Reactions of a carbosilylated methylenephosphonium ion with π-conjugated hydrocarbons [1]

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Abstract

In the C-silylated methylenephosphonium salt [$^tBu_2$P=CHSiMe$_3$]$^+$AlCl$_4^-$ (6) cation and anion are separated in the solid state and in solution. Adding an excess of AlCl$_3$, however, does not allow the synthesis of the methylenephosphonium salt 6' with Al$_2$Cl$_7^-$ as counteranion but leads to the adduct $^tBu_2$PCl–CHSiMe$_3 \cdot$ Al$_2$Cl$_6$ (7) which was characterized by an X-ray analysis. Electron-rich π-conjugated hydrocarbons like fulvene 9 or anthracene 10 react with 6 (or 7) under formation of [2 + 4]-cycloadducts 11a,b and 12, respectively, while electron-poor systems (benzene, naphthalene, C$_{60}$) are unreactive. © 1997 Elsevier Science S.A.

Keywords: Methylenephosphonium salts; Aluminium compounds; Cycloadditions; Phosphonium salts

1. Introduction

Methylenephosphonium ions 1,2 may be formally regarded as phosphanyl-substituted carbenium ions in which the phosphorus as well as the carbon centres adopt trigonal planar coordination sites [1–4]. Generally, the inversion barriers of alkyl- and aryl-substituted pyramidal phosphines PR$_3$ are high. [2] The observation of trigonal planar coordinated phosphorus centres indicate, apart from σ-donation, effective π-charge donation from the phosphorus to the carbon centre. Calculations on the parent compound 1a [5–7] and the C-silyl derivative 1b [7] show that σ- and π-donation from the phosphorus centre leads to a total electron distribution within the P=C double bond that leaves considerable positive charge on the phosphorus centre and negative charge on the carbon centre which is enhanced by C-silyl substitution (Scheme 1).

This electron distribution is inverse to the one observed in the homologous iminium ions, [R$_2$N=CR$_2^1$]$^+$
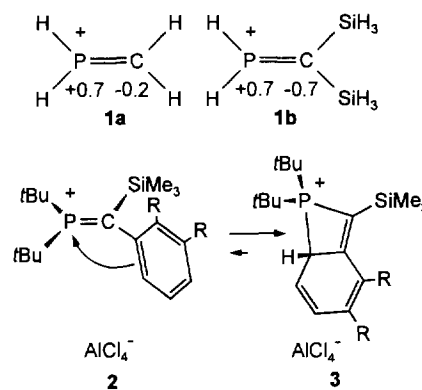
Scheme 1.

which are attacked by nucleophiles at the carbon centre [8,9]. In contrast, simple nucleophiles like F$^-$ or Cl$^-$ bind to the phosphorus centre of methylenephosphonium ions to yield the corresponding ylides [1]. The high electrophilicity of the phosphorus centre in methylenephosphonium salts 2 is demonstrated by *intra*molecular electrophilic attack on the conjugated π-system bonded to the carbon atom of the P=C double bond which proceeds under formation of cyclic four-membered phosphonium salts 3 [8,9]. In solution, compounds 3 are in equilibrium with 2. In this paper, we

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[2] PH$_3$: 155.6 kJ mol^{-1} vs. 22.3 kJ mol^{-1} in NH$_3$.

report our findings obtained studying *inter*molecular reactions of the *C*-silylated methylene phosphonium salt [^{t}Bu$_2$P=CHSiMe$_3$]$^+$AlCl$_4^-$ (6) [2] with hydrocarbon π-systems.

2. Results and discussion

As originally reported, **6** is easily prepared from the *P*-chloro ylide ^{t}Bu$_2$PCl=CH(SiMe$_3$) (4) and a slight excess (ca. 10%) of freshly sublimed AlCl$_3$ (5) in CH$_2$Cl$_2$ at low temperature. However, if a larger excess of AlCl$_3$ is used, the AlCl$_3$ is partly dissolved and a new product **7** is formed beside smaller amounts of **6**, as indicated by a new resonance signal at 135 ppm in the ^{31}P NMR spectrum which lies within the typical range of *P*-chlorophosphonium salts (Scheme 2).

Layering the filtered CH$_2$Cl$_2$ solution with *n*-hexane and cooling to −30°C leads to precipitation of large colourless cubic crystals of **7** which were suitable for an X-ray analysis. The result is shown as a SCHAKAL [10] plot in Fig. 1. Selected bond lengths and angles are given in the figure caption.

Compound **7** is best described as an adduct formed by addition of the negatively charged carbon centre of **4** to the Lewis acid Al$_2$Cl$_6$. To our knowledge, ^{t}Bu$_2$PCl–CH(SiMe$_3$) · Al$_2$Cl$_6$ **7** is unique in the sense that it represents the only structurally characterized example of a Y–Al$_2$Cl$_6$ adduct were Y is different from chlorine [11]. In **7** the Al1,C3,Cl2,Cl3 and Al2,Cl5,Cl6,Cl7 moieties adopt a staggered conformation with respect to the Al1–Al2 vector and are linked by a bent chloro bridge (Al1–Cl2–Al2 115.05°). The averaged distances of the aluminium centres to the terminal chlorine atoms Cl$_t$
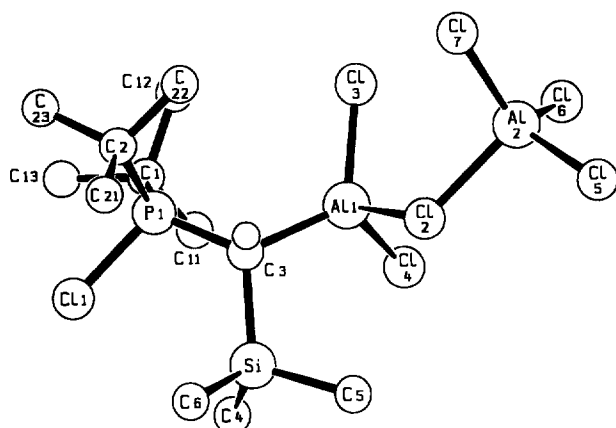

