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On the Reaction of 1,3-Diaza-2-azoniaallene Salts with 1,3-Butadienes and Cumulenes

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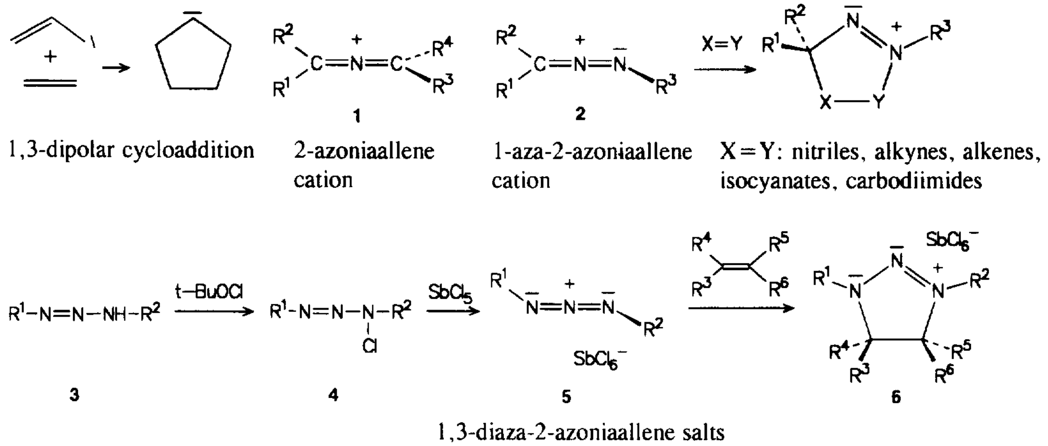
Abstract - 1,3-Disubstituted triazenes **3** are oxidized with *tert*-butyl hypochlorite to N-chlorotriazenes **4**, which at low temperatures with antimony pentachloride afford 1,3-diaza-2-azoniaallene salts **5** as reactive intermediates. Cations **5** undergo cycloadditions to one or both double bonds of 1,3-butadienes to furnish 4,5-dihydro-*1H*-1,2,3-triazolium salts (**6a-k**) (1,3-dipolar cycloaddition with inverse electron demand). With an allene, a butatriene, and a pentatetraene the 4,5-dihydro-*1H*-1,2,3-triazolium salts **6l-n** were obtained. Some of the products undergo consecutive reactions to 1,2,3-triazolium salts (**8a,b**). The constitutions of **6n** and **8b** were secured by X-ray structural analyses. 4,5-Dihydro-*1H*-1,2,3-triazolium salts (**6**) and *1H*-1,2,3-triazolium salts (**8**) are aza analogues of Arduengo's nucleophilic carbenes (imidazolidine-2-ylidenes, imidazole-2-ylidenes). © 1997 Elsevier Science Ltd.

While 1,3-dipolar cycloadditions of electrically neutral 1,3-dipoles are widely used in preparative organic chemistry,[1] reports on cycloadditions of cationic four-electron-three-center components to multiple bonds seem to be scarce.

An interesting inorganic example of a cationic "1,3-dipole" is the $S=N^+=S$ ion prepared by Passmore et al.[2-4] In contrast to the well-known nitronium ion $O=N^+=O$, which reacts as an electrophile effecting, for instance, aromatic nitration, the ion $S=N^+=S$ acts as a four-electron component in cycloadditions to alkenes such as ethene to afford 1,3,2-dithiazolium salts.

In a short communication without experimental details Shatzmiller et al. reported stereoselective cycloadditions of cations $R^1R^2C^+\text{-}C=N\text{-}R^3$ to olefins.[5]

Recently, we reported cycloadditions of 1-aza-2-azoniaallene cations **2** to nitriles,[6,7] acetylenes,[8] carbodiimides,[9] isocyanates,[10] and alkenes.[11] Cations **2** behave as positively charged 1,3-dipoles undergoing cycloadditions to electron-rich olefins with complete conservation of the configuration of the alkene. At least reactions of **2** with alkynes and alkenes are believed to be concerted 1,3-dipolar cycloadditions with inverse electron demand,[12] a view, which is supported by semi empirical AM1 calculations.[13] Corresponding cycloadditions are not to be expected and have not been observed experimentally for 2-azoniaallene cations **1**.[14-17] However, 1,3-diaza-2-azoniaallene cations **5** bearing a lone pair in conjugation to a double bond similar to cations **2**, should be qualified to undergo concerted cycloadditions to multiple bonds. Recently, we reported in situ preparations of first cumulenes **5** reacting with both electron-rich and electron-deficient alkenes to afford 4,5-dihydro-*1H*-1,2,3-triazolium salts **6** with complete conservation of the configuration of the alkene (Scheme 1). This was regarded as an argument for a concerted process, in agreement with results of AM1 calculations.[18]



