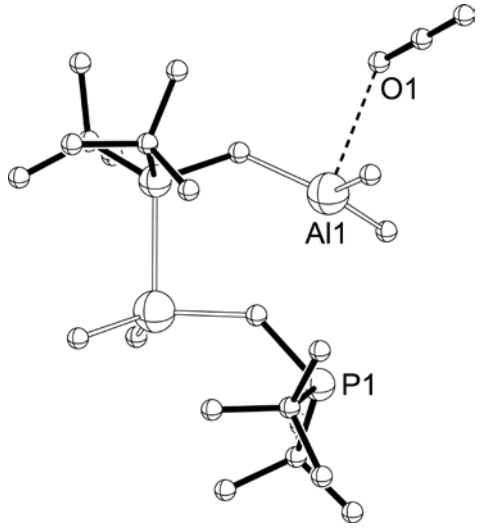
C_1

Selected bond lengths [Å] and angles [°]: Al1-O1 3.52264, Al1-P1 2.51829.

C	-0.23050	-2.37798	-0.18374
C	-0.29380	1.50743	-0.05959
H	-0.26202	-3.40658	-0.57245
H	-0.39712	1.59422	-1.14739
H	-0.26177	2.53475	0.32701
H	-0.11423	-2.46823	0.90298
P	1.28584	-1.56613	-0.78021
P	-1.81325	0.69946	0.52502
Al	-2.11591	-1.63293	-0.33781
C	2.79226	1.70805	-1.17436
H	3.26655	2.56659	-0.67906
H	3.62511	1.07355	-1.50413
H	2.30260	2.09640	-2.07511
C	2.47131	0.73142	1.90393
H	3.53482	0.48392	1.79070
H	2.44466	1.74929	2.32036
H	2.06940	0.08183	2.68689
C	-1.66072	0.69665	2.40766
C	-3.24678	1.80062	-0.03524
C	-2.99467	-1.64892	-2.12870
H	-3.07855	-2.70712	-2.41865
H	-4.02651	-1.28221	-2.05351
H	-2.52605	-1.13046	-2.97042
C	-3.31985	-2.56895	0.94386

H	-4.28733	-2.05785	1.03719
H	-3.54143	-3.56195	0.52822
H	-2.93873	-2.73216	1.95775
C	1.11599	-1.54673	-2.66419
C	2.72570	-2.67544	-0.25322
C	2.56168	-2.91964	1.25735
H	3.46115	-3.42276	1.63123
H	2.44806	-1.98476	1.81600
H	1.70552	-3.56430	1.47264
C	4.06047	-1.94545	-0.47035
H	4.08408	-0.98889	0.06149
H	4.87408	-2.56560	-0.07481
H	4.27268	-1.75414	-1.52375
C	2.74368	-4.03810	-0.95433
H	2.97742	-3.95954	-2.01884
H	3.51656	-4.66596	-0.49364
H	1.78768	-4.56159	-0.84520
C	2.46843	-1.39944	-3.37318
H	3.09161	-2.29205	-3.27920
H	2.28129	-1.24221	-4.44238
H	3.02899	-0.53466	-3.00550
C	0.39154	-2.79500	-3.18600
H	0.34318	-2.74117	-4.28058
H	0.90604	-3.72251	-2.92102

5



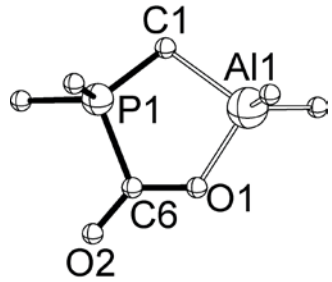
C₁

Selected bond lengths [Å] and angles [°]: Al1-O1 2.78366.