Fig. 1. Molecular structure of **7**. Selected bond lengths (Å) and angles (deg) for compound **7**: P–C1 1.873(4), P–C2 1.867(4), P–C3 1.784(3), P–Cl1 2.021(1), Al1–C3 2.012(3), Al1–Cl2 2.296(1), Al1–Cl3 2.108(2), Al1–Cl4 2.112(2), Al2–Cl2 2.288(1), Al2–Cl5 2.097(2), Al2–Cl6 2.084(2), Al2–Cl7 2.100(2), C3–Si 1.954(3); C1–P–C3 116.5(2), C1–P–C2 116.5(2), C2–P–C3 109.2(2), Cl1–P–C1 101.6(2), Cl1–P–C2 102.3(1), Cl1–P–C3 109.2(1), Cl2–Al1–C3 102.9(1), Cl2–Al1–Cl4 104.8(1), Cl2–Al1–Cl3 102.8(1), Cl3–Al1–C3 120.1(1), C3–Al1–Cl4 115.3(1), Cl3–Al1–Cl4 111.0(1), Cl2–Al2–Cl5 101.9(1), Cl2–Al2–Cl6 107.4(1), Cl2–Al2–Cl7 103.6(1), Cl5–Al2–Cl6 111.4(1), Cl5–Al2–Cl7 112.8(1), Cl6–Al2–Cl7 117.9(1), Al1–Cl2–Al2 115.0(1), Si–C3–P 116.9(2), Al1–C3–P 122.3(2), Al1–C3–Si 111.2(2). Hydrogen atoms have been omitted for clarity.

(2.100 Å) as well as to the bridging chloro centre Cl$_b$ (2.292 Å) resemble closely the averaged values observed in Al$_2$Cl$_7^-$ anions which were structurally characterized by X-ray analysis in several salts (Al$_2$Cl$_7^-$: Al–Cl$_t$ 2.084 Å, Al–Cl$_b$ 2.270 Å). The Cl$_t$–Al–Cl$_t$ (114.7°) and Cl$_t$–Al–Cl$_b$ (103.4°) angles are also comparable (Al$_2$Cl$_7^-$: Cl$_t$–Al–Cl$_t$ 114.1°, Cl$_t$–Al–Cl$_b$
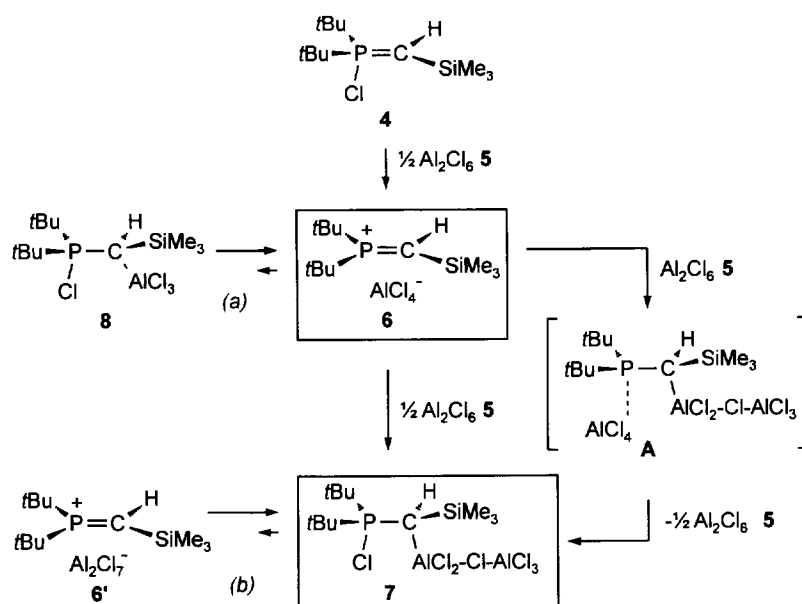
Scheme 2.

104.7°][11]. Noteworthy is the P–C3 distance which is ca. 0.1 Å shorter than the P–C1 and P–C2 bonds, although all carbon centres may be described by an sp^3 valence electron configuration. This effect can be explained by Coulomb attractions between the positively charged phosphorus atom and the enhanced negative charge on C3 which bears two additional electropositive substituents (Si, Al). In contrast to P-chloro-substituted ylides, $^t Bu_2 ClP=CR^1 R^2$, which possess considerably elongated P–Cl bonds (> 2.15 Å) [3,9] the P–Cl bond in **7** falls within the usual range $(2.021(1)$ Å). The Al1–C3 distance $(2.012(3)$ Å) is slightly longer than the terminal Al–C distance in Al_2Me_6 $(1.95$ Å) [12].