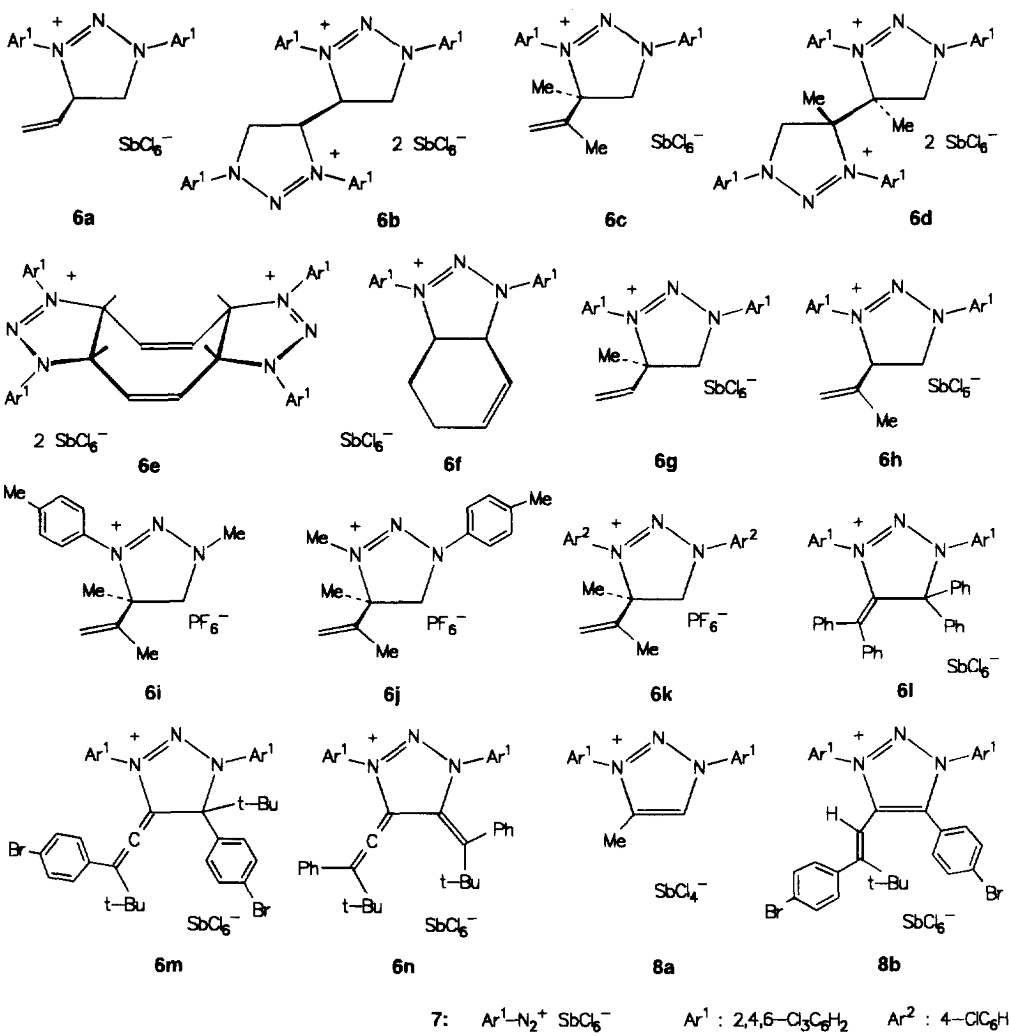
Scheme 1

In this study we set out to extend this work to cycloadditions of salts **5** to 1,3-butadienes, an allene, a butatriene, and a pentatetraene.

Oxidation of the triazene **3**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) with *tert*-butyl hypochlorite afforded the yellow N-chlorotriazene **4**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$). On addition at -60°C of antimony pentachloride to a solution of this compound in dichloromethane a red-orange solid **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) precipitated, the ^{1}H NMR spectrum of which (at -35°C in CD_3CN) showed only one singlet at 7.93 ppm. In the ^{13}C NMR spectrum four resonances for two equivalent aryl substituents were found. The IR spectrum (at -50°C in CH_3CN) is dominated by a very strong band at 2018 cm^{-1} assigned to the asymmetric stretching vibration of the $N=N^+=N$ unit. These data together with a correct elemental analysis support the proposed structure. At -80°C the cumulene is stable over months but above -25°C it decomposes into equal amounts of the diazonium salt **7** and azo(2,4,6-trichlorobenzene).[18]

On addition of 1,3-butadiene to a cold (-60°C) suspension of **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) in dichloromethane the cumulene went into solution. Warming up to room temperature and workup afforded the cycloadduct **6a** in 59% yield (after recrystallization). The crude product was contaminated by a small amount of the diazonium salt **7**. When pure **6a** in dichloromethane was treated with the cumulene **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) the pale yellow bistriazolium salt **6b** was formed in 67% yield showing that even the vinyl group of a cation is able to add a cation **5**.

Correspondingly, from 2,3-dimethyl-1,3-butadiene the vinyl triazolium salt **6c** (52%) and the dimer **6d** (59%) were prepared. Formation of **6d** suggests that moderate steric constraints do not prevent the cycloaddition. However, in solution the *hexachloro*antimonate **6d** slowly decomposed into two molecules of the triazolium *tetrachloro*antimonate **8a**. We believe that homolytic cleavage of the bond connecting the two rings of **6b** led to free radicals, which were oxidized by the Sb(V)-counterion.



Scheme 2. Products prepared

With cyclooctatetraene not more than twofold cycloaddition to **6e** could be achieved. Large amounts of **7** were formed as byproduct. The symmetries of the NMR spectra suggest point group C_{2v} or C_{2h} for the dication **6e**. According to AM1 calculations the cis form (C_{2v}) is 75 $kJmol^{-1}$ more stable than the trans form (C_{2h}). With no better arguments at hand we assign the cis form drawn to **6e**.

The salts **6f-h** were prepared by reactions of equimolecular mixtures of **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) and the corresponding butadienes (55-81%). Preparations of 2:1 adducts were not attempted. With isoprene an almost equimolecular mixture of the regioisomers **6g,h** was obtained. With 2,3-dimethylbutadiene the unsymmetrically substituted heterocumulene **5**(R^1=p-tolyl; R^2=Me)[19] afforded a 1:5 mixture **6i,j** of the regioisomers in respect to the triazenium ion. By reason of better crystallization the counterion $SbCl_6^-$ of **6i-k** was exchanged against PF_6^-. No reactions were observed between hexachloro-1,3-butadiene and cumulenes **5**.

Only occasionally 4,5-dihydro-*1H*-1,2,3-triazolium salts have been mentioned in the literature.[20,21]

In addition to 1,3-butadienes we studied reactions of **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) with a few cumulenes. Tetraphenylallene afforded the triazolium salt **6l**. With (E)-1,4-bis(4-bromophenyl)-1,4-di-*tert*-butylbutatriene[22] the allene **6m** was formed. No cycloaddition across the central double bond of the butatriene was observed. According to AM1 calculations **6m** is 12 to 46 kJmol^{-1} more stable than any stereoisomer, which could have been formed by cycloaddition onto the central double bond of the butatriene. Recrystallization of **6m** resulted in loss of isobutene and formation of the triazolium salt **8b**. AM1 calculations suggest elimination of Me_3C^+ from the 4-position of **6m** leaving back an ylide. The cation Me_3C^+ decomposes to isobutene and a proton, which protonates the ylide to give **8b**. The cation **8b** was calculated to be 75 kJmol^{-1} more stable than the cation **6m**.

