An Ylide-Substituted Tetraphosphene, Cyclotetraphosphane, and Bicyclotetraphosphane

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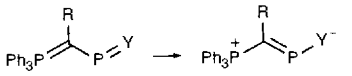
The reaction of two specific ylidyl dichlorophosphanes, $Ph_3P{=}CR{-}PCl_2$, with $P(SiMe_3)_3$ yields the ylidyl trimethylsilyl diphosphenes $Ph_3P{=}CR{-}P{=}P{-}SiMe_3$ as primary products which form two different types of dimers: the cyclotetraphosphane **9** (R = $SiMe_3$), and the tetraphosphene **10** (R = 2,6-$Cl_2C_6H_3$). The latter compound is readily converted to the bis(ylidyl)bicyclotetraphosphane **11**. The molecular structures of **9** and **11** allow a strong transanular interaction between the ylide-substituted phosphorus atoms, which results in very large two-bond coupling constants ($^2J_{PP}$ = 184 and 332 Hz respectively). The central PP bond in **11** is relatively long (220.7 pm); quantum chemical calculations show the lengthening to be a consequence of the perpendicular orientation of the ylidic donor p-orbital.

Ylide substituents strongly influence P^{III} towards dicoordination[1][2]. They stabilize thioxophosphanes **1**,[3] selenoxophosphanes **2**,[3] silyliminophosphanes **3**,[4] and silylphosphaalkenes **4**[5][6] as monomers, but not however phenyldiphosphenes **5**. In the latter case their dimers, i.e. cyclotetraphosphanes, are obtained instead.[7] However, different results are achieved in the case of some silyldiphosphenes **6**, which are reported here.



	Y
1	S
2	Se
3	$NSiMe_3$
4	$C(SiMe_3)_2$
5	PPh
6	$PSiMe_3$

Synthesis

The reaction of ylidyl dichlorophosphanes (dichlorophosphanyl triphenylphosphonium ylides) **7**[2] with tris(trimethylsilyl)phosphane leads to the known[1] bis(ylidyl)phosphenium chlorides **8**, R = Et, Ph, 3-MeC_6H_4, 4-MeC_6H_4. However, for R = $SiMe_3$ and 2,6-$Cl_2C_6H_3$, the condensation occurs as intended and yields the diphosphenes **6**. These are readily identified by their ^{31}P-NMR spectra.

The spectra reflect the strong contribution of the polar resonance formula (see above): The ^{31}P-NMR signal of the Me_3Si-bonded phosphorus atom in **6** is found at exceptionally high field (δ = 233 and 192, respectively) and the shift difference of the two adjacent phosphorus atoms ($\Delta\delta$ = 324 and 297 respectively) is significantly larger than in any other polar diphosphene reported so far.[8] At the same time the coupling constant ($^1J_{PP}$ = 537 and 511 Hz respectively) is among the smallest observed for diphosphenes so far (525–640 Hz).[8]

The diphosphenes **6** are not stable in solution but dimerize within approximately 1 day. In the case of R = $SiMe_3$ the dimer has the tetraphosphetane (cyclotetraphosphane) structure **9** as shown by the X-ray structure analysis (see below) and by the ^{31}P-NMR spectrum, which demonstrates an $AA'BB'C_2$ spin system. In case of R = 2,6-$Cl_2C_6H_3$, however, the dimer has the open chain tetraphosphene structure **10** as infered from the ^{31}P-NMR spectrum. In particular the large two-bond coupling constant $^2J_{CE}$, and the considerably smaller one-bond coupling constant $^1J_{DE}$, are analogous to the corresponding constants $^2J_{PP}$ and $^1J_{PP}$ found for triphosphenes.[10] To our knowledge no tetraphosphene has yet been described.[11] The alternative formation of dimers **9** and **10** may be governed by the steric demands of R. It seems that the bulky 2,6-dichlorophenyl groups are easier accommodated in the flexible structure **10** than in the rigid structure **9**.