Formation of **7** can be assumed to take place via formation of $Al_2Cl_7^-$ from excess $AlCl_3$ and $AlCl_4^-$. Subsequently, rapid 1,2-addition of $Al_2Cl_7^-$ to $[^t Bu_2 P=CH(SiMe_3)]^+$ occurs which indicates that equilibrium *(b)* (in Scheme 2) lies to the right side in favour of **7** over **6'**. Alternatively, one can assume addition of Al_2Cl_6 to the nucleophilic carbon centre of methylene phosphonium ion **6** under formation of an adduct **A** as intermediate which subsequently leads to **7**. In contrast to equilibrium *(b)*, we have no indication for reaction *(a)* (in Scheme 2) taking place between cation $[^t Bu_2 P=CH(SiMe_3)]^+$ and anion $AlCl_4^-$ which would yield the comparable adduct $^t Bu_2 PCl-CH(SiMe_3)$ · $AlCl_3$ **8**. No close contact between $AlCl_4^-$ and $[^t Bu_2 P=CH(SiMe_3)]^+$ is observed in crystals of **6** (shortest Al–Cl distance 4.5 Å). The ^{31}P NMR and ^{27}Al NMR spectra of **6** in CD_2Cl_2 solution are temperature independent, giving rise only to sharp signals at 245 ppm and 104 ppm respectively $(\nu_{\frac{1}{2}} < 3$ Hz) [2]. If there were considerable amounts of adduct $^t Bu_2 PCl-CH(SiMe_3)$ · $AlCl_3$ **8** present in rapid equilibrium with ion separated $[^t Bu_2 P=CH(SiMe_3)]^+$ and $AlCl_4^-$ no distinct species can be detected within the NMR time scale and we expect a significant temperature dependence of the ^{31}P chemical shift because the chemical shift difference between **6** and **8** should be as large as between **6** and **7** $(\Delta\delta(^{31}P) = 110$ ppm). It may be therefore concluded, that the chloride affinity of **6** lies in between that of $AlCl_3$ and Al_2Cl_6.

In contrast to $Al_2Cl_7^-$, which is in rapid equilibrium with other aluminium chloride anions [13–15], adduct **7** is rather stable. Freshly dissolved crystals of **7** in CH_2Cl_2 show only one signal in the ^{31}P NMR spectrum and one broad resonance signal at 113.2 ppm $(\nu_{\frac{1}{2}} \approx 193$ Hz) in the ^{27}Al NMR spectrum. This chemical shift compares well with the signal at $\delta \approx 115$ observed for a minor component in an n-butylpyridiniumchloride–$AlCl_3$ melt at elevated temperature. This signal was tentatively assigned to the $Al_2Cl_7^-$ anion [15]. However, leaving a solution of **7** in CH_2Cl_2 at ambient temperature leads to decomposition. Primarily, a mixture of mainly **6** and **7** is formed. In the ^{27}Al NMR spectrum of this mixture, the resonance signal of the $AlCl_4^-$ ion at

about 104 ppm is broad $(\nu_{\frac{1}{2}} \approx 100$ Hz) indicating relatively slow chemical exchange with the aluminium centres in **7** on the NMR time scale. In the ^{31}P NMR spectrum, two sharp resonance signals for **6** and **7** are observed. Solutions in CH_2Cl_2 of **6** and/or **7** decompose to yield several products after hours at room temperature.

2.1. Reactions with hydrocarbon π-systems

C-Silylated methylenephosphonium ions are very dienophilic and react exothermically with butadienes to yield [2 + 4]-cycloadducts and products of ene-reactions [2,8]. Although we have not performed quantitative measurements, we found qualitatively that C,C-diaryl-substituted methylenephosphonium ions react much slower with dienes [16]. We have now investigated the reaction of the mono-C-silylated methylenephosphonium salt **6** with some π-conjugated and aromatic hydrocarbons.

There is no rapid reaction between **6** and benzene, naphthalene, biflurenylidene, or C_{60} and after several days only an inseparable mixture of compounds is obtained, probably formed from decomposition products of the methylenephosphonium salt **6** itself. However, the reaction of **6** with 6,6-dimethylfulvene **9** and anthracene **10** proceeds smoothly and the cycloadducts **11a,b** and **12** are obtained in good yields (Scheme 3).

In the reaction with **9**, two [2 + 4]-cycloaddition products are formed in a 1:1 ratio which were identified as the endo- and exo-isomers **11a** and **11b**. By fractional recrystallization of the crude mixture of **11a,b** from CH_2Cl_2–n-hexane the endo isomer **11a** was obtained in analytically pure form. The exo-isomer **11b** was characterized by NMR-spectra of mixtures contaminated with small amounts of **11a**.

