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AN EXAMPLE OF CHELETROPIC REACTIVITY OF A METHYLENE PHOSPHANE

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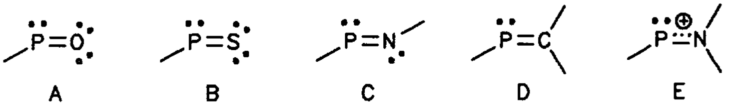
Abstract: In the reaction of a 2-phosphonio-1-phospha-1-alkene with tetrachloro-orthobenzoquinone, a [4+1] cycloaddition is observed. In the presence of a Lewis acid, however, [4+2] cycloaddition takes place.

In the reactions of the isovalent electronic compounds A - E (scheme 1) with dienes, [4+2]-cycloadditions as well as [4+1] cycloadditions are expected. Oxophosphanes A and thiooxophosphanes B react predominantly,[1] phosphenium ions E exclusively,[2] in a [4+1] fashion, while imino phosphanes C and methylene phosphanes D represent interesting borderline cases.

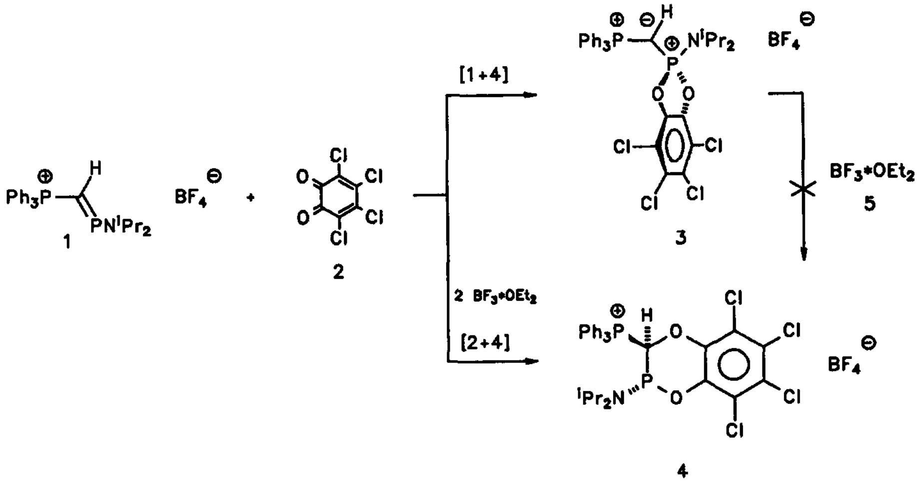


scheme 1

Assuming a HOMO (Y=P; Y=NR or CR_2) - LUMO (diene) interaction,[3] this can be explained by a HOMO with σ symmetry (lone pair of electrons at the phosphorus atom) for A, B and E, while in C and D a crossing of the closely spaced frontier orbitals $(\sigma^2, \pi^2, \pi^* \rightarrow \pi^2, \sigma^2, \pi^*)$[4] gives rise to ambiphilic reactivity. Indeed, for imino phosphanes, depending on the substituents attached to them, [4+1] as well as [4+2] cycloadditions are reported.[5] Methylene phosphanes studied so far, to our knowledge, only yielded [4+2] cycloaddition products.[6] Herein we describe both cycloaddition patterns in the reaction of a methylene phosphane with tetrachloro-orthobenzoquinone 2.

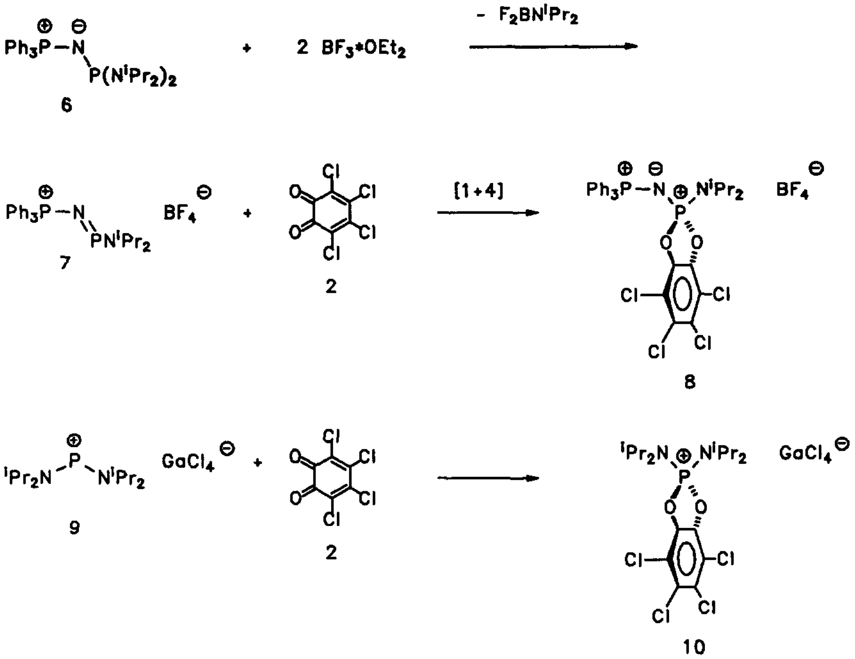
The P-amino substituted 2-phosphonio-1-phospha-alkene[7] 1 reacts with 2 in CH_2Cl_2 to yield a mixture of approximately 90% [2-Diisopropylamino-2-(triphen-ylphosphoranylidene-methyl)-tetrachlorobenzo-1,3,2-dioxaphospholanium] tetra-fluoroborate 3 and 10% [1-Diisopropylamino-6-triphenylphosphonio-tetrachloro-benzo-1-phospha-2,5-dioxa-cyclohexane] tetrafluoroborate 4.