Table 1. Selected bond lengths [pm], bond angles, and torsional angles [deg] for the cation **6n**[24]

Atoms	X-ray	AM1	Atoms	X-ray	AM1
N1-N2	130(1)	129.4	N1-C1-C14	117(1)	120.9
N2-N3	130(1)	130.2	C1-C14-C15	176(1)	173.3
N3-C2	145(1)	147.9	N1-N2-N3-C2	-1(1)	2.2
C2-C1	147(2)	150.0	N2-N3-C2-C1	2(1)	-0.2
C1-N1	143(1)	148.2	N3-C2-C1-N1	-1(1)	-1.6
C2-C3	135(2)	135.6	C2-C1-N1-N2	1(1)	3.1
C1-C14	131(2)	130.6	C1-N1-N2-N3	0(1)	-3.4
C14-C15	134(2)	131.3	N1-N2-N3-C26	-172(1)	-179.8
N1-C20	144(1)	143.5	N1-C1-C2-C3	-179(1)	178.4
N3-C26	143(1)	143.9	N2-N3-C26-C27	90(1)	86.6
N1-N2-N3	108(1)	110.1	N2-N1-C20-C21	80(1)	80.4
N2-N3-C2	114(1)	113.0	N2-N1-C1-C14	-172(1)	-175.5
N3-C2-C1	102(1)	101.8	N2-N3-C2-C3	180(1)	179.8
C2-C1-N1	104(1)	102.7	N3-C2-C3-C4	-11(2)	2.9
C1-N1-N2	113(1)	112.4	N3-C2-C3-C10	175(1)	-175.2
C20-N1-N2	119(1)	122.3	N3-C2-C1-C14	169(2)	176.7
C20-N1-C1	128(1)	125.2	C2-C3-C4-C5	104(2)	90.8
C26-N3-N2	114(1)	117.9	C2-N3-C26-C27	-78(2)	-95.9
C26-N3-C2	132(1)	129.1	C1-N1-C20-C21	-92(2)	-93.6
N3-C2-C3	123(1)	125.1	C1-C2-C3-C4	167(1)	-177.1
C2-C3-C4	121(1)	122.4	C10-C3-C4-C5	-81(2)	-91.0
C2-C3-C10	123(1)	124.3	C16-C15-C32-C33	-96(2)	-87.8

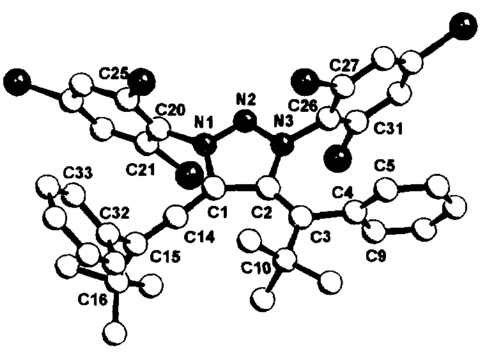


Figure 1. SCHAKAL Plot of the Cation **6n**

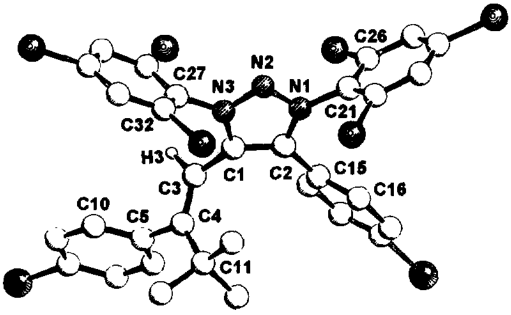


Figure 2. SCHAKAL Plot of the Cation **8b**

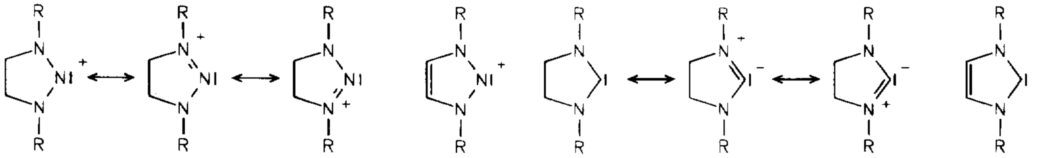
Table 2. Selected bond lengths [pm], bond angles, and torsional angles [deg] for the cation **8b**[24]

Atoms	X-ray	AM1	Atoms	X-ray	AM1
N1-N2	132.9(6)	132.0	N1-N2-N3-C1	-0.2(5)	0.2
N2-N3	132.4(6)	132.2	N2-N3-C1-C2	0.8(6)	-0.6
N3-C1	136.6(6)	142.4	N3-C1-C2-N1	-1.0(5)	0.7
C1-C2	137.9(7)	141.9	C1-C2-N1-N2	0.9(6)	-0.7
C2-N1	135.6(6)	142.0	C2-N1-N2-N3	-0.5(5)	0.2
C1-C3	146.8(7)	144.0	N1-N2-N3-C27	180.0(4)	-177.6
C3-C4	134.4(7)	134.7	N1-C2-C1-C3	170.7(5)	173.0
C2-C15	146.9(7)	144.9	N1-C2-C15-C16	51.7(7)	33.9
N1-C21	143.9(6)	143.9	N2-N3-C27-C32	-77.0(6)	-76.1
N3-C27	144.6(6)	143.9	N2-N1-C21-C26	-100.9(6)	-95.1
N1-N2-N3	102.5(4)	107.2	N2-N1-C2-C15	-178.2(4)	-178.5
N2-N3-C1	114.5(4)	112.0	N2-N3-C1-C3	-171.9(5)	-173.6
N3-C1-C2	103.8(4)	104.2	N3-C1-C3-C4	-116.2(6)	-111.5
C1-C2-N1	105.6(4)	104.6	N3-N2-N1-C21	176.0(4)	179.8
C2-N1-N2	113.6(4)	112.0	N3-C1-C2-C15	178.1(5)	-178.3
C21-N1-N2	117.4(4)	122.1	C1-C3-C4-C5	-175.5(5)	-177.1
C21-N1-C2	128.9(4)	125.9	C1-C3-C4-C11	7(1)	2.5
C27-N3-N2	117.0(4)	122.2	C1-N3-C27-C32	103.3(6)	106.3
C27-N3-C1	128.5(4)	125.7	C1-C2-C15-C16	-127.2(6)	-117.3
N3-C1-C3	123.0(5)	124.3	C2-N1-C21-C26	74.9(7)	84.5
C1-C3-C4	130.6(5)	130.4	C2-C1-C3-C4	73.5(9)	77.6
C15-C2-N1	123.2(5)	125.1	C11-C4-C5-C10	103.9(7)	91.7
C15-C2-C1	131.2(5)	130.2			

In contrast to the butatriene, the central double bond of 1,5-di-*tert*-butyl-1,5-diphenylpentatetraene[23] was attacked by **5**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) to afford the allene **6n**. The cycloaddition of the butatriene leading to **6m** was calculated (AM1) to be exothermic by 80 $kJmol^{-1}$, while the formation of **6n** is even more exothermic (169 $kJmol^{-1}$).

The structural assignments of the triazolium salts **6** and **8** are based on their ^1H,^{13}C NMR, and the IR spectra (Experimental Section). In most cases the assignments were straightforward. However, no allene bands could be observed in the IR spectra of **6m,n**. Also, the configurations of the isolated double bonds of **6n** and **8b** could not be established. Therefore, X-ray structural analyses were carried out for these two compounds. The results are shown in Figures 1,2. Selected molecular data are collected in Tables 1,2.