The structure of **11a** was determined by an X-ray analysis. The result is shown as a SCHAKAL plot in Fig. 2; selected bond lengths and angles are given in the figure caption.
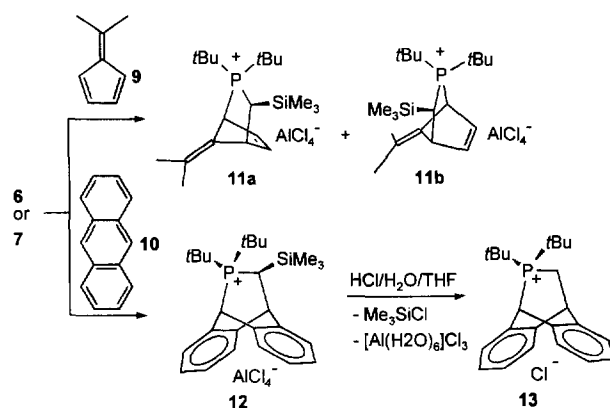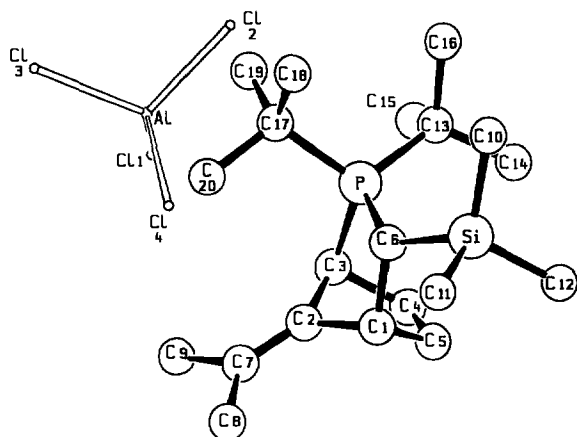

Scheme 3.

Fig. 2. Molecular structure of 11a. Selected bond lengths (Å) and angles (deg) for compound 11a: P–C3 1.873(3), P–C6 1.843(3), P–C13 1.880(3), P–C17 1.866(4), C1–C2 1.513(4), C1–C5 1.512(5), C1–C6 1.587(4), C2–C3 1.530(4), C2–C7 1.319(5), C3–C4 1.514(5), C4–C5 1.316(5), C6–Si 1.915(3); C3–P–C6 93.2(1), C3–P–C17 111.1(2), C13–P–C3 110.2(3), C13–P–C6 119.7(2), C13–P–C17 111.7(2), C2–C1–C5 98.9(3), C6–C1–C2 104.8(3), C6–C1–C5 110.2(3), C1–C2–C7 130.6(3), C3–C2–C1 97.9(3), C3–C2–C7 130.7(3), C2–C3–C4 98.3(3), P–C3–C2 100.6(2), P–C3–C4 104.3(2), C3–C4–C5 109.0(3), C1–C5–C4 108.7(3), P–C6–C1 101.7(2), Si–C6–C1 113.0(2), Si–C6–P 131.3(2). Hydrogen atoms have been omitted for clarity.

Almost all P–C distances lie within the expected single bond range (1.85 Å); only the phosphorus bridgehead distance P–C3 is elongated (1.873(3) Å). The C1–C6 bond (1.587(4) Å) opposing the P–C3 bond is also significantly longer than a C–C single bond. The C2=C7 and C4=C5 distances (1.317 Å) correspond with isolated C=C double bond lengths. As expected, all endocyclic angles within the bicyclic frame of 11a are considerably narrowed, imposing strain energy on the cation.

The reaction of 6 with anthracene 10 in CH_2Cl_2 is complete after 2 h. In the ^{31}P NMR spectrum of the reaction mixture only one resonance signal at 55.2 ppm is detected. The same result is obtained when adduct 7 is used instead of methylenephosphonium salt 6. The [2 + 4]-cycloadduct 12 is obtained in analytically pure form after recrystallization from THF and was characterized by NMR spectroscopy. In order to destroy the $AlCl_4^-$ counter anion which we felt might disturb in subsequent reactions, phosphonium salt 12 was hydrolysed. We could never prevent partial cleavage of the carbon silicon bond and formation of 13. This fragmentation can be driven to completeness if diluted hydrochloric acid is used and 13 is obtained as colourless crystals in almost quantitative yield. Both 12 and 13 are remarkably stable towards thermolysis up to 200 °C and we have no indication for retro [2 + 4]-cycloaddition reactions. As well, in the mass spectra of 12 and 13 there is no ion present corresponding to m/z of

$^1Bu_2P=CHR^+$, $^1BuHP=CHR^+$, or $H_2P=CHR^+$ (R = $SiMe_3$, H).

From the findings described above, it can be concluded that silylated methylenephosphonium ions are strong Lewis-acids with a chloride affinity in between $AlCl_3$ and Al_2Cl_6. They can be used as reagents in [2 + 4]-cycloaddition reactions to functionalize rather electron-rich π-conjugated hydrocarbons while electron-poor π-systems are unreactive. The resulting phosphonium salts 11a,b, 12, and 13 not being prepared easily by other methods and obtained in good yields could serve as valuable starting materials for further manipulations which are under current investigation.

3. Experimental

3.1. X-ray data collection and structure determinations

Diffraction data were collected on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and with an ω scan mode. Intensities were corrected for Lorentz, polarization and background effects. An empirical correction for absorption was done by the psi-scan method. Lattice parameters were received from centring 25 high angle reflections (25 < 2θ < 30°). For both compounds, heavy atoms were located by direct methods (SHELXS86 [17]), and coordinates for the remaining non-metal atoms were determined from subsequent difference electron density calculations. All refinements were performed using the program SHELXL93 [18]. All non-hydrogen atoms were refined anisotropically. Except H3 in 7, all hydrogen atoms were placed in calculated positions and refined as riding atoms. Complete lists of bond lengths and angles and tables of atomic coordinates and displacement parameters have been deposited at Fachinformationszentrum Karlsruhe, Geselschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany, quoting the depository number CSD406693, the name of the author and the journal citation. Crystallographic data for 7 and 11a are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters of 7 and 11a are given in Tables 2 and 3 respectively.