C	0.56175	-1.05539	-0.27039
C	-0.53570	2.10172	-0.64200
H	0.69902	-0.43489	0.62976
H	-0.64911	1.98731	-1.72917
H	-0.67729	3.16909	-0.42823
H	0.73031	-0.42300	-1.16235
P	2.06042	-2.17336	-0.25236
P	-1.89643	1.12020	0.07731
Al	-1.45337	-1.32271	-0.45176
C	2.36806	1.36885	-2.13466
H	2.83610	2.30675	-2.45824
H	3.16871	0.62889	-2.01548
H	1.72322	1.02971	-2.95448
C	2.42997	1.82356	1.21982
H	2.63808	0.87211	1.72205
H	3.41333	2.24514	0.97109
H	1.95986	2.48345	1.95940
C	-1.86735	1.49472	1.93254
C	-3.49038	1.78726	-0.69982
C	-2.03999	-1.54969	-2.34324
H	-1.83062	-2.57385	-2.67978
H	-3.12111	-1.40397	-2.45986
H	-1.54011	-0.87948	-3.05483
C	-2.57758	-2.34046	0.83163
H	-3.63502	-2.12567	0.62466
H	-2.44458	-3.42028	0.68390
H	-2.40803	-2.14595	1.89649
C	1.67678	-3.41585	-1.63044
C	1.90366	-3.01969	1.44027
C	2.43119	-1.98678	2.45158
H	2.44137	-2.42842	3.45634
H	3.44751	-1.66152	2.20658
H	1.78669	-1.10039	2.49474
C	2.82594	-4.24450	1.48550
H	3.82952	-4.01316	1.11057
H	2.92403	-4.58814	2.52309
H	2.42226	-5.07784	0.90267
C	0.49423	-3.42151	1.87849
H	0.02964	-4.14684	1.20731
H	0.53826	-3.87227	2.87939
H	-0.16434	-2.55176	1.93727

C	2.94396	-4.23774	-1.91620
H	3.21282	-4.89897	-1.08947
H	2.77867	-4.86391	-2.80224
H	3.79753	-3.58222	-2.11744
C	0.49572	-4.35983	-1.39513
H	0.26473	-4.90217	-2.32189
H	0.72008	-5.10463	-0.62551
H	-0.41237	-3.82567	-1.09464
C	1.40357	-2.55660	-2.87706
H	2.21109	-1.83462	-3.04905
H	1.33908	-3.20574	-3.75938
H	0.46107	-2.00970	-2.80067
C	-3.89321	3.18547	-0.21956
H	-3.07907	3.90667	-0.35061
H	-4.74167	3.53473	-0.82094
H	-4.20667	3.19969	0.82699
C	-3.25509	1.86349	-2.21866
H	-2.58002	2.68169	-2.48370
H	-2.85239	0.93017	-2.62250
H	-4.21632	2.05240	-2.71079
C	-4.62861	0.78408	-0.45123
H	-5.53517	1.13856	-0.95676
H	-4.38233	-0.20164	-0.85872
H	-4.86595	0.66172	0.60722
C	-3.19461	1.09178	2.59111
H	-3.08658	1.17975	3.67879
H	-4.02435	1.73673	2.29293
H	-3.45981	0.05308	2.36639
C	-1.54728	2.96347	2.23889
H	-2.28423	3.65579	1.82693
H	-1.52985	3.10245	3.32693
H	-0.55967	3.24137	1.85661
C	-0.75972	0.63394	2.56289
H	-0.74577	0.81214	3.64496
H	-0.92715	-0.43569	2.40144
H	0.22930	0.90131	2.18095
Al	1.39505	1.59310	-0.44412
O	1.80276	4.34527	-0.53378
C	2.64279	4.83659	0.11083
O	3.47350	5.33590	0.74626

2-Me

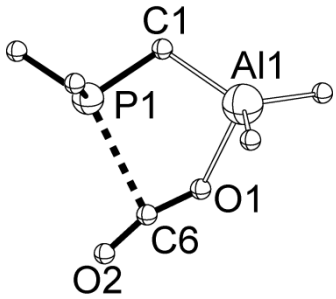


C_1

Selected bond lengths [Å] and angles [°]: P1-C6 1.89346, C6-O1 1.28221, C6-O2 1.21142, Al1-O1 1.88697, P1-C1 1.75742, Al1-C1 2.09961, O2-C6-O1 130.669, P1-C1-Al1 101.175.

O	1.621216	-0.542960	1.413808
C	0.344093	-0.454005	1.485199
C	0.842793	-0.586563	-1.364129
H	0.797415	-1.655397	-1.597188
H	0.785781	-0.000525	-2.284172
O	-0.399232	-0.512647	2.439965
P	-0.419352	-0.151688	-0.221145
Al	2.565177	-0.290545	-0.200465
C	3.135898	1.602093	-0.262828
H	4.150712	1.722524	0.133536
H	3.147979	1.998494	-1.286106
H	2.492839	2.261318	0.334764
C	3.841283	-1.762658	-0.448253
H	4.279817	-1.751874	-1.453448
H	4.672363	-1.702239	0.263376
H	3.367262	-2.741521	-0.309762
C	-0.772027	1.626480	-0.301671
C	-2.009385	-1.026167	-0.226353
H	-1.321449	1.853827	-1.218406
H	-1.363840	1.915923	0.569714
H	0.175719	2.170368	-0.300426
H	-2.591166	-0.753860	-1.109660
H	-2.549322	-0.760597	0.686211
H	-1.825988	-2.102794	-0.228239