Repeated recrystallization of **10** from a mixture of benzene and dichloromethane resulted in the loss of the trimethylsilyl groups and the formation of the *exo*,*exo*-con-

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[+] X-ray structure analysis.

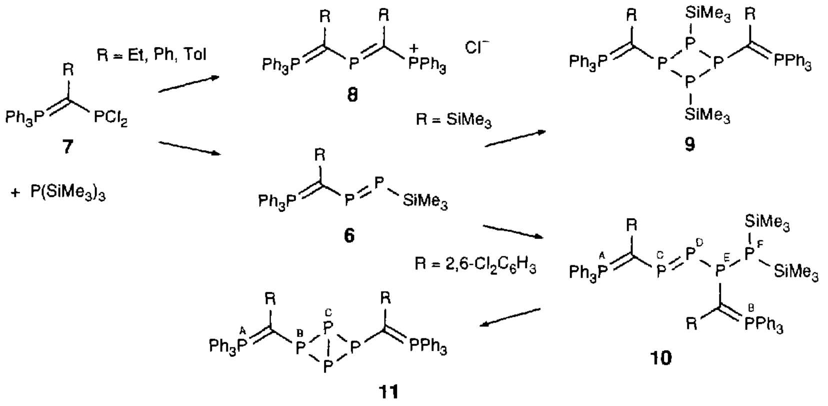
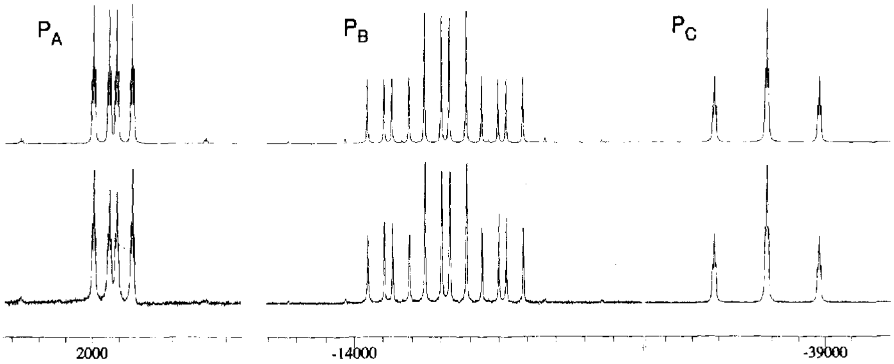


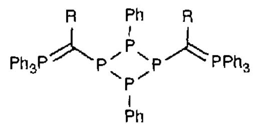
Figure 1. Experimental (bottom) and calculated[26] (top) ^{31}P-NMR spectrum of **11** in CD_2Cl_2 (ν_0 = 109.379 MHz); scale graduation: 100 Hz



figurated bicyclotetraphosphane **11**.[12] Its identity follows from the ^{31}P-NMR spectrum (Figure 1) which displays a AA'BB'C_2 spin system, and shows the characteristic upfield shift (δ = −355) of the bridgehead phosphorus atoms P_C. The original coupling constants are confirmed by the calculated spectrum (Figure 1). All attempts to convert the cyclotetraphosphane **9**, by heating or by oxidation, to a bicyclotetraphosphane analogue of **11** with R = $SiMe_3$ failed.