3.2. Preparation of compounds

3.2.1. General remarks

All solvents were dry and free of oxygen. They were freshly distilled before use. All procedures were carried out under a dry, nitrogen-atmosphere by use of modified Schlenk-techniques. Tetramethylsilane (^1H, ^{13}C, ^{29}Si), 85% H_3PO_4 (ext.) (^{31}P), and aqueous solutions of $AlCl_3$ (ext.) (^{27}Al) were used as standards for NMR spectroscopy.

Table 1

Crystallographic data for compounds **7** and **11a**

	7	11a
Formula	$C_{12}H_{28}Al_2Cl_7PSi$	$C_{20}H_{38}AlCl_4PSi$
Weight	533.51	506.34
Colour/habit	colourless cubes	colourless rhombic platelet
Crystal size (mm³)	0.5×0.5×0.5	1.5×0.4×0.4
Space group	$C2/c$ No. 15	$P2_1/n$ No. 14
a (Å)	29.439(2)	11.903(3)
b (Å)	9.3186(11)	17.128(4)
c (Å)	22.825(2)	13.557(3)
β (deg)	127.60(1)	96.96(2)
V (Å³)	4961.1(9)	2743.5(11)
Calc. density (g cm⁻³)	1.429	1.226
μ (mm⁻¹)	0.98	0.57
$F(000)$	2192	1072
Z	8	4
Scan speed (deg min⁻¹)	2–20	2–20
Θ-range in (deg)	2–23	2–25
h, k, l range	±32, 10, 25	±14, −9, 15
Refl. collected	3793	4893
Unique refl.	3439	4510
Observed refl. ($I > 0$)	3099	3934
No. of parameters	222	255
$wR2(I)$ [a]	0.0952	0.1221
$R1(F)$ [a] ($F > 4\sigma(F)$)	0.0378 (2716)	0.0484 (3259)
GooF	1.071	1.057
Largest diff. values (e⁻ Å⁻³)	+0.59/−0.49	+0.64/−0.53

[a] According to SHELXL-93.

Table 2

Atomic coordinates and equivalent isotropic displacement parameters (Å²) for **7**

Atom	x	y	z	U_{equ}
P	0.37119(4)	0.16993(10)	0.49384(5)	0.0306(5)
Si	0.26031(4)	0.33557(11)	0.36112(6)	0.0378(5)
Al1	0.37704(5)	0.35463(12)	0.37387(6)	0.0354(6)
Al2	0.38067(5)	0.28266(13)	0.20993(6)	0.0432(6)
Cl1	0.31722(4)	0.16251(12)	0.52058(5)	0.0498(6)
Cl2	0.32719(4)	0.29188(11)	0.25179(5)	0.0456(5)
Cl3	0.46009(4)	0.28959(15)	0.41432(6)	0.0658(6)
Cl4	0.37112(5)	0.58055(11)	0.37311(6)	0.0617(8)
Cl5	0.31778(5)	0.30632(13)	0.09551(5)	0.0587(6)
Cl6	0.43646(6)	0.4573(2)	0.25517(7)	0.0930(9)
Cl7	0.41643(7)	0.0759(2)	0.23981(8)	0.0931(11)
C1	0.4329(2)	0.2735(4)	0.5735(2)	0.043(2)
C11	0.4179(2)	0.4325(5)	0.5573(2)	0.075(4)
C12	0.4886(2)	0.2410(6)	0.5843(2)	0.071(2)
C13	0.4435(2)	0.2358(6)	0.6462(2)	0.066(3)
C2	0.3841(2)	−0.0243(4)	0.4887(2)	0.039(2)
C21	0.3256(2)	−0.0983(4)	0.4375(2)	0.054(3)
C22	0.4164(2)	−0.0381(4)	0.4562(2)	0.049(2)
C23	0.4180(2)	−0.0939(5)	0.5648(2)	0.059(3)
C3	0.3350(2)	0.2486(4)	0.4045(2)	0.030(2)
C4	0.2648(2)	0.4841(4)	0.4182(2)	0.056(3)
C5	0.2299(2)	0.4109(5)	0.2679(2)	0.056(2)
C6	0.2076(2)	0.1952(5)	0.3413(2)	0.057(2)

Table 3

Atomic coordinates and equivalent isotropic displacement parameters (Å²) for **11a**