The crystal structures of both **6n** and **8b** show planar 1,2,3-triazolium rings. In **8b** the olefinic double bond C3=C4 has (E)-configuration (C1 and C5 trans with respect to each other). Due to the poor quality of the crystal the structural analysis of **6n** led to rather poor agreement factors [$R_F(I > 2\sigma(I)) = 8.38\%$; $R_F(\text{all data}) = 16.14\%$]. However, there is no doubt about the structure of the cation, which has an exocyclic double bond C2=C3 with (Z)-configuration (C4 and N3 cis with respect to each other). The allene unit is almost linear (C1-C14-C15: 176(1)°). For reason of comparison structural data calculated by the AM1 method are included in the Tables. While agreement between most of the calculated and measured parameters is satisfactory, the C-N and C-C bond lenghts of the triazolium ring of **8b** were calculated too long (ca 6 pm). For **8b** the (Z)-form was calculated to be 16 $kJmol^{-1}$ more stable than the (E)-form found in the crystal, while for **6n** the (E)-isomer should be 38 $kJmol^{-1}$ less stable than the (Z)-form found by X-ray crystallography.



6 **6'** **6"** **8** **9** **9'** **9"** **10**

Recent publications of Arduengo et al. on stable nucleophilic carbenes **9** and **10** attract much attention.[25-30] The work is based on earlier observation of Wanzlick et al., who postulated carbene character for **9** and **10** but did not isolate such compounds.[31-36] 1,2,3-Triazolium cations **6** and 1,2,3-triazoles **8** are isoelectronic to Wanzlick-Arduengo carbenes **9**, **10**. Arguments put forward in favor of the singlet carbene character of **9**,**10** and against important ylidic contributions **9'**,**9"** etc are small bond angles N-C-N (**9**: 105°,[25] **10**: ca 102° [27]), and long nitrogen bonds to the carbene center (132-137 pm). It is of some note that rather small bond angles were observed also for **6n** [N1-N2-N3: 108(1)], and **8b** [N1-N2- N3: 102.5(4)]. These angles and the N-N bond distances in **6n** (N1-N2: 130(1) pm) and **8b** (N1-N2: 132.7(6) pm) may be compared with those of 1-substituted 4,5-dihydro-1,2,3-triazoles (N1-N2-N3: 112-113°; N1-N2: 135-136 pm; N2=N3: 125-126 pm[37,38]), and 1-substituted 1,2,3-triazoles (N1-N2-N3: 106-108°; N1-N2: ca 135 pm; N2=N3: ca 130 pm[39,40]). Thus, while π-interaction (**6'**,**6"** etc) is certainly important in compounds **6** and **8**, the small N-N-N -bond angles may suggest some singlet nitrenium character of these compounds.

Experimental Section

X-Ray Diffraction Analyses of **6n** and **8b**:[24] Reflections were measured with an Enraf-Nonius CAD4 diffractometer (graphite monochromator, $\lambda_{Mo\text{-}K\alpha}$ = 71.069 pm). Solution by direct methods with subsequent difference-Fourier syntheses and full-matrix least-squares refinement using programs SHELXS-86 and SHELXL-93, respectively. **6n**, $[C_{37}H_{32}Cl_6N_3]^+SbCl_6^-\cdot CCl_4$; MW = 1219.6; crystal size [mm]: 0.40 x 0.40 x 0.20; space group $P2_1/c$; Z = 4; monoclinic; a = 1309.0(4) pm, b = 1516.5(2) pm, c = 2558.4(7) pm; β = 96.79(1)°; V = 5043.10^6 pm^3; d_{calcd} = 1.61 Mg m^{-3}; ω-scan; scan width (in ω) 1.0 + 0.35 tanΘ; $3 \leq 2\Theta \leq 50°$; $F(000)$ = 2416; μ(Mo-Kα) = 1.426 mm^{-1}; T = 153(2) K; 8892 reflections collected; 8478 independent reflections; 5152 observed reflections ($I > 2\sigma(I)$); positions of 8 hydrogen atoms were located by difference Fourier synthesis. The other hydrogen atoms were included in calculated positions. Anisotropic refinement of all non-H atoms with exception of disordered CCl_4 converged to $R_F(I > 2\sigma(I))$ = 8.38% and R_F(all data) = 16.14%.

8b, $[C_{32}H_{22}Br_2Cl_3N_3]^+SbCl_6^-$; MW = 1155.6; crystal size [mm]: 0.40 x 0.20 x 0.21; space group $P2_1/n$; Z = 4; monoclinic; a = 943.1(3) pm, b = 1954.7(6) pm, c = 2274(1) pm; β = 94.34(2)°; V = 4181(3)·10^6 pm^3; d_{calcd} = 1.84 Mg m^{-3}; ω/2Θ-scan; scan width (in ω) 0.9 + 0.35 tanΘ; $3 \leq 2\Theta \leq 50°$; $3.6 \leq 2\Theta \leq 56°$; $F(000)$ = 2240; μ(Mo-Kα) = 3.367 mm^{-1}; T = 153(2) K; 10624 reflections collected; 10032 independent reflections; 6201 observed reflections ($I > 2\sigma(I)$); positions of five hydrogen atoms calculated; the other hydrogen atoms were located by difference Fourier synthesis; CH_3 groups were refined as rigid groups (riding model) with idealized geometry. The anisotropic refinement of all non-H atoms converged to $R_F(I > 2\sigma(I))$ = 4.91%; R_F(all data) = 12.37%.

All experiments were carried out with exclusion of moisture. ^1H, ^{13}C NMR spectra: Bruker AC-250 and WM-250 spectrometers; CD_3CN; 295 K; internal reference TMS; δ-scale; coupling constants J in Hz. IR spectra: Perkin-Elmer FTIR 1600 spectrometer; CH_2Cl_2; absorptions in cm^{-1}. m: multiplet; br: broad; dd: doublet of doublets; t: triplet; sh: shoulder; w: weak.

4,5-Dihydro-1,3-bis(2,4,6-trichlorophenyl)-4-vinyl-*1H*-1,2,3-triazolium Hexachloroantimonate (**6a**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (-60°C) solution of **4**($R^1=R^2$=2,4,6-$Cl_3C_6H_2$)[18] (4.39 g, 10 mmol) in CH_2Cl_2 (40 ml). Excess of 1,3-butadiene (2 ml) in CH_2Cl_2 (20 ml) was added to the resulting orange-red suspension. The reaction mixture was warmed to -30°C over the course of the next 1 h. Stirring was continued at 0°C for 30 min, then at 23°C for 15 min. Addition of CCl_4 (120 ml) afforded a yellow precipitate, which was contaminated by **7** (^1H NMR: singlet at 8.11 ppm[18]). Crystallization at 23°C from CH_2Cl_2 (20 ml)/MeCN (48 ml)/ Et_2O (360 ml) afforded colorless prisms (4.64 g, 59%); mp 175-177°C (dec). IR: 1559, 1571. ^1H NMR: 4.88(m,1H), 5.25(m,1H), 5.63(m,2H), 6.11(m,2H)(vinyl,H4,5,5'), 7.81, 7.82(aryl). ^{13}C NMR: 60.9, 73.6(C4,5), 128.2, 128.6, 129.6, 130.3, 130.9, 131.1, 135.0, 135.3(br), 140.7, 140.8(vinyl,aryl). (Found: C, 24.34; H, 1.50; N, 5.20. Calcd for $C_{15}H_{10}Cl_{12}N_3Sb$ (MW = 791.5): C, 24.28; H, 1.27; N, 5.31%).