TS1-Me

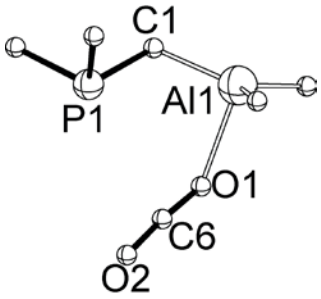


C_1

Selected bond lengths [Å] and angles [°]: P1-C6 2.75342, C6-O1 1.19113, C6-O2 1.15920, O1-Al1 2.11814, O2-C6-O2 162.027,P1-C1-Al1 108.252.

O	2.142750	-0.906323	1.312231
C	1.307496	-0.678851	2.130395
C	0.509120	-0.801875	-1.151582
H	0.405262	-1.895198	-1.111855
H	0.174351	-0.472603	-2.143726
O	0.764432	-0.556086	3.147133
P	-0.531495	-0.090817	0.167324
Al	2.420976	-0.400454	-0.725711
C	2.921933	1.493494	-0.496223
H	3.998746	1.604063	-0.326709
H	2.673676	2.090690	-1.382508
H	2.414357	1.965506	0.354974
C	3.767540	-1.745543	-1.201538
H	4.028860	-1.692815	-2.265269
H	4.697014	-1.602596	-0.638783
H	3.416613	-2.765712	-1.008913
C	-0.767570	1.646761	-0.408279
C	-2.233226	-0.758138	-0.114009
H	0.194293	2.164024	-0.434732
H	-1.430449	2.180622	0.277473
H	-1.204921	1.660572	-1.412554
H	-2.941804	-0.285335	0.571831
H	-2.551239	-0.574137	-1.145677
H	-2.240102	-1.834844	0.072322

vdW-Me

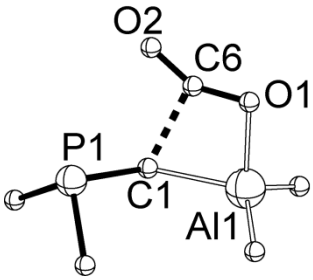


C_1

Selected bond lengths [Å] and angles [°]: P1-C6 3.21268, C6-O1 1.17551, C6-O2 1.15324, Al1-O1 2.26874, O2-C6-O1 174.775, P1-C1-Al1 110.861.

O	2.249447	-1.096832	1.354081
C	1.693624	-0.707444	2.313902
C	0.422709	-0.849283	-1.075122
H	0.336094	-1.935419	-0.927210
H	0.051483	-0.634058	-2.087280
O	1.228365	-0.364081	3.311702
P	-0.620583	-0.020930	0.193885
Al	2.340290	-0.413789	-0.807485
C	2.850126	1.436302	-0.356450
H	3.908425	1.502310	-0.079847
H	2.698945	2.118286	-1.202459
H	2.266118	1.843403	0.479395
C	3.690842	-1.699255	-1.415888
H	3.910951	-1.569367	-2.482535
H	4.638619	-1.579753	-0.879346
H	3.358741	-2.734908	-1.283678
C	-0.797617	1.657664	-0.568325
C	-2.317279	-0.673789	-0.175139
H	-1.500032	2.259242	0.014829
H	0.167361	2.170652	-0.574711
H	-1.164820	1.581514	-1.598244
H	-3.065023	-0.131162	0.410910
H	-2.552577	-0.571800	-1.240321
H	-2.371187	-1.730618	0.099083

TS2-Me

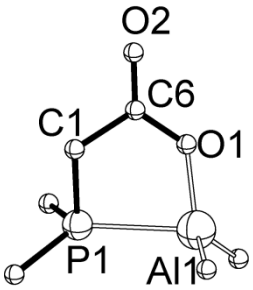


C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.86296, C1-Al1 2.10815, Al-O1 1.93843, O1-C61.22670, C6-O2 1.16388, C1-C6 2.18233.