Molecular Structure of 9

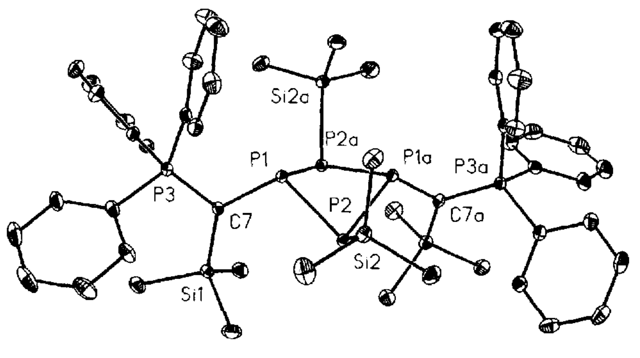
The ^{31}P-NMR data of **9** compare well to those of the known 1,3-bis(ylidyl)tetraphosphetanes **12** and **13**.[7] As in their case the large coupling constant $^2J_{AB}$ indicates a predominantly synperiplanar orientation of the lone electron pair at P_B to the phosphonio group P_A. Remarkably large, indicative of the folding of the four-membered ring and characteristic for donor-substituted phosphorus ring members,[7] is the transanular coupling constant $^2J_{BB'}$ = 183.9 Hz. It exceeds that of compound **13** (179.7 Hz)[7] which had been the largest in bicyclotetraphosphanes reported to date.



	R
12	Me
13	m-Tol

Single crystal X-ray structure analyses reveal further details of the molecular structure of the cyclotetraphosphane **9** and the bicyclotetraphosphane **11**. Crystals of **9** were grown from tetrahydrofuran and contain two molecules of the solvent per molecule of **9**. The structure of **9** (Figure 2) may be compared to that of many other cyclotetraphosphanes,[17][18][19][20][21][22][23] and in particular to that of the 1,3-bis(ylidyl)cyclotetraphosphane **12**.[7] The four-membered ring of **9** is folded, and the folding angle of 119.1° is, in accord with the large coupling constant $^2J_{BB'}$ (see above), smaller than that of **12** (140°). The ring substituents take up equatorial positions in an all-*trans* configuration. The ylidic carbon atom C7 shows a planar coordination with the phosphonio group P3 synperiplanar to the lone pair of electrons at P1.

Figure 2. Molecular structure of **9** (thermal ellipsoids with 25% probability)



The coordination of the ylide-substituted phosphorus atom P1 in **9** is much less pyramidal (sum of angles 303°) than that of P2 (sum of angles 282°). In this manner the ylide substituents achieve a maximum distance from each other. The same difference, although less pronounced, has been observed for **12**.[7] In other known cyclotetraphosphanes the sum of bond angles at the phosphorus ring members are either equal or do not differ by more than 11°.[17][18][19][20][21][22][23]

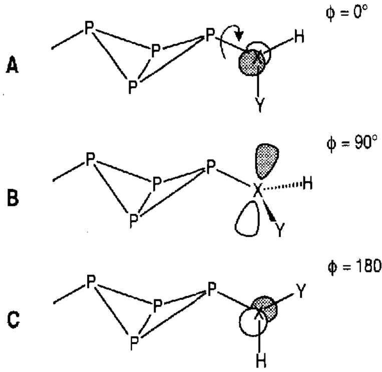
Molecular Structure of 11

Generally the coupling constant $^2J_{PP}$ between the two non-bridgehead phosphorus atoms of a bicyclotetraphosphane allows differentiation between an *endo,exo*-isomer, for which the coupling constant is found in a range up to 42 Hz,[13][14][15][24][25] and an *exo,exo*-isomer, for which a range of 157–249 Hz[13][14][15][16][25] has been found. For compound **11** $^2J_{BB'}$ = 332.3 Hz clearly indicates the *exo,exo*-configuration,which was already inferred from the symmetry of the spin system. Moreover $^2J_{BB'}$ of **11** is the largest two-bond coupling constant in such a system so far observed. It is roughly twice that found for the monocyclic compounds **9**, **12**, and **13**. It indicates a strong transanular interaction of the two phosphorus atoms involved, and this is possibly intensified by a charge transfer from the ylidic carbon atoms.