Atom	x	y	z	U_{equ}
P	0.34076(7)	0.20560(5)	0.30737(6)	0.0365(2)
Si	0.09695(8)	0.11153(6)	0.34877(8)	0.0465(3)
C1	0.1585(3)	0.2769(2)	0.3606(2)	0.0416(8)
C2	0.2590(3)	0.3304(2)	0.3861(2)	0.0395(7)
C3	0.3194(3)	0.3137(2)	0.2950(2)	0.0395(7)
C4	0.2188(3)	0.3223(2)	0.2160(3)	0.0471(8)
C5	0.1264(3)	0.3010(2)	0.2535(3)	0.0478(8)
C6	0.2102(3)	0.1915(2)	0.3658(2)	0.0379(7)
C7	0.2785(3)	0.3839(2)	0.4560(2)	0.0426(8)
C8	0.1999(3)	0.3956(2)	0.5339(3)	0.0572(10)
C9	0.3778(3)	0.4377(2)	0.4642(3)	0.0543(9)
C10	0.1601(4)	0.0125(2)	0.3424(4)	0.0700(12)
C11	0.0272(4)	0.1173(3)	0.4643(4)	0.0786(14)
C12	−0.0140(4)	0.1296(3)	0.2423(4)	0.0762(13)
C13	0.3533(3)	0.1610(2)	0.1825(3)	0.0508(9)
C14	0.2375(4)	0.1516(3)	0.1217(3)	0.0657(11)
C15	0.4257(4)	0.2160(3)	0.1266(3)	0.0677(12)
C16	0.4065(4)	0.0791(2)	0.1899(3)	0.0705(12)
C17	0.4659(3)	0.1822(2)	0.3993(3)	0.0474(8)
C18	0.4556(4)	0.0979(2)	0.4378(3)	0.0655(11)
C19	0.5777(3)	0.1932(3)	0.3557(3)	0.0620(10)
C20	0.4690(3)	0.2383(3)	0.4881(3)	0.0599(10)
Al	0.76819(9)	0.40116(7)	0.25018(9)	0.0522(3)
Cl1	0.78682(14)	0.49452(9)	0.15087(11)	0.1038(5)
Cl2	0.76156(12)	0.29369(7)	0.17152(10)	0.0890(4)
Cl3	0.90512(12)	0.40181(9)	0.36645(11)	0.0994(5)
Cl4	0.61497(10)	0.41599(7)	0.31269(11)	0.0861(4)

3.2.2. Preparation of the adduct 7

The methylenephosphonium salt **6** (1 g; 2.5 mmol) was dissolved in ca. 10 ml methylene chloride and was added to an equimolar amount of anhydrous aluminium trichloride **5** (0.33 g; 2.5 mmol) in ca. 10 ml methylene chloride at −78 °C. After stirring for some minutes the solvent was removed and the colourless residue was recrystallized from *n*-hexane–methylene chloride by adding methylene chloride dropwise to a suspension of the crude reaction product in *n*-hexane until a clear solution was obtained. After layering this solution with additional *n*-hexane and cooling to 4 °C for several days, colourless, sometimes slightly yellowish, crystals were collected. Yield: 90–95%; m.p. 100–103 °C m/z: 401.5 (29%), 347.4 (22%), 253 (10%), 147.3 (31%), 120.3 (32%), 75.2 (22%), 57.2 (100%), 41 (22%). ^{1}H NMR (CD_2Cl_2, 300 K, 200.133 MHz): $\delta = 0.46$ (s, 9 H, $SiCH_3$), 1.53 (d, $J_{PH} = 18$ Hz, 9 H, CCH_3), 1.67 (d, $J_{PH} = 19$ Hz, 9 H, CCH_3), 5.32 (s, 1H, PCHSi). ^{13}C NMR (CD_2Cl_2, 300 K, 75.429 MHz): $\delta = 5.3$ (d, $J_{PC} = 2.25$ Hz, $SiCH_3$), 27.5 (CH_3), 29.2 (CH_3), 30.8 (d, $J_{PC} = 1.51$ Hz), 43.5 (d, $J_{PC} = 30.5$ Hz, CMe_3), 43.9 (d, $J_{PC} = 33.68$ Hz, CMe_3). ^{31}P NMR (CD_2Cl_2, 300 K, 81.012 MHz): $\delta = 134.8$. ^{27}Al NMR (CD_2Cl_2, 300 K, 78.157 MHz): $\delta = 113.2$. ^{29}Si NMR (CD_2Cl_2, 300 K, 59.591 MHz): $\delta = 9.4$ (d, $J_{PSi} = 9.6$ Hz).

3.2.3. Preparation of cycloadducts 11a,b

6,6-Dimethylfulvene (**9**) was prepared according to procedures described in the literature [19]. To a solution of 1 g methylenephosphonium salt **6** (2.5 mmol) in ca. 10 ml methylene chloride, an equimolar amount (0.27 g; 2.5 mmol) of 6,6-dimethylfulvene **9** dilluted with ca. 5 ml of methylene chloride was added via syringe at −78 °C. After warming to ambient temperature the solvent was removed in vacuo. The colourless residue was recrystallized from n-hexane–methylene chloride by the procedure described above for **7**. NMR-spectra of dissolved crystals revealed the presence of endo-compound **11a** exclusively. In the mother liquor beside some endo-isomer mainly the exo-isomer **11b** was present which was not isolated seperately.