Al	2.716491	-0.722762	0.693397
C	3.177467	1.161411	0.467351
C	3.180710	-1.814926	2.244888
C	0.755140	-1.209080	0.092642
P	-0.389168	-0.285897	-1.051427
C	2.242264	-2.001499	-1.294114
O	3.346554	-1.665792	-0.878612
O	1.578924	-2.563030	-2.068243
H	2.568720	1.823221	1.093016
H	4.223146	1.319911	0.756222
H	3.072922	1.496194	-0.570216
H	2.830275	-2.847855	2.139667
H	4.265696	-1.852386	2.394707
H	2.744877	-1.416037	3.168095
H	0.411625	-2.244826	0.181193
H	0.588716	-0.799831	1.115004
C	-2.005997	-0.710722	-0.241551
H	-2.807767	-0.125058	-0.701087
H	-2.228860	-1.768878	-0.403167
H	-1.991957	-0.509581	0.835810
C	-0.206697	1.430034	-0.368749
H	0.742400	1.869971	-0.682144
H	-1.011476	2.050484	-0.773877
H	-0.266316	1.453725	0.726169

3-Me

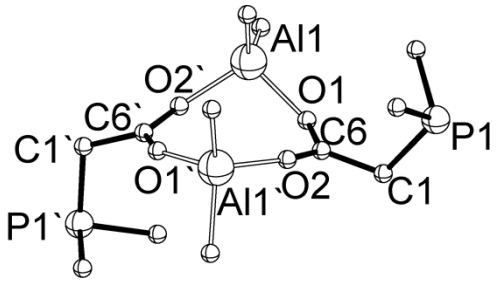


C_1

Selected bond lengths [Å] and angles [°]: P1-Al1 2.51469, P1-C1 1.84005, C1-C6 1.54341, C6-O2 1.20840, C6-O1 1.31513, O1-Al1 1.80962, C1-C6-O1 114.863, O1-C6-O2 124.811.

P	0.949097	-0.790067	0.024514
C	1.886550	-1.977007	-1.010176
H	2.944891	-1.706532	-1.055782
H	1.789483	-2.981854	-0.592501
H	1.469111	-1.981599	-2.020005
C	1.821545	-0.778079	1.636752
H	1.668695	-1.730685	2.149065
H	2.892478	-0.601818	1.503393
H	1.400680	0.018662	2.256451
C	1.309903	0.871486	-0.678927
H	2.336273	1.208672	-0.515344
H	1.131924	0.820660	-1.760439
C	0.323572	1.904558	-0.094106
O	0.660540	3.055985	0.050448
O	-0.863643	1.426163	0.207932
Al	-1.508353	-0.257081	0.047374
C	-2.108745	-0.709135	-1.767450
H	-2.231006	-1.790840	-1.897276
H	-3.079427	-0.248948	-1.985856
H	-1.414166	-0.359322	-2.540905
C	-2.339374	-0.903353	1.696452
H	-3.330065	-0.457938	1.841220
H	-2.473758	-1.990786	1.689164
H	-1.742173	-0.644858	2.577966

[3-Me]$_2$

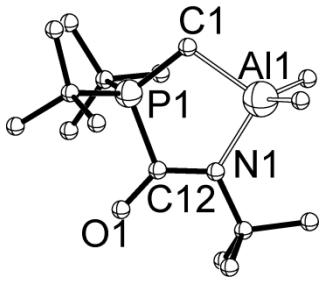


C_1

Selected bond lengths [Å] and angles [°]: Al1-O1 1.86392, O1-C6 1.26853, C6-O2 1.26244, O2-Al1` 1.84472, Al1`-O1` 1.85428, O1`-C6` 1.26399, C6`-O2` 1.85600, O2`-Al1 3.19872, O2`-Al1-O1 102.442, O2-Al2-O1` 105.676, O1-C6-O2 123.502, O1`-C6`-O2` 124.125.