Yellow octahedral crystals of **11** were grown from a solution in equal volumes of benzene and dichloromethane. They contain two molecules of the latter per molecule of **11**. The X-ray structure determination also confirms the *exo,exo*-bicyclotetraphosphane structure for the solid state (Figure 3). The environment of the ylidic carbon atoms C1 and C2 is planar, with the phosphonio groups P5 and P6 being synperiplanar to the lone pair of electrons at P2 and P4 respectively, as in **9**. The planes of C1 and C2 coincide and the central bond P1 P3 stands perpendicular to them. The bonds between the ylidic carbon atom and the phosphorus(III) atom in **11** [P2–C1 and P4–C2, average 178.8(4) pm, Table 1] are as long as those in the monocyclic compounds **9** [179.5(2) pm] and **12** [177.7(5) pm]. As a result of the transanular bond, the sum of angles at the non-bridgehead phosphorus atoms P2 and P4 (average 271°) is considerably smaller than in **9** or **12**. The structural data of **11** can be further compared to those of two known bicyclotetraphosphanes **14** (R = 2,4,6-tBu$_3$C$_6$H$_2$[27]) and **15** (R = (Me$_3$Si)$_2$N[25]). The folding angle between the planes of the three-membered rings P1–P2–P3 and P1–P3–P4 in **11** is 96.7°, and only marginally wider than that of **14** (95.5°) and **15** (95.2°). The peripheral PP-bond lengths of **11** are somewhat shorter than those of **9** but similar to those of **14** and **15** (220–224 pm). While the peripheral PP-bonds of bicyclotetraphosphanes seem to be quite uniform in length, the central bond varies and is longer in **11** [220.7(2) pm] than in **14** [216.6(2) pm] and **15** (212.9 pm).

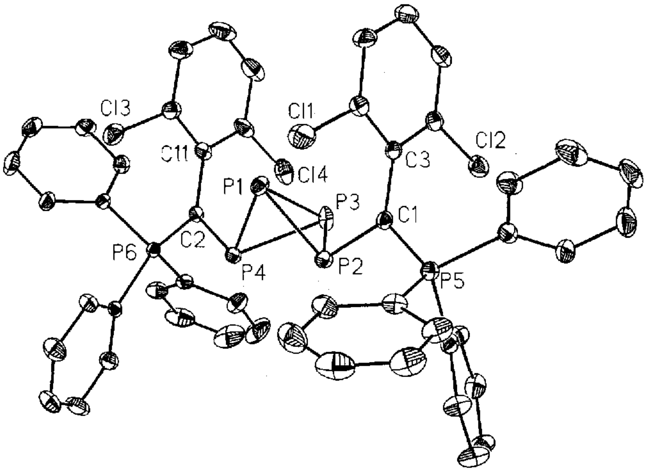
In order to analyze the bonding situation in **11** in more detail we performed quantum chemical calculations[28a] on several model-substituted bicyclotetraphosphanes P$_4$R$_2$. The various rotamers **A**, **B**, **C** of a donor-substituted bicyclotetraphosphane (X = N, Y = H, and X = C, Y = PH$_3$) can be characterized by the dihedral angle ϕ between the electron lone pair at the substituent atom X and the central PP bond. The view is analogous to the study of the rotational barrier in vinylphosphane.[29]

Scheme



According to symmetry considerations a donor-orbital which is parallel to the central PP-bond, as in rotamer **B**, lengthens and a donor orbital perpendicular to the central bond, as in rotamers A and C, shortens the central bond.[30] Conformations with differing rotational angles ϕ were explored at the MP2(fc)/6-31g** level for a variety of model disubstituted bicyclotetraphosphanes.[28b] The computational results are collected in Table 2.

Figure 3. Molecular structure of **11** (thermal ellipsoids with 25% probability)



In reference to the parent compound, with R = H, the central PP distance (218 pm) was elongated for the cases R = F, NH$_2$ (rotamer **A**, **C**) and CHPH$_3$ (rotamers **A** and **C**). On the contrary for R = NH$_2$ (rotamer **B**) the central PP bond is slightly decreased, in agreement with experimental investigations on the tetrakis(trimethylsilyl) derivative of the diaminobicyclotetraphosphane.[25] Two methyl groups for R induce a slight extension of the central bond (219.4 pm), comparable with that for the known diaryl bicyclotetraphosphane (216.6 pm[27]). We note that the computed equilibrium geometries result in slightly (approx. 4 pm) longer PP distances as compared to the experimental val-