11a; yield: 50% by ^{31}P NMR, 30% isolated; m.p.: 154–156 °C. MS (EI, 70 eV) m/z: 262 (90%, M − SiMe$_3$), 183 (69%), 57 (100%, ^{t}Bu). ^{1}H NMR (CD$_3$CN, 300 K, 200.133 MHz): δ = 0.32 (s, 9 H, SiCH$_3$), 1.40 (d, $^3J_{PH}$ = 10.9 Hz, 9 H, CH$_3$), 1.48 (d, $^3J_{PH}$ = 11.9 Hz, 9 H, CH$_3$), 1.59 (d, $^5J_{PH}$ = 1.2 Hz, 3 H, =CCH$_3$), 1.60 (d, $^5J_{PH}$ = 2 Hz, 3 H, =CCH$_3$), 1.79 (dd, $^2J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 2.5 Hz, 1 H, P–CHSi), 4.09 (d, $^3J_{PH}$ = 21.5 Hz, 1 H, broad, SiC–CH), 4.57 (m, $^2J_{HH}$ = 2.2 Hz, 1 H, P–CH), 6.51 (m, $^3J_{HH}$ = 2.94 Hz, 1 H, –C=CHC), 6.78 (m, $^3J_{HH}$ = 2.52 Hz, 1 H, –C=CHCP). ^{13}C NMR (CD$_3$CN, 300 K, 75.429 MHz): δ = 1.2 (d, $^3J_{PC}$ = 2.2 Hz, SiCH$_3$), 19.7 (d, $^4J_{PC}$ = 1.65 Hz, =CCH$_3$), 21.4 (=CCH$_3$), 27.1 (d, $^1J_{PC}$ = 45.6 Hz, P–C–Si), 28.8 (CH$_3$), 31.4 (CH$_3$), 37.9 (d, $^1J_{PC}$ = 25.82 Hz,CMe$_3$), 38.0 (d, $^1J_{PC}$ = 29.67 Hz, CMe$_3$), 45.0 (d, $^1J_{PC}$ = 30.19 Hz, –SiC–CH), 47.7 (d, $^2J_{PC}$ = 2.75 Hz, P–CH), 120.4 (d, $^3J_{PC}$ = 11.5 Hz, =CMe$_2$), 133.0 (d, $^3J_{PC}$ = 13.19 Hz, –C=CHP), 141.0 (d, $^2J_{PC}$ = 7.14 Hz, =C$\diagdown$), 145.2 (d, $^2J_{PC}$ = 11 Hz, –C=CHP). ^{31}P NMR (CD$_3$CN, 300 K, 81.012 MHz): δ = 74.8. ^{29}Si NMR (CD$_3$CN, 300 K, 59.591 MHz): δ = 10.7.

11b; yield: 50% by ^{31}P NMR, not isolated. ^{1}H NMR (CD$_3$CN, 300 K, 200.133 MHz): δ = 0.35 (s, 9 H, SiCH$_3$), 1.40 (d, $^3J_{PH}$ = 14.9 Hz, 9 H, CCH$_3$), 1.50 (d, $^3J_{PH}$ = 15.4 Hz, 9 H, CCH$_3$), 1.64 (d, $^5J_{PH}$ = 1.94 Hz, 3 H, =CCH$_3$), 1.67 (d, $^5J_{PH}$ = 2.97 Hz, 3 H, = CCH$_3$), 3.98 (d, $^3J_{PH}$ = 20.5 Hz, 1 H, broad, SiC–CH), 4.63 (m, $^2J_{HH}$ = 3.16 Hz, 1 H, P–CH), 6.39 (m, $^3J_{HH}$ = 2.86 Hz, 1 H, –C=CHC), 6.70 (m, $^3J_{HH}$ = 3.39 Hz, 1 H, –C=CHCP), the proton of P–CHSi could not be located. ^{13}C NMR (CDCl$_3$, 300 K, 50.323 MHz): δ = 1.3 (SiCH$_3$), 20.8 (=CCH$_3$), 22.0 (C=CCH$_3$), 25.4 (d, $^1J_{PC}$ = 34.1 Hz, P–C–Si), 30.4 (CH$_3$), 30.5 (CH$_3$), 37.5 (d, $^1J_{PC}$ = 27.4 Hz, CMe$_3$), 37.6 (d, $^1J_{PC}$ = 31.8 Hz, CMe$_3$), 45.7 (d, $^1J_{PC}$ = 43.3 Hz, PCH), 46.8 (s, SiC–CH), 119.7 (d, $^3J_{PC}$ = 10.5 Hz, =CMe$_2$), 131.2 (d, $^3J_{PC}$ = 16.2 Hz, –C=CHCP), 139.1 (d, $^2J_{PC}$ = 9.0 Hz, =C$\diagdown$), 143.4 (d, $^2J_{PC}$ = 11.4 Hz, –C=CHCP). ^{31}P NMR (CD$_3$CN, 300 K, 81.012 MHz): δ = 66.0.
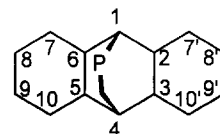

Fig. 3. Assignment of resonances.