Al	0.240945	0.470142	0.898781
C	-0.202499	-1.394807	0.504723
C	1.534164	1.484007	-0.174398
O	-1.319670	1.471455	0.884501
O	0.898774	0.596888	2.617554
C	-2.181499	2.133835	1.529622
C	0.957810	0.985864	3.817119
O	-0.052335	1.378435	4.476418
O	-2.294570	2.114115	2.790973
Al	-1.856217	0.995307	4.205489
C	-2.020479	-0.879292	3.627074
C	-2.776035	1.723634	5.766218
C	2.264353	0.909264	4.523511
C	-3.070743	3.063374	0.779502
P	2.547312	-0.775004	5.336366
P	-2.232905	4.731045	0.446626
C	2.313845	-1.902052	3.884572
C	0.920591	-1.030375	6.188827
C	-1.089289	4.846368	1.904076
C	-1.008170	4.211669	-0.840179
H	-0.125350	-1.587774	-0.571737
H	0.484468	-2.090824	1.001569
H	-1.217191	-1.664849	0.814375
H	1.734153	2.483777	0.231247
H	2.495066	0.955604	-0.205811
H	1.209266	1.612129	-1.213848
H	-1.092325	-1.306069	3.228257
H	-2.331768	-1.511693	4.467699
H	-2.779541	-1.001039	2.844065
H	-2.487419	1.200242	6.685339
H	-2.538569	2.784222	5.909184
H	-3.865370	1.642569	5.678802
H	3.087413	1.063737	3.822947
H	2.301236	1.653641	5.321059
H	-3.324589	2.645418	-0.197201
H	-3.975868	3.251326	1.357558
H	1.345193	-1.778104	3.390906
H	3.108194	-1.732835	3.152151
H	2.398951	-2.932608	4.240844
H	0.074717	-1.092636	5.496551
H	0.978350	-1.965796	6.752190
H	0.740190	-0.217757	6.897849
H	-0.515873	5.772378	1.807273
H	-1.662017	4.894414	2.833559
H	-0.385572	4.007507	1.963362
H	-1.528637	3.994605	-1.776907
H	-0.326373	5.047505	-1.022670
H	-0.425015	3.336590	-0.541408

7

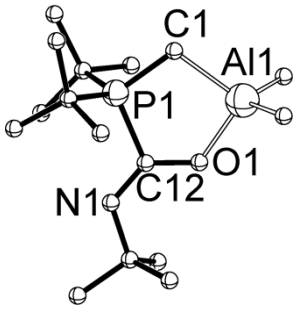


C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.77105, C1-Al1 2.06896, Al1-N1 1.97770, N1-C12 1.33046, C12-O1 1.23685, C12-P1 1.87660, P1-C1-Al1 104.574, P1-C12-O1 116.250, O1-C12-N1 131.201.

C	-0.503030	1.205514	1.472962
H	-0.685673	0.764098	2.457385
H	-0.939538	2.207008	1.449217
C	0.247848	-0.819517	-0.509431
P	-1.180115	0.159726	0.214186
C	-2.366439	-1.106348	0.900788
C	-3.101079	-1.887489	-0.196508
H	-2.400387	-2.311188	-0.919990
H	-3.652344	-2.707280	0.279018
H	-3.832213	-1.261719	-0.717288
C	-3.379587	-0.420007	1.828550
H	-2.890855	0.103674	2.654792
H	-4.015571	0.293360	1.298064
H	-4.030932	-1.190222	2.257059
C	-1.501997	-2.080200	1.723961
H	-0.830382	-2.654576	1.080557
H	-0.907484	-1.566473	2.487569
H	-2.168095	-2.780564	2.240097
C	-1.813483	1.192135	-1.207381
C	-0.755916	2.280126	-1.465086
H	-0.636161	2.964607	-0.621304
H	0.222860	1.845293	-1.691784
H	-1.074454	2.866978	-2.333827
C	-3.150070	1.845660	-0.832811
H	-3.415218	2.569210	-1.611970
H	-3.958965	1.111452	-0.774909
H	-3.095748	2.385256	0.118767
C	-1.970164	0.360926	-2.490002
H	-2.699030	-0.443990	-2.385916
H	-2.318938	1.032844	-3.282861
H	-1.022756	-0.083229	-2.804069
O	-0.055621	-1.786288	-1.218689
N	1.432532	-0.308642	-0.184397
Al	1.541948	1.130186	1.168042
C	2.262652	2.814823	0.401408
H	2.242099	2.834934	-0.695801
H	1.695934	3.689946	0.746535
H	3.304456	2.974976	0.705974
C	2.357775	0.441828	2.842328
H	3.443128	0.588106	2.895885
H	1.931353	0.950151	3.717631
H	2.168618	-0.631978	2.976935
C	2.639893	-0.948490	-0.786019
C	3.875299	-0.164142	-0.335273
H	3.989016	-0.187458	0.753386
H	4.770773	-0.615024	-0.773569
H	3.825338	0.878879	-0.663935
C	2.560832	-0.886752	-2.317715
H	3.487686	-1.279313	-2.748943
H	1.722114	-1.472115	-2.697014
H	2.449720	0.154389	-2.641953
C	2.762357	-2.396905	-0.295552
H	1.912077	-2.996001	-0.626456
H	3.682369	-2.843054	-0.688194
H	2.811503	-2.415461	0.798556