Table 1. Selected bond lengths [pm] and angles [°] of **9** and **11**

9		**11**	
P2−Si2	225.3(1)	P1−P3	220.7(2)
P2−P1	224.2(1)	P1−P2	219.8(2)
P2−P1a	226.6(1)	P1−P4	221.7(2)
		P2−P3	224.1(2)
		P3−P4	223.8(2)
P1−C7	179.5(2)	P2−C1	179.4(4)
C7−Si1	185.6(2)	C1−C3	148.0(6)
C7−P3	182.8(2)	C1−P5	169.8(4)
		P4−C2	178.1(4)
		C2−C11	148.4(6)
		C2−P6	170.3(4)
P1−P2−P1a	81.1(1)	P2−P1−P4	81.5(1)
		P2−P3−P4	80.1(1)
		P1−P3−P4	59.8(1)
Si2−P2−P1	98.9(1)	P1−P3−P2	59.2(1)
Si2−P2−P1a	102.4(1)	P3−P1−P4	60.8(1)
		P2−P1−P3	61.1(1)
P2−P1−P2a	82.0(1)	P1−P2−P3	59.6(1)
P2−P1−C7	108.1(1)	P1−P2−C1	104.8(2)
P2a−P1−C7	112.1(1)	P3−P2−C1	106.9(2)
		P1−P4−P3	59.4(1)
		P1−P4−C2	104.1(2)
		P3−P4−C2	106.9(1)
		P6−C2−P4	118.5(2)
		P4−C2−C11	121.5(3)
P1−C7−P3	111.4(1)	P6−C2−C11	120.0(3)
P3−C7−Si1	122.5(1)	P2−C1−P5	114.2(2)
Si1−C7−P1	125.9(1)	P5−C1−C3	121.7(3)
		C3−C1−P2	123.9(3)

Table 2. Disubstituted bicyclotetraphosphanes P_4R_2

R	*d*PP [pm] central		*d*PP [pm] peripheral	∡ PPPP [°] folding angle		Δ*E* [kcal mol^{-1}]
	calcd.	exp.	calcd.	calcd.	exp.	
H	218.0		222.6	96.0		
F	223.0		221.1	100.3		
NH_2 (rotamer **B**)[a]	216.3	212.9	224.6	98.1	95.2	2.8
NH_2 (rotamer **A**,**C**)	227.4		221.2	103.9		0
CH_3[b]	219.4	216.6	222.0	98.6	95.5	
$CHPH_3$ (rotamer **C**)[c]	224.7	220.7	221.8	102.9	96.6	0
$CHPH_3$ (rotamer **A**)	226.0		222.2	105.3		1.5

[a] The experimental values refer to $P_4[N(SiMe_3)_2]_2$.[25] – [b] The experimental values refer to $P_4(2,4,6\text{-}t\mathrm{Bu}_3C_6H_2)_2$.[27] – [c] The experimental values refer to compound **11**.

ues. Furthermore the folding angle between the two three-membered rings results are too large as compared with the experimental values. This may be attributed to the MP2 procedure, which tends to somewhat overestimate the lengthening of the PP bonds as well as the folding angles. The trends resulting from the quantum chemical calculations are, however, in good agreement with the experimental findings and the predications of the qualitative model.[30a,b] The calculations also indicate that the energy differences between the various rotamers are fairly small and may well be dictated by steric effects exerted by bulky substituents at X.

Experimental Section

All reactions were carried out in flame-dried glassware under argon and dry solvents. NMR spectra were measured with a GSX 270 (^{31}P) or an EX 400 (^1H) NMR spectrometer using 85% H_3PO_4 and $SiMe_4$ as standards.