Admixing $BF_3 \cdot OEt_2$ to a solution of 1 before 2 is added leads to an increase in 4. The formation of 4 increases as the concentration of $BF_3 \cdot OEt_2$ 5 is increased until only 4 can be detected by NMR spectroscopy if the reaction is performed in the presence of 2 equivalents of the Lewis acid. The [4+1] cycloadduct 3 is not isomerized to 4 by subsequent $BF_3 \cdot OEt_2$ addition and is stable thermally and photochemically (scheme 2).



scheme 2

The structures of the cycloadducts are proven by a) their characteristic coupling constants $^2J(P^V-P^V)$ = 29.3 Hz for 3 and $^2J(P^V-P^{III})$ = 95.3 Hz for 4 (Tab. 1), b) the proton resonance of the proton bonded to the carbon bridging the phosphorus atoms (3: δ = 2.73 ppm, J(PH) = 3.9 Hz; 4: δ = 6.86 ppm, J(PH) = 8.8 Hz) and c) the ^{13}C-NMR resonance of the bridging carbon (3: δ = 12.9 ppm, J(PC) = 230.1 Hz, J(PC) = 111.4 Hz; 4: δ = 71.6 ppm, J(PC) = 60.2 Hz, J(PC) = 52.9 Hz). The X-ray structure of compound 3[8] is given in the figure The amino substituted phosphonio imino phosphane 7 has been synthesized as shown in scheme 3. For comparison, 7 and the phosphenium ion[2] 9 are treated with 2. In both cases only the [4+1] cycloadducts [2-Diisopropylamino-2-(triphenylphosphoranylidene-amino)-tetrachlorobenzo-1,3,2-dioxaphospholanium] tetrafluoroborate 8 and [2,2-Bis(diisopropylamino)-1,3,2-dioxaphospholanium] tetrachlorogallate 10 are obtained and a large excess of $BF_3 \cdot OEt_2$ does not alter the reactivity of 7 (scheme 3). However, in contrast to 1, the imino phosphane 7 is more reactive and combines with 9,10-phenanthrenequinone to a [4+1] cycloadduct. Both 1 and 7 do not react with benzil, norcampherdione and oxalyl chloride even at elevated temperatures. Cycloadduct 6 has been characterized by means of a single crystal X-ray diffraction study as well (figure 1).



scheme 3

In the cyclovoltammogramm of 1 (CH_2Cl_2, platinum disk electrode), a irreversible oxidation peak is found at 2.04 V (vs. SCE). However, 7 could not be oxidized within the electrochemical window of CH_2Cl_2 (+2.5 V/ -2.2 V). Under similar conditions, tetrachloro-orthobenzoquinone 2 shows a first reversible reduction peak at 0.15 V and hence, formation of a radical cation/anion pair, which has been suggested for the reactions of aryl substituted phosphaalkenes with 2,[9] is very unlikely. In these investigations, [4+2] cycloadducts have been found exclusively.