***E*-7$_{C=O}$**



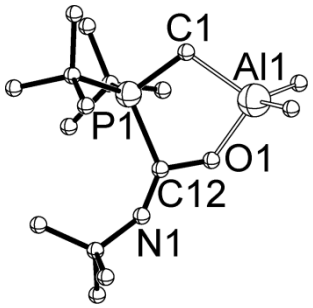
C₁

Selected bond lengths [Å] and angles [°]: P1-C1 1.77778, C1-Al1 2.08097, P1-C12 1.86833, C12-O1 1.30393, C12-N1 1.27471, Al1-O1 1.86351, P1-C1-Al1 105.101, P1-C12-N1 115.739, N1-C12-O1 131.006, P1-C12-O1 113.236.

C	1.605126	1.528605	-0.432863
H	1.934769	1.603528	-1.473176
H	2.432123	1.829893	0.214204
O	-1.211857	1.217643	0.073301
C	-0.780008	-0.011473	0.018496
P	1.081234	-0.134756	-0.087487
C	1.509508	-1.294861	-1.486327
C	1.236543	-2.762518	-1.132895
H	0.230636	-2.893749	-0.724688
H	1.326280	-3.357253	-2.049613
H	1.974095	-3.146260	-0.421265
C	2.983697	-1.117276	-1.880375
H	3.199861	-0.103242	-2.226897
H	3.666928	-1.353456	-1.060629
H	3.202166	-1.806355	-2.704007
C	0.613799	-0.876630	-2.666805

H	-0.436316	-1.098504	-2.461589
H	0.707498	0.189166	-2.903739
H	0.922760	-1.442036	-3.552968
C	1.645686	-0.639021	1.620314
C	1.249149	0.524380	2.548556
H	1.764945	1.455719	2.300453
H	0.169991	0.713532	2.523496
H	1.518236	0.252025	3.574960
C	3.167763	-0.831670	1.638024
H	3.493842	-0.947906	2.677786
H	3.464174	-1.735780	1.097340
H	3.703359	0.023460	1.212975
C	0.954571	-1.916183	2.120555
H	1.232375	-2.796920	1.539632
H	1.273453	-2.083684	3.155946
H	-0.133118	-1.824923	2.096836
N	-1.407158	-1.120683	0.053498
Al	-0.111844	2.688632	-0.241096
C	-0.582858	3.443528	-2.005681
H	0.150704	4.186082	-2.344383
H	-0.636952	2.666813	-2.780288
H	-1.557704	3.945463	-1.990216
C	-0.104792	3.873255	1.339682
H	0.710330	4.606253	1.284218
H	-1.037403	4.446570	1.405506
H	0.007629	3.335547	2.288549
C	-2.877953	-1.144901	0.168586
C	-3.274413	-2.622960	0.178649
H	-2.795870	-3.137393	1.018614
H	-4.359716	-2.735161	0.270327
H	-2.948371	-3.108135	-0.747319
C	-3.526910	-0.447476	-1.034396
H	-3.277875	0.615678	-1.053523
H	-3.182875	-0.907605	-1.967137
H	-4.615836	-0.554547	-0.984479
C	-3.321926	-0.484683	1.480738
H	-2.836500	-0.975955	2.331533
H	-3.063374	0.576449	1.490479
H	-4.405713	-0.585269	1.603189

Z-7$_{C=O}$



C_1

Selected bond lengths [Å] and angles [°]: P1-C1 1.78558, C1-Al1 2.05953, Al1-O1 1.84037, P1-C12 2.00126, C12-N1 1.24736, P1-C1-Al1 106.271, P1-C12-N1 135.041, N1-C12-O1 122.680, P1-C12-O1 102.101.