4,4'-Bis[4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium] Dihexachloroantimonate (**6b**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a cold (-60°C) solution of **4**($R^1=R^2$=2,4,6-$Cl_3C_6H_2$) (4.39 g, 10 mmol) in CH_2Cl_2 (50 ml). At -60°C a solution of

6a (7.92 g, 10 mmol) in CH_2Cl_2 (50 ml) was added. The reaction mixture was warmed to -30°C over the course of the next 1 h. Stirring was continued at 0°C for 30 min, then at 23°C for 15 min. Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (500 ml)/MeCN (120 ml)/Et_2O (1500 ml) afforded a pale yellow powder (10.20 g, 67%); mp 164-165°C (dec). IR(KBr): 1558, 1567. ^1H NMR: 5.17(dd,J=10.9 and 15.9, 2H), 5.63(t,J=15.9, 2H), 6.31(m,2H), 7.91(4H), 7.83-7.94(m,4H). ^{13}C NMR: 59.6, 67.8(C4,5,4',5'), 127.7, 129.4, 131.2, 131.8, 134.5, 134.7, 135.4, 135.6, 141.8, 142.1(aryl). (Found: C, 22.29; H, 1.04; N, 5.82. Calcd for $C_{28}H_{14}Cl_{24}N_6Sb_2$ (MW = 1528.8): C, 22.00; H, 0.92; N, 5.50%).

4,5-Dihydro-4-isopropenyl-4-methyl-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**6c**): From 2,3-dimethyl-1,3-butadiene (0.83 g, 10 mmol) as described for **6a**. The brown reaction mixture was evaporated to furnish a yellow-brown foam, which was suspended in CH_2Cl_2 (60 ml). Addition of CCl_4 (60 ml), filtration from **7**, addition of further CCl_4 (200 ml) to the filtrate, and storing at -15°C for 12 h afforded a yellowish powder (4.92 g, 60%), which was precipitated at 23°C from CH_2Cl_2 (20 ml)/CCl_4 (80 ml) to furnish a pale yellow powder (4.28 g, 52%); mp 168-170°C (dec). IR: 1558, 1569. ^1H NMR: 2.07, 2.08(CH_3), 4.88(d,J=15.1), 5.26(d,J=15.1)(H5,5'), 5.38 (m), 5.51(m)(vinyl), 7.76(br), 7.82(aryl). ^{13}C NMR: 22.2, 26.5(CH_3), 65.0, 85.4(C5,4), 123.7-140.6 (11 lines: vinyl,aryl). (Found: C, 26.08; H, 1.76; N, 5.03. Calcd for $C_{18}H_{14}Cl_{12}N_3Sb$ (MW = 819.5): C, 26.38; H, 1.72; N, 5.13%).

4,4'-Bis[4,5-dihydro-4-methyl-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium] Dihexachloroantimonate (**6d**): From **6c** (8.20 g, 10 mmol) as described for **6b**. The product crystallized during the reaction and was isolated by filtration. Yield: 9.19 g (59%) of a colorless powder; mp 135-136°C (dec). IR(KBr): 1561(sh), 1570. ^1H NMR (333 K): 2.56(CH_3), 5.16(d,J=16.2), 5.56(d,J=16.2) (CH_2), 7.81, 7.89(aryl). ^{13}C NMR (333 K): 23.2(CH_3), 65.0, 84.3(CH_2,C), 128.7, 129.9, 131.5, 132.7, 133.1, 134.2, 135.9, 139.0, 141.5, 142.4(aryl). (Found: C, 23.23; H, 1.22; N, 5.59. Calcd for $C_{30}H_{18}Cl_{24}N_6Sb_2$ (MW = 1556.9): C, 23.14; H, 1.17; N, 5.40%). Evaporation of the filtrate of the isolation of **6d** afforded almost pure **6c**.

(3aR,5aS,8aR,10aS,4Z,9Z)-1,3a,5a,6,8a,10a-Hexahydro-1,3,6,8-tetrakis(2,4,6-trichlorophenyl)cycloocta[1,2-d:5,6-d']bis(-*1H*-1,2,3-triazolium] Dihexachloroantimonate (**6e**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (-60°C) solution of **4**($R^1=R^2=2,4,6\text{-}Cl_3C_6H_2$) (4.39 g, 10 mmol) in CH_2Cl_2 (50 ml). At -60°C a solution of cyclooctatetraene (0.52 g, 5 mmol) in CH_2Cl_2 (5 ml) was added. The reaction mixture was warmed to -30°C over the course of the next 1 h. Stirring was continued at 0°C for 30 min, then at 23°C for 15 min. Filtration afforded a grey powder (5.16 g, 65%), which contained considerable amounts (ca 30%) of **7**. Stirring for 5 min in MeCN (15 ml) and filtration furnished **6e** as pale yellow powder (2.41 g, 31%); mp 177-178°C (dec). IR(KBr): 1450, 1558, 1569. ^1H NMR: 6.25, 6.60(vinyl), 7.86(aryl). ^{13}C NMR(gated decoupling): 70.0(br,m,J=162.4,CH), 126.5(br,d,J=173.3,vinyl), 127.4(t,J=9,i-C), 130.3(dd,J=178.1 and 5.7,m-C), 134.1(t,J=2.4,o-C), 140.5(t,J=4.3,p-C). (Found: C, 24.61; H, 1.03; N, 5.46. Calcd for $C_{32}H_{16}Cl_{24}N_6Sb_2$ (MW = 1578.9): C, 24.34; H, 1.02; N, 5.32%).

c-3a,4,5,7a-Tetrahydro-1,3-bis(2,4,6-trichlorophenyl)cyclohexa[d]-*1H*-1,2,3-triazolium Hexachloroantimonate (**6f**): From 1,3-cyclohexadiene (0.96 g, 12 mmol) as described for **6a**. Addition of CCl_4 (120 ml) to the brown reaction mixture, filtration from a small amount of **7**, and addition of further