Obviously the triphenylphosphonium group in 1 and 7 has a strong electron withdrawing ability,[10] that causes, in spite of the conjugated bonded amino group (strong π donor) at the low coordinated phosphorus atom, a HOMO of σ symmetry. Consequentely, cheletropic reaction behavior is observed. [1+1] Adducts of methylene phosphanes and Lewis acids such as BCl_3, $AlCl_3$ and $GaCl_3$ through the lone pair of electrons at phosphorus are known.[11] A possible equilibrium $1 + BF_3{\cdot}OEt_2 \rightleftarrows 1{\cdot}BF_3 + OEt_2$ would evoke a "masking" (decrease in energy) of the HOMO with σ symmetry. In this case, 1 can only use frontier orbitals of π symmetry in the reaction with the heterodiene and a [4+2] cycloadduct 4 will be the product.[12]

Cycloadducts 3 and 6 are members of a long known family of phosphorus compounds[13] and there structural features do not differ remarkable from the ones previously described.[14] In comparison to 1, the P2-C1 bond length is shortened from 1.684 Å to 1.647 Å in 3 due to strong electrostatic attractions. The angles P1-C1-C2 as well as C1-P2-N1 are widened from 115.5(8) and 105.3(7) in 1 to 128.0(2) and 113.8 (2) in 3, respectively.

Table 1. $^{31}P\{^{1}H\}$-NMR-data of compounds 1,3,4,6,7,8,9 and 10[a]

compound No.	δ[ppm] P_A	P_B	J(P-P)[Hz]
1	19.5	303.5	^2J = 124.6
3	15.7	71.8	^2J = 36.6
4	17.2	91.7	^2J = 95.3
6	-2.5	70.1	^2J = 124.0
7	29.3	311.4	^2J = 71.1
8	21.6	22.9	^2J = 14.6
9		305.4	
10		52.9	

[a] In CDC13, Jeol FX 90 Q, 36.19 MHz, H3PO4 as external standard.

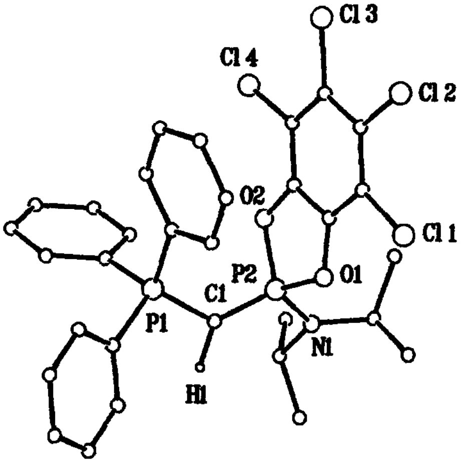
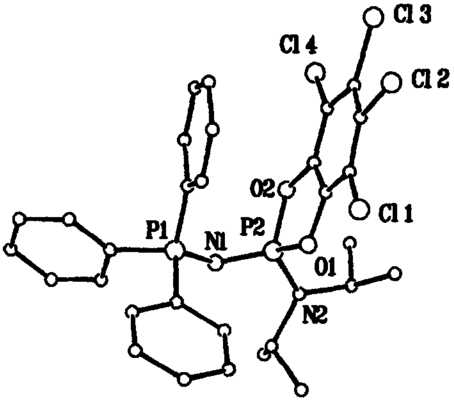


figure 1. Structure of the cation in 3



Structure of the cation in 8

Important bond lengths (Å) and angles (°): 3: P1-C1 1.721(5), P2-C1 1.647(5), P2-O1 1.637(4), P2-O2 1.645(3), P2-N1 1.601(4); P1-C1-P2 128.0(3), C1-P1-N1 113.8(2), C1-P2-O1 119.4(2), C1-P2-O2 108.2(2), N1-P2-O1 103.9(2), N1-P2-O2 116.5(2).

8: P1-N1 1.580(15), P2-N1 1.554(15); P1-N1-P2 135.1(11).

EXPERIMENTAL

^{31}P-NMR, ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Jeol FX 90 Q (36.19, 89.55 and 22.49 MHz); H_3PO_4 (ext.) and tetramethylsilane (int.) as standards. All reactions were carried out in carefully dried glassware and solvents under an atmosphere of nitrogen.
Melting points are uncorrected. Elemental analyses were performed by the microanalytical laboratory of the Chemische Institute der Universität Heidelberg.

[2-Diisopropylamino-2-(triphenylphosphoranylidene-methyl)-tetrachlorobenzo-1,3,2-dioxaphospholanium] tetrafluoroborate 3: compound 1 (2.46 g, 5 mmol) was dissolved in 15 ml of methylene chloride and a solution of 2 (1.23 g, 5 mmol) in 10 ml of methylene chloride was added dropwise. The colourless solution was evaporated to dryness and the residue was suspended in 20 ml of diethyl ether. Methylene chloride was slowely added until a clear solution was obtained. After cooling to -30°C for 3 d the white precipitate was filtered off and dried under vacuum. 2.66 g (72%) 3, m.p. 214°-216°C, was isolated. Found: C, 49.94; H, 4.11; Calc: C, 50.37; H, 4.09% for $C_{31}H_{30}BCl_4F_4NP_2O_2$ (739.15 g/mol).