6 (R = $SiMe_3$) *and* **9**: $P(SiMe_3)_3$ (1.69 ml, 5.82 mmol) was added via a syringe to a suspension of **7**, R = $SiMe_3$, (2.62 g, 5.82 mmol) in 15 ml of tetrahydrofuran at room temp. A ^{31}P-NMR spectrum recorded after 5 h shows the signals of **6**, R = $SiMe_3$: $\delta_A = 23.7$ (PPh_3), $\delta_B = 556.1$ (P−C), $\delta_C = 232.6$ (P−Si), $J_{AB} = 100.0$, $J_{AC} = 18.4$, $J_{BC} = 536.7$ Hz. After stirring for 2 d at room temp. and refluxing for 2 d the red solution was reduced in vacuo to half of its volume. In a first fraction 490 mg (0.44 mmol, 15%) of **9** was isolated, which crystallized with 2 mol of tetrahydrofuran, one of which was lost by drying in vacuo. – $^{31}P\{^1H\}$ NMR (CH_2Cl_2): $AA'BB'C_2$, $\delta_A = 29.2$ (PPh_3), $\delta_B = -74.1$ (P−C), $\delta_C = -35.7$ (P−Si), $J_{AB} = 208.1$, $J_{AB'} \leq 3$, $J_{AC} = 11.8$, $J_{BB'} = 183.9$, $J_{BC} = -124.1$ Hz.[9] – $C_{50}H_{66}P_6Si_4 \cdot C_4H_8O$ (1037.37): calcd. C 62.52, H 7.19; found C 62.23, H 7.31.

6 (R = 2,6-$Cl_2C_6H_3$) *and* **10**: $P(SiMe_3)_3$ (0.81 g, 3.22 mmol) in 3 ml of tetrahydrofuran was added dropwise to a solution of **7**, R = 2,6-$Cl_2C_6H_3$ (1.68 g, 3.22 mmol) in 16 ml of tetrahydrofuran at 0°. A ^{31}P-NMR spectrum recorded after 3 h showed, besides the signals of the starting materials, those of **6**, R = 2,6-$Cl_2C_6H_3$ with 40% of the total intensity: $\delta_A = 13.6$ (PPh_3), $\delta_B = 488.7$ (P−C), $\delta_C = 191.8$ (P−Si), $J_{AB} = 107.8$, $J_{AC} = 16.3$, $J_{BC} = 510.7$ Hz. After stirring for 3 d at ambient temp. the red solution was reduced to half of its volume and mixed with 5 ml of pentane. An orange precipitate, which had formed after 18 h, was filtered off, washed twice with a 1:1 mixture of pentane/tetrahydrofuran, and dried in vacuo. Yield 1.32 g (37%, 1.19 mmol). – $^{31}P\{^1H\}$ NMR (C_6D_6, CH_2Cl_2 4:1): $\delta_A = 10.8$, $\delta_B = 15.6$, $\delta_C = 456.5$, $\delta_D = 303.4$, $\delta_E = -26.8$, $\delta_F = -138.3$, $^2J_{AC} = 105.1$, $^2J_{BE}$ no break (required) space = 178.9, $^3J_{BF}$ no break (required) space = 25.0, $^1J_{CD} = 540.0$, $^2J_{CE} = 393.7$, $^1J_{DE} = 217.7$, $^2J_{DF} = 15$, $^1J_{EF} = 331.6$ Hz. – ^1H NMR (C_6D_6, THF): δ = 7.76 (m, 6 H, 3,4-H), 7.03 (m, 30 H, *o,m,p*-H), 3.56 (*m*, 2-H, THF), 1.41 (m, 3-H, THF), 0.30 (d, $J_{PH} = 4.4$ Hz, 18 H, Me_3Si). – $C_{56}H_{54}Cl_4P_6Si_2$ (1110.87): calcd. C 60.55, H 4.99; found C 62.07, H 4.86.