CCl_4 (100 ml) to the filtrate furnished a pale brown precipitate (5.48 g, 67%). Reprecipitation from CH_2Cl_2 (40 ml)/Et_2O (140 ml) afforded a pale yellow powder (5.12 g, 63%), which had to be dried at 60°C for 7 d at 10^{-1} torr; mp 198-199°C (dec). IR: 1558, 1571. ^{1}H NMR: 2.11-2.46(m,4H), 5.78 (m,3H), 6.53(m,1H)(H3a,7a,6,7), 7.81, 7.82(aryl). ^{13}C NMR: 20.9, 21.5(CH_2), 66.9, 68.5 (C3a,7a), 115.3(vinyl), 129.2, 129.3, 131.1, 131.3, 135.0, 135.4, 139.7, 140.4, 140.7(vinyl,aryl). (Found: C, 26.47; H, 1.72; N, 5.13. Calcd for $C_{18}H_{12}Cl_{12}N_3Sb$ (MW = 817.5): C, 26.45; H, 1.48; N, 5.14%).

4,5-Dihydro-4-methyl-1,3-bis(2,4,6-trichlorophenyl)-4-vinyl-*1H*-1,2,3-triazolium Hexachloroantimonate (**6g**) + 4,5-Dihydro-4-isopropenyl-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**6h**): From isoprene (0.82 g, 12 mmol) as described for **6a**. Evaporation of the reaction mixture afforded a brown oil, which was suspended in CH_2Cl_2 (40 ml). Addition of CCl_4 (120 ml), filtration from **7**, and addition of further CCl_4 (120 ml) to the filtrate resulted in precipitation of a pale brown powder (4.92 g, 61%). Reprecipitation from CH_2Cl_2 (20 ml)/Et_2O (60 ml) gave an orange-brown powder (4.44 g, 55%); mp 183-184°C (dec). IR: 1559, 1571. ^{1}H NMR: mixture (ca 1.3:1) of **6g,h**: main component: 2.03(CH_3), 6.45(dd,J=10.6 and 17.1,1H,vinyl); minor component: 2.01(d,J=0.4, CH_3), 6.24(dd,J=11.8 and 14.8,1H,vinyl). ^{13}C NMR: 19.0, 23.5(CH_3), 58.9, 66.2, 75.7, 83.7(C4,5), 124.5-140.7(18 signals: vinyl,aryl). (Found: C, 25.31; H, 1.59; N, 5.20. Calcd for $C_{14}H_{12}Cl_{12}N_3Sb$ (MW = 805.5): C, 25.35; H, 1.50; N, 5.22%).

4,5-Dihydro-1,4-dimethyl-3-(4-methylphenyl)-4-isopropenyl-*1H*-1,2,3-triazolium Hexafluorophosphate (**6i**) + 4,5-Dihydro-3,4-dimethyl-1-(4-methylphenyl)-4-isopropenyl-*1H*-1,2,3-triazolium Hexafluorophosphate (**6j**): With exclusion of light *tert*-butylhypochlorite (1.52 g, 15 mmol) was added to a cold (-60°C) suspension of 2,3-dimethyl-1,3-butadiene (1.64 g, 20 mmol), $3(R^1=4\text{-}MeC_6H_4, R^2=Me)$[19] (1.49 g, 10 mmol) and KPF_6 (3.68 g, 20 mmol) in CH_2Cl_2 (100 ml). The reaction mixture was warmed to -10°C over the course of the next 2 h. Stirring was continued at 0°C for 30 min, then at 23°C for 15 min. The orange suspension was filtered and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (15 ml). Slow addition of Et_2O (100 ml) afforded an oily precipitate, which was dried at 60°C i. vac. to give an orange sirup (3.04 g, 81%). IR: 1508, 1525. ^{1}H NMR ($CDCl_3$): 1:5 mixture of **6i,j**: main component: 1.79, 1.87, 2.37, 3.88(CH_3), 4.44(CH_2), 5.28(br), 5.32(br)(vinyl), 7.23(m), 7.33(m)(aryl); minor component: 1.78, 3.69(CH_3), 4.65(AB-q,CH_2), 7.39(m,2H,aryl). ^{13}C NMR ($CDCl_3$): main component: 18.2, 21.1, 22.4, 40.1(CH_3), 65.7(CH_2), 77.6(?)(C), 117.8, 120.8, 130.5, 132.2, 140.4, 141.4(aryl,vinyl); minor component: 17.8, 21.0, 34.9(CH_3), 61.3 (CH_2), 76.9(C), 118.0, 118.5, 130.7, 133.6, 138.7, 140.1(aryl,vinyl). (Found: C, 44.78; H, 5.35; N, 11.16. Calcd for $C_{14}H_{20}F_6N_3P$ (MW = 375.3): C, 44.81; H,5.37; N, 11.20%).

1,3-Bis(4-chlorophenyl)-4,5-dihydro-4-isopropenyl-4-methyl-*1H*-1,2,3-triazolium Hexafluorophosphate (**6k**): From $3(R^1=R^2=4\text{-}ClC_6H_4)$[41] (2.66 g, 10 mmol) as described for **6i,j**. The orange suspension was evaporated and the residue was suspended in CH_2Cl_2 (60 ml)/MeCN (15 ml). Filtration and addition of Et_2O (100 ml) to the filtrate afforded an orange-yellow powder (4.28 g, 87%), which was reprecipitated from MeCN (20 ml)/Et_2O (100 ml) to give a dark yellow powder (3.90 g, 79%); mp 218-220°C (dec). IR: 1475, 1489. ^{1}H NMR: 1.90(br), 1.97(CH_3), 4.91(AB-q,J=14.2,H5,5'), 5.47 (vinyl), 7.57-7.75(m,aryl). ^{13}C NMR: 18.7, 23.2(CH_3), 64.5, 80.0(C4,5), 119.7, 121.6, 123.7, 131.2, 131.3, 134.6, 135.9, 136.7, 137.1, 141.8(aryl,vinyl). (Found: C, 43.85; H, 3.70; N, 8.53. Calcd for $C_{18}H_{18}Cl_2F_6N_3P$ (MW = 492.2): C, 43.92; H, 3.69; N, 8.54%).