1-Diisopropylamino-6-triphenylphosphonio-tetrachlorobenzo-1-phospha-2,5-dioxacyclohexane 4: The applied procedure resembled the one described for 3. However, two equivalents of 5 (1.42 g, 10 mmol) had been added before reacting 1 with 2. 2.98 g (80%) 4, m.p. 179°-182°C, were obtained. Found: C, 50.91; H, 3.98; Calc: C, 50.37; H, 4.09% for $C_{31}H_{30}BCl_4F_4NP_2O_2$ (739.15 g/mol).

Bis(diisopropylamino)phosphano-imino triphenylphosphorane 6: To a suspension of lithium(triphenylphosphoranylimide) (2.83 g, 10 mmol) in 20 ml of THF a solution of diisopropylamino-chloro-phosphane (2.66 g, 10 mmol) was added and the reaction mixture was stirred for 7 d at room temperature. Heating led to substancial decomposition. After evaporation under vacuum to dryness the residue was taken up in 40 ml of methylene chloride and filtered. The filtrate was again evaporated and the remaining yellow oil disolved in a minimum amount of hot acetonitril (ca. 30 ml). Cooling to 0°C afforded 3.1 g (60 %) crude 6, which after recrystallisation showed satisfying analytical data. Pale yellow crystals, m.p. 95°C. Found: C, 73.62; H, 8.81; N, 5.42; Calc.: C,73.49; H, 8.75; N, 5.53 % for $C_{31}H_{44}N_2P_2$ (506.655 g/mol).

[P-Diisopropylamino-N-triphenylphosphonio-imino phosphane] tetrafluoroborate 7: To compound 6 (1.52 g, 3 mmol), solved in 10 ml methylene chloride, freshly distilled 5 (0.85 g, 6 mmol) was added at -78°C. The reaction mixture was allowed to warm up to room temperature and stirred for 10 h. All volatile components were pumped off under vacuum and the residue was suspended in diethyl ether. After filtration the slightly brown solid was recrystallized from diethyl ether/methylene chloride at -80°C to yield 1.1 g (73 %) of 7, m.p. 85 °C. ^{1}H-NMR (CDCl3, T = 297.5 K): δ = 1.39-1.51 (m, 12H, CH3); 4.05 (sept., 1H, CH); 4.67 (sept., 1H, CH); 7.4-7.84 (m, 15H, aryl H). ^{13}C-NMR (CD_2Cl_2; T = 300 K): δ = 22.4 (s, CH3); 25.7 (d, CH3, J(P-C) = 10.25 Hz); 51.1 (d, CH, J(P-C) = 13.2 Hz); 52.1 (d, CH, J(P-C) = 7.3 Hz); 125.1 (d, ipso-C, J(P-C) = 104.0 Hz); 130.4 (d, m-C, J(P-C) = 13.2 Hz); 133.0 (d, o-C, J(P-C) = 10.3 Hz); 135.0 (d, p-C, J(P-C) = 2.9 Hz). Found: C, 57.89; H, 5.89; N, 5.71; Calc.: C, 58.32; H, 5.91; H, 5.67% for $C_{24}H_{29}BF_4N_2P_2$ (494.26 g/mol).

[2-Diisopropylamino-2-(triphenylphosphoranylidene-amino)-tetrachlorobenzo-1,3,2-dioxaphospholanium] tetrafluoroborate 8: Compound 7 (1 g, 2 mmol) was dissolved in 10 ml of methylene chloride and 2 (0.49 g, 2 mmol) in 5 ml methylene chloride was added slowly at 0°C. After evaporation of the solvent the oily residue was treated with diethyl ether. After several days the compound began to crystallize. Found: C, 49.01; H, 4.06; N, 3.64; Calc.: C, 48.68; H, 3.95; N, 3.78% for $C_{30}H_{29}BCl_4F_4N_2P_2O_2$ (740.136 g/mol).

[2,2-Bis(diisopropylamino)-1,3,2-dioxaphospholanium] tetrachlorogalate 10: Compound 10 was synthesized as described above and characterized by means of NMR spectroscopy. ^{1}H-NMR ($CDCl_3$): δ = 1.33 (d, 24H, CH3, J(H-H) = 6.8 Hz); 4.01 (dsept., 4H, CH, J(P-H) = 23.2 Hz, J(H-H) = 6.83 Hz).