11: From **7** (R = 2,6-$Cl_2C_6H_3$) (1.26 g, 2.42 mmol) and $P(SiMe_3)_3$ (0.61 g, 2.42 mmol) a mixture of **6**, R = 2,6-$Cl_2C_6H_3$ (20%) and **10** (70%) was obtained as before. Attempts to recrystallize this mixture from a solution of benzene and dichloromethane by warming it up to 50°C gave 104 mg (9%, 0.10 mmol) of **11**. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta_A = 17.6$ (PPh_3), $\delta_B = -130.9$ (P−C), $\delta_C = -354.5$ (P−P), $J_{AB} = 140.6$, $J_{AB'} = 2.9$, $J_{AC} = 6.1$, $J_{BB'} = 332.3$, $J_{BC} = -197.2$ Hz. – ^1H NMR (CD_2Cl_2): δ = 7.54 (m, 12 H, *o*-H), 7.48 (m, 6 H, *p*-H), 7.36 (m, 12 H, *m*-H), 7.00 (d, 4 H, $J_{HH} = 7.9$ Hz, 3,5-H), 6.76 (dt, 2 H, $J_{HH} = 7.8$ Hz, $J_{PH} = 1.8$ Hz, 4-H). – $C_{50}H_{36}Cl_4P_6 \cdot CH_2Cl_2$ (1049.42): calcd. C 58.37, H 3.65; found C 58.08, H 3.83.

X-ray Structure Analysis of 9 and 11: For the structure determination, a Siemens *P*4 X-ray diffractometer with a SMART area detector was used employing Mo-K_α radiation and a graphite monochromator. Crystal data and data collection parameters (at 193 K) are given in Table 3. Structure solution program: XS (SHELXTL Vers. 5), direct methods and refinement with full-matrix least-squares on F^2 (SHELX 93) for nonhydrogen atoms in anisotropic description and hydrogen atoms refined as a riding model. Additional information of the crystal structure determination are deposited at the Cambridge Crystallographic Data Center

Table 3. Crystal and analysis data

	1	**2**
Compound	9 $(C_4H_8O)_2$	11 $(CH_2Cl_2)_2$
Formula	$(C_{29}H_{41}OP_3Si_2)_2$	$C_{52}H_{40}Cl_8P_6$
Crystal habit	yellow cube	yellow octahedron
Crystal size	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.35 mm^3
Crystal system	monoclinic	monoclinic
Space group	*C*2/c	*P*2(1)/c
a	15.1241(2)	18.131(3) Å
b	15.1491(2)	16.724(3) Å
c	27.7437(5)	17.809(3) Å
β	90.26°	93.66(2)°
V	6356.5(2)	5389.1(16) $Å^3$
Z	4	4
d(calcd.)	1.157	1.393 Mg m^{-3}
μ	0.282	0.631 mm^{-1}
F(000)	2360	2296
2θ range for data collection	2.94 to 58.18°	2.26 to 49.00°
Index ranges	$-19 \leq h \leq 19$ $-18 \leq k \leq 19$ $-28 \leq l \leq 35$	$-21 \leq h \leq 21$ $-19 \leq k \leq 0$ $0 \leq l \leq 20$
Reflections collected	17840	8680
Independent reflections	5654 (R_{int} = 0.0357)	8355 (R_{int} = 0.0368)
Observed reflections	4060 ($F > 4\sigma(F)$)	5622 ($F > 4\sigma(F)$)
Weighting scheme	$w^{-1} = \sigma^2F_o^2 + (0.0098P)^2 + (16.030P)$[a]	$w^{-1} = \sigma^2F_o^2 + (0.0536P)^2 + (7.8511P)$[a]
Data / restraints / parameters	4533 / 0 / 322	8353 / 36 / 633
goodness-of-fit of F^2	1.238	1.034
Final *R*1 (4σ)	0.0480	0.0549
Final w*R*2	0.0919	0.1231
Largest difference peak	0.293	0.671 e$Å^{-3}$
Largest difference hole	−0.260	−0.583 e$Å^{-3}$

[a] $P = (F_o^2 + 2\ F_c^2)/3$.

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