4,5-Dihydro-4,4-diphenyl-5-(diphenylmethylene)-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**6l**): From tetraphenylallene[42] (3.44 g, 10 mmol) as described for **6a**. The solvent of the reaction mixture was evaporated. The green residue was suspended in MeCN (20 ml). Slow addition of Et_2O (240 ml) afforded a green precipitate (6.85 g, 61%). Crystallization from hot MeCN (80 ml) afforded yellow prisms (5.61 g, 50%); mp 146-148°C (dec). IR: 1552(sh), 1567. ^1H NMR (CD_2Cl_2,258K): 2.01(MeCN), 7.30, 7.37($Cl_3C_6H_2$), broad lines for one phenyl group (rotational hindrance). ^{13}C NMR (CD_2Cl_2,258K): 2.5, 117.5(MeCN), 94.7, 126.2, 126.9, 128.1, 128.2, 128.3, 129.0, 129.2, 129.59, 129.63, 129.69, 129.9, 130.3, 130.4, 131.6, 132.0, 133.4, 133.8, 135.5, 135.6, 136.1, 138.1, 139.7, 139.8, 140.8(C=,aryl). (Found: C, 43.76; H, 2.43; N, 4.97. Calcd for $C_{39}H_{24}Cl_{12}N_3Sb\cdot CH_3CN$ (MW = 1122.9): C, 43.85; H, 2.42; N, 4.99%).

4-(4-Bromophenyl)-5-[2-(4-bromophenyl)-3,3-dimethylbut-1-en-1-ylidene]-4-*tert*-butyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**6m**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (-60°C) suspension of 1,4-bis-(4-bromophenyl)-1,4-di-*tert*-butylbutatriene[22] (4.74 g, 10 mmol) and $4(R^1=R^2=2,4,6\text{-}Cl_3C_6H_2)$ (4.39 g, 10 mmol) in CH_2Cl_2 (40 ml). After stirring between -40 and -30°C for 1 h and at -10°C for another h, then at 0°C for 30 min, and finally at 23°C for 15 min, CCl_4 (40 ml) was added. The mixture was filtered from **7**, and the filtrate was cooled to -20°C. Further CCl_4 (160 ml) was added. The suspension was stirred at -20°C for 1 h, then at 23°C for 2 h. A pale yellow powder (8.84 g, 73%) was isolated by filtration; the color of the compound disappeared at 180-185°C; mp 294-297°C (dec). Attempts to recrystallize the product from MeCN resulted in decomposition. FAB-MS (3-nitrobenzyl alcohol, m/e): 876(100%, M - $SbCl_6$), 820(63%, M - $SbCl_6$ - $Me_2C=CH_2$). IR: 1549(sh), 1567, 1586(sh), no allene band. ^1H NMR (350 K): 1.14(br,9H), 1.19(9H)(*tert*-butyl), 6.87(m,2H), 7.51-7.97(10H)(aryl;some lines br). ^{13}C NMR (350 K,slow decomposition to **8b**): 28.3, 29.7, 29.8(?), 39.9, 45.8(CH_3,C), 96.9(C4), 191.3(allene), 120.0-142.3(25 lines:aryl,allene). (Found: C, 35.36; H, 2.53; N, 3.54. Calcd for $C_{36}H_{30}Br_2Cl_{12}N_3Sb$ (MW = 1211.6): C, 35.69; H, 2.50; N, 3.47%).

5-(3,3-Dimethyl-2-phenylbut-1-en-1-ylidene)-4-[(Z)-2,2-dimethyl-1-phenylpropyl-1-idene]-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**6n**): From 2,2,8,8-tetramethyl-3,7-diphenyl-3,4,5,6-nonatetraene[23] (3.29 g, 10 mmol) in CH_2Cl_2 (20 ml) as described for **6a**. The solvent of the dark red reaction mixture was evaporated, and the red residue was dissolved in CH_2Cl_2 (80 ml). Addition of CCl_4 (200 ml) and filtration of the precipitate afforded a red crystalline powder (7.60 g, 71%), which was dissolved in CH_2Cl_2 (20 ml). After slow addition of Et_2O (20 ml) a small amount of **7** was removed by filtration. Addition of Et_2O (60 ml) to the filtrate furnished a red crystalline powder (6.44 g, 60%); mp 140-170°C (dec). Crystals of low quality but suitable for X-ray analysis were obtained by crystallization at -15°C from $MeCN/CCl_4$. For **6n** a correct elemental analysis could not be obtained because of easy loss of isobutene. - FAB-MS (3-nitrobenzyl alcohol, m/e): 731(65%, M - $SbCl_6$). IR: 1561, 1906(w,allene?). ^1H NMR: 1.11, 1.17(CH_3), 6.92-8.10(14 H,aryl). ^{13}C NMR: 26.6, 28.8(CH_3), 38.1, 40.7(C), 194.2(allene), 117.5-149.8(23 lines: aryl, C4,5,allene). (Found: C, 40.30; H, 2.80; N, 4.12. Calcd for $C_{37}H_{32}Cl_{12}N_3Sb$ (MW = 1065.9): C, 41.69; H, 3.03; N, 3.94%).

4-Methyl-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Tetrachloroantimonate (**8a**): A solution of **6d** (1.56 g, 1 mmol) in MeCN (50 ml) was boiled under reflux for 24 h. The solvent was evaporated and the brown residue was dissolved in CH_2Cl_2 (25 ml). Slow addition of CCl_4 (150 ml) afforded a pale brown crystalline powder, which was recrystallized from hot MeCN (15 ml) to furnish a colorless crystalline powder (1.25 g, 88%); mp 186-188°C (dec). IR(KBr): 1563, 1572. ^1H NMR (323 K): 2.55(CH_3), 7.86, 7.90(aryl), 8.88(H-5). ^{13}C NMR (323 K): 9.91(CH_3), 127.8, 130.2, 130.9, 131.4, 134.0, 134.5, 134.8, 141.3, 141.8, 146.6(aryl,C4,5). (Found: C, 25.43; H, 1.19; N, 6.06. Calcd for $C_{15}H_8Cl_{10}N_3Sb$ (MW = 706.5): C, 25.50; H,1.14; N, 5.95%).

4-(4-Bromophenyl)-5-[(E)-2-(4-bromophenyl)-3,3-dimethylbut-1-enyl]-1,3-bis(2,4,6-trichlorophenyl)-*1H*-1,2,3-triazolium Hexachloroantimonate (**8b**): A solution of **6m** (1.21 g, 1 mmol) in MeCN (30 ml) was boiled under reflux for 12 h. After cooling to 23°C Et_2O (40 ml) was added and the colorless precipitate (0.75 g, 65%) was isolated by filtration; mp 303-305°C (dec). Crystals suitable for X-ray analysis were obtained by crystallization from boiling MeCN. IR(KBr): 1564, 1598(sh). ^1H NMR (CD_3CN/D_6-DMSO(2:1)): 0.79(CH_3), 6.07(vinyl), 8.04(br), 8.12($Cl_3C_6H_2$), 6.92(m,2H), 7.51(m, 4H), 7.89(m,2H)(BrC_6H_4). ^{13}C NMR(CD_3CN/D_6-DMSO (2:1)): 29.3(CH_3), 38.4(C), 106.3, 170.6 (vinyl), 120.5-143.4(16 lines: aryl,C4,5). (Found: C, 33.28; H, 1.98; N, 3.72. Calcd for $C_{32}H_{22}Br_2Cl_{12}N_3Sb$ (MW = 1155.6): C, 33.26; H, 1.92; N, 3.64%).