C	2.043099	0.455849	0.808857
H	2.010089	0.514755	1.901163
H	2.734094	1.221287	0.442375
O	0.825662	-1.778611	-0.345912
C	-0.278765	-1.108215	-0.152006
P	0.405436	0.746503	0.159349
C	-0.508491	1.878028	1.364850
C	-1.652089	2.706609	0.762125
H	-2.368663	2.123915	0.192190
H	-2.193811	3.189337	1.584212
H	-1.268291	3.502752	0.118046
C	0.489140	2.880585	1.978155
H	1.268621	2.391056	2.563038
H	0.970205	3.505669	1.220895
H	-0.071558	3.541391	2.649694
C	-1.014138	0.956231	2.489030
H	-1.746545	0.226290	2.137411
H	-0.188806	0.401103	2.949146
H	-1.480175	1.566931	3.270770
C	0.596085	1.467106	-1.560454
C	1.573141	0.568421	-2.337986
H	2.560294	0.524778	-1.870327
H	1.201097	-0.455056	-2.434124
H	1.692152	0.989398	-3.342882
C	1.175660	2.887358	-1.491725
H	1.365091	3.232648	-2.514596
H	0.488391	3.599031	-1.027611

H	2.127764	2.917243	-0.953386
C	-0.745593	1.478933	-2.303762
H	-1.479595	2.142616	-1.840478
H	-0.572699	1.839055	-3.324411
H	-1.168389	0.471643	-2.373155
N	-1.408564	-1.625619	-0.260393
Al	2.499887	-1.503142	0.366853
C	2.679017	-2.494467	2.069357
H	3.586662	-2.205890	2.615304
H	1.827736	-2.311395	2.739041
H	2.733355	-3.577968	1.911370
C	3.871299	-1.764131	-1.039295
H	4.551528	-0.906048	-1.124981
H	4.494854	-2.641023	-0.829678
H	3.420964	-1.918383	-2.027487
C	-2.841139	-1.480486	-0.253984
C	-3.355080	-2.287742	0.948028
H	-4.449867	-2.299987	0.955931
H	-2.984730	-3.314069	0.892767
H	-3.004639	-1.847483	1.887299
C	-3.330210	-2.146084	-1.551958
H	-4.424375	-2.180777	-1.575837
H	-2.980776	-1.582521	-2.423587
H	-2.934004	-3.161551	-1.620322
C	-3.418029	-0.065013	-0.191860
H	-3.220392	0.407634	0.771336
H	-3.019547	0.558077	-0.997578
H	-4.504894	-0.110826	-0.315046

[1] Gaussian 09, Revision A.02, Frisch M. J.; Trucks G. W.; Schlegel H. B.; Scuseria G. E.; Robb M. A.; Cheeseman J. R.; Scalmani G.; Barone V.; Mennucci B.; Petersson G. A.; Nakatsuji H.; Caricato M.; Li X.; Hratchian H. P.; Izmaylov A. F.; Bloino J.; Zheng G.; Sonnenberg J. L.; Hada M.; Ehara M.; Toyota K.; Fukuda R.; Hasegawa J.; Ishida M.; Nakajima T.; Honda Y.; Kitao O.; Nakai H.; Vreven T.; Montgomery J. A. Jr.; Peralta J. E.; Ogliaro F.; Bearpark M.; Heyd J. J.; Brothers E.; Kudin K. N.; Staroverov V. N.; Kobayashi R.; Normand J.; Raghavachari K.; Rendell A.; Burant J. C.; Iyengar S. S.; Tomasi J.; Cossi M.; Rega N.; Millam J. M.; Klene M.; Knox J. E.; Cross J. B.; Bakken V.; Adamo C.; Jaramillo J.; Gomperts R.; Stratmann R. E.; Yazyev O.; Austin A. J.; Cammi R.; Pomelli C.; Ochterski J. W.; Martin R. L.; Morokuma K.; Zakrzewski V. G.; Voth G. A.; Salvador P.; Dannenberg J. J.; Dapprich S.; Daniels A. D.; Farkas O.; Foresman J. B.; Ortiz J. V.; Cioslowski J.; Fox D. J. Gaussian, Inc., Wallingford CT, 2009.

[2] (a) Zhao Y.; Truhlar D. G. *Acc. Chem. Res*. **2008**, *41*, 157–167; (b) Zhao Y.; Truhlar D. G. *Theor Chem Account* **2008**, *120*, 215–241; (c) Janesko B. G.; *J. Chem. Theory Comput*. **2010**, *6*, 1825–1833. DFT calculations were carried out with Gaussian 09 (Revision A.02).

[3] Boudreau J.; Courtemanche M. A.; Fontaine F. G. *Chem. Commun*. **2011**, *47*, 11131–11133.