3.2.4. Preparation of dibenzo-7-phosphonium-bicylo[2.2.2]octadiene tetrachloroaluminate 12

To a solution of 1 g (2.5 mmol) **6** in 10 ml methylene chloride were added 0.45 g (2.5 mmol) anthracene **10** dissolved in 10 ml methylene chloride at ambient temperature. The slightly yellow reaction mixture was stirred for 2 h and all volatiles were evaporated in vacuo. The residue was recrystallized from a minimum amount of THF to yield 0.74 g (51%) of colourless crystals. M.p. 200–205 °C. MS (EI, 70 eV) m/z: 353 (10%, M − ^{t}Bu), 296 (5%, M − 2^{t}Bu), 191 (25%, dibenzotropylium), 178 (54%, anthracenium), 73 (40%, Me$_3$Si), 57 (80%, ^{t}Bu), 41 (100%, C$_3$H$_5$). ^{1}H NMR (CD$_2$Cl$_2$, 300 K, 200.133 MHz): δ = 0.48 (s, 9 H, SiCH$_3$), 1.14 (d, $^3J_{PH}$ = 6.61 Hz, 9 H, CH$_3$), 1.22 (d, $^3J_{PH}$ = 7.5 Hz, 9 H, CH$_3$), 1.67 (d, $^2J_{PH}$ = 17.2 Hz, 1 H, CHSi), 4.90 (d, $^3J_{PH}$ = 25 Hz, 1 H, C4H), 5.55 (d, $^2J_{PH}$ = 3.9 Hz, 1 H, PC1H), 7.23–7.36 (m, 5 H, H$_{aryl}$), 7.48–7.53 (m, 1H, H$_{aryl}$), 7.56–7.63 (m, 2 H, H$_{aryl}$). ^{13}C NMR (CD$_3$CN, 300 K, 50.323 MHz). Assignment of resonances as shown in Fig. 3. δ = 1.2 (s, SiCH$_3$), 24.0 (d, $^1J_{PC}$ = 30.2 Hz, CHSi), 28.5 (s, CH$_3$), 29.9 (s, CH$_3$), 38.6 (d, $^1J_{PC}$ = 29.7 Hz, CMe$_3$), 39.3 (d, $^1J_{PC}$ = 27.5 Hz, CMe$_3$), 42.1 (d, $^1J_{PC}$ = 29.1 Hz, PC1), 46.6 (d, $^2J_{PC}$ = 6.6 Hz, C4), 125.1 [d, $^5J_{PC}$ = 2.7 Hz, C9(9')], 128.1 [s, C10(10')], 128.5 [d, $^3J_{PC}$ = 6.0 Hz, C7(7')], 128.7 [s, C10(10')], 128.8 [d, $^4J_{PC}$ = 2.7 Hz, C8(8')], 129.1 (d, $^5J_{PC}$ = 2.2 Hz, C9(9')), 129.4 [d, $^4J_{PC}$ = 2.7 Hz, C8(8')], 137.1 [d, $^3J_{PC}$ = 6.0 Hz, C3(5)], 137.5 [d, $^3J_{PC}$ = 7.7 Hz, C3(5)], 143.9 [d, $^2J_{PC}$ = 12.1 Hz, C2(6)PC–Car), 146.8 (d, $^2J_{PC}$ = 7.7 Hz, C2(6)]. ^{31}P NMR (CD$_3$CN, 300 K, 81.012 MHz): δ = 55.2 ^{29}Si NMR (CD$_3$CN, 300 K, 59.591 MHz): δ = 13.2 (d, $^2J_{PSi}$ = 2.1 Hz).

3.2.5. Preparation of dibenzo-7-phosphonium-bicylo[2.2.2]octadiene chloride 13 by hydrolysis of 12

To a solution of 1 g (1.73 mmol) **12** in methylene chloride 4 ml diluted hydrochloric acid (0.5 N) was added and the biphasic mixture was stirred overnight. Solids were filtered off and the methylene chloride layer checked by ^{31}P NMR. In the case that starting material **12** was still present, another 4 ml HCl (0.5 N) were added. Additionally, sufficient THF was added to produce a homogeneous mixture. The hydrolysis was monitored by ^{31}P NMR and when complete all volatiles were evaporated in vacuo. The remaining residue was recrystallized from a minimum amount of THF. In most experiments, up to 0.8 g (90%) colourless crystals of **13**

were obtained. M.p. 195–197 °C. ^{1}H NMR (CD$_3$CN, 300 K, 200.133 MHz): $\delta = 1.07$ (s, 18 H, CH$_3$), 2.67 (dd, $^2J_{PH} = 8.0$ Hz, $^3J_{HH} = 3.4$ Hz, 2 H, PCH$_2$), 5.01 (dt, $^3J_{PH} = 26.0$ Hz, $^3J_{HH} = 3.4$ Hz, 1 H, C4H), 6.31 (d, $^2J_{PH} = 5.3$ Hz, 1 H, PC1H), 7.20–7.30 (m, 4 H, H$_{aryl}$), 7.46–7.50 (m, 2H, H$_{aryl}$), 7.64–7.69 (m, 2 H, H$_{aryl}$). ^{13}C NMR (CD3CN, 300 K, 50.323 MHz) Assignment of resonances as shown in Fig. 3. $\delta = 20.8$ (d, $^1J_{PC} = 48.5$ Hz, PCH$_2$), 28.6 (s, CH$_3$), 37.8 (d, $^1J_{PC} = 28.1$ Hz, CMe$_3$), 40.6 (d, $^1J_{PC} = 29.3$ Hz, PC1), 43.5 (d, $^2J_{PC} = 8.3$ Hz, C4), 127.1 (d, $^4J_{PC} = 2.7$ Hz, C8), 128.4 (d, $^3J_{PC} = 5.9$ Hz, C7), 128.5 (s, C9), 129.4 (d, $^4J_{PC} = 2.4$ Hz, C10), 137.1 [d, $^3J_{PC} = 7.0$ Hz, C5(3)], 144.7 [d, $^2J_{PC} = 9.8$ Hz, C2(6)]. ^{31}P NMR (CD$_3$CN, 300 K, 81.012 MHz): $\delta = 46.6$.

Acknowledgements

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