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References

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1. Padwa, A. (Ed.) *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1 and 2, John Wiley and Sons Inc.: New York 1984.
2. Parsons, S.; .Passmore, J.; Shriver, M.J.; Sun, X. *Inorg.Chem.* **1991**, *30*, 3342-3348.
3. Burford, N.; Johnson, J.P.; Passmore, J.; Shriver, M.J.; White, P.S. *J.Chem.Soc.Chem.Commun.* **1986**, 966-968.
4. Liblong, S.W.; Oakley, R.T.; Cordes, A.W.; Noble, M.C. *Can.J.Chem.* **1983**, *61*, 2062-2067.
5. Shatzmiller, S.; Shalom, E.; Bahar, E. *J.Chem.Soc.Chem.Commun.* **1984**, 1522-1523.
6. Wang, Q.; Jochims, J.C.; Köhlbrandt, St.; Dahlenburg, L.; Al-Talib, M.; Hamed, A.; Ismail, A.E. *Synthesis* **1992**, 710-718.
7. Guo, Y.; Wang, Q.; Jochims, J.C. *Synthesis* **1996**, 274-280.
8. Wang, Q.; Al-Talib, M.; Jochims, J.C. *Chem.Ber.* **1994**, *127*, 541-547.
9. Wang, Q.; Amer, A.; Troll, C.; Fischer, H.; Jochims, J.C. *Chem.Ber.* **1993**, *126*, 2519-2524.
10. Wang, Q.; Mohr, S.; Jochims, J.C. *Chem.Ber.* **1994**, *127*, 947-953.
11. Wang, Q.; Amer, A.; Mohr, S.; Ertel, E.; Jochims, J.C. *Tetrahedron* **1993**, *49*, 9973-9986.
12. Sustmann, R. *Tetrahedron Lett.* **1971**, 2721-2724.

13. MOPAC program, version 6.0, Stewart, J.J.P., QCPE # 455; all calculations were carried out with complete optimization of all bond lengths, bond angles and dihedral angles.
14. Geisler, A.; Würthwein, E.-U. *Tetrahedron Lett.* **1994**, *35*, 77-80.
15. Schleimer, R.; Hornig, K.; Möller, M.H.; Würthwein, E.-U. *Chem.Ber.* **1993**, *126*, 133-141.
16. Liebscher, J. *Synthesis* **1988**, 655-669.
17. Hitzler, M.G.; Freyhardt, C.C.; Jochims, J.C. *Synthesis* **1994**, 509-515.
18. Wirschun, W.; Jochims, J.C. *Synthesis* **1997**, 233-242.
19. Commercially available from FLUKA
20. Mohr, R.; Hertel, H. *Chem.Ber.* **1963**, *96*, 114-129.
21. Hansen, H.; Hünig, S.; Kishi, K. *Chem.Ber.* **1979**, *112*, 445-461.
22. Bertsch, K.; Rahman, M.A.; Jochims, J.C. *Chem.Ber.* **1979**, *112*, 567-576.
23. Karich, G.; Jochims, J.C. *Chem.Ber.* **1977**, *110*, 2680-2694.
24. A computer print-out of refined coordinates, structure factors, bond distances etc. is available from the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW, respectively from the British Library, Lending Devision, on request.
25. Arduengo, A.J.; Goerlich, J.R.; Marshall, W.J. *J.Am.Chem.Soc.* **1995**, *117*, 11027-11028.
26. Arduengo, A.J.; Harlow, R.L.; Kline, M. *J.Am.Chem.Soc.* **1991**, *113*, 361-363.
27. Arduengo, A.J.; Dias, H.V.R.; Harlow, R.L.; Kline, M. *J.Am.Chem.Soc.* **1992**, *114*, 5530-5534.
28. Arduengo, A.J.; Dias, H.V.R.; Dixon, D.A.; Harlow, R.L.; Kloosters, W.T.; Koetzle, T.F. *J.Am.Chem.Soc.* **1994**, *116*, 6812-6822.
29. Arduengo, A.J.; Bock, H.; Chen, H.; Denk, M.; Dixon, D.A.; Green, J.C.; Herrmann, W.A.; Jones, N.L.; Wagner, M.; West, R. *J.Am.Chem.Soc.* **1994**, *116*, 6641-6649.
30. Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J.H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew.Chem.* **1995**, *107*, 1119-1122; *Angew.Chem.Int.Ed.Engl.* **1995**, *34*, 1021.
31. Wanzlick, H.-W.; Lachmann, B.; Schikora, E. *Chem.Ber.* **1965**, *98*, 2170-2177.
32. Lachmann, B.; Wanzlick, H.-W. *Liebigs Ann.Chem.* **1969**, *729*, 27-32.
33. Wanzlick, H.-W.; Schönherr, H.-J. *Angew.Chem.* **1968**, *80*, 154; *Angew.Chem.Int.Ed.Engl.* **1968**, *7*, 141.
34. Schönherr, H.-J.; Wanzlick, H.-W. *Liebigs Ann.Chem.* **1970**, *731*, 176-179.
35. Schönherr, H.-J.; Wanzlick, H.-W. *Chem.Ber.* **1970**, *103*, 1037-1046.
36. Walentowski, R.; Wanzlick, H.-W. *Z.Naturforsch.* **1970**, *25B*, 1421-1423.
37. Eagan, R.L.; Ogliaruso, M.A.; Springer, J.P. *J.Org.Chem.* **1986**, *51*, 1544-1547.
38. Adam, W.; Carballeira, N.; Crämer, E.; Lucchini, V.; Peters, E.-M.; Peters, K.; von Schnering, H.G. *Chem.Ber.* **1987**, *120*, 695-703.
39. Bettison, R.M.; Hitchcock, P.B.; Walton, D.R.M. *J.Organomet.Chem.* **1988**, *341*, 247-254.
40. Nagawa, Y.; Goto, M.; Honda, K.; Nakanishi, H. *Acta Crystallogr.,Sect.C* **1987**, *43*, 147-149.
41. Vernin, G.; Siv, C.; Metzger, J.; Parkanyi, C. *Synthesis* **1977**, 691-693.
42. Ubbelohde, A.R.; Burgess, J.A. *J.Chem.Soc.(B)* **1970**, 1106-1113.

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