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REFERENCES AND NOTES

1. Yoshifuji, M.; Nakayama, S.; Okazaki, R.; Inamoto, N. *J. Chem. Soc. Perkin I* 1973, 2065; Hussong, R.; Heydt, H.; Maas, G.; Regitz, M. *Chem.Ber.* 1987, *120*, 1263 and lit. cited.
2. Cowley, A.H.; Kemp, R.A.; Lasch, J.G.; Norman, N.C.; Stewart, C.A.; Whittlesey, B.R.; Wright, T.C. *Inorg. Chem.* 1986, *25*, 740; Cowley, A.H.; Kemp, R.A. *Chem. Rev.* 1985, *85*, 367.

3. This corresponds to a Diels-Alder reaction of inverse electron demand. Due to the high nucleophility of phosphaalkenes, a [4+2] cycloaddition of normal electron demand (HOMO(diene)-LUMO(en)) has to be considered at least in cases electronrich dienes are employed: Schoeller, W.W. *J. Chem. Soc., Chem. Commun.* 1985, 334 (see also D. Gudat, dissertation, Bielefeld, (1987).
4. Schoeller, W.W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* 1982, 569; Bock, H.; Bankmann, M. *Angew. Chem.* 1986, *98*, 951; *Angew. Chem. Int. Ed. Engl.* 1986, *25*, 265.
5. Niecke, E.; Gudat. D.; Schoeller, W.W.; Rademacher, P. *J. Chem.Soc., Chem. Commun.* 1985, 1050; Romanenko, V.D.; Drapailo, A.B.; Ruban, A.V.; Markovskii, L.N. *Zh. Obshch. Khim.* 1987, *57*, 1402; engl. 1253.
6. i.e.: Yeung Lam Ko, Y.Y.C.; Carrié, R. *J. Chem. Soc., Chem. Commun.* 1984, 1640; Grobe, J.; Le Van, D. *Z. Naturforsch.* 1985, *40b*, 467; Appel, R.; Menzel, J.; Knoch, F. *Chem. Ber.* 1985, *118*, 4068.
7. Grützmacher, H.; Pritzkow, H. *Angew. Chem.* 1989, *101*, 768; *Angew. Chem. Int. Ed. Engl.* 1989, *28*, 740.
8. 3: Space group $P2_1$, a = 8.951(3), b = 15.022(6), c = 12.952(4) Å, β = 95.46(3)°, Z = 2, V = 1733.5 $Å^3$; 2361 observed reflections (four-circle diffractometer, MoKα-radiation, ω-scan), R = 0.042 (non-hydrogen atoms were refined anisotropically, phenyl rings and methyl groups as rigid groups with hydrogens in calculated positions, H1 was located and refined isotropically, the BF_4 anion is disordered and was refined by two rigid BF_4tetrahedra).

   8: Isotypic to 3; space group $P2_1$, a = 8.885(19), b= 15.35(4),C = 12.80(3) β= 97.93(18)°, Z = 2, V = 1730 $Å^3$; 1233 observed reflections (four-circle diffractometer, MoKα-radiation, ω-scan), R = 0.079 (P, Cl atoms were refined anisotropically, phenyl rings and methyl groups as rigid groups including hydrogens in calculated positions). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-54344, the name of the authors and the journal citation.
9. van der Knaap, T.A.; Bickelhaupt, F. *Tetrahedron* 1983, *39*, 3189; Heinicke,J.; Tzschach, A. *Tetrahedron Lett.* 1983, *24*, 5481; Hausen, H.-D.; Weckler, G. *Z. Naturforsch.* 1984, *39b*, 628.
10. This has been expressed by Karsch et. al. in terms of the resonance structures: $R_3P^+\text{-}CR{=}P\text{-}R \leftrightarrow R_3P{=}CR\text{-}P^+\text{-}R \leftrightarrow R_3P^+\text{-}CR^-\text{-}P^+\text{-}R$: Karsch, H.H.; Reissacher, H.-U.; Müller, G. *Angew. Chem.* 1986, *98*, 467; *Angew. Chem. Int. Ed. Engl.* 1986, *25*, 454. See also: Bock, H.; Bankmann, M.; Hänel, P.;

Lechner-Knoblauch, U. *Phosphorus Sulfur* 1987, *30*, 109 and literature cited therein.

11. Nixon, J.F. cites a personal communication of Niecke, E. in: Nixon, J.F. *Chem. Rev.* 1988, *88*, 1327.
12. Note, that no proof for this hypothesis can be obtained from spectroscopic data. However, an complexative interaction of $BF_3 \cdot OEt_2$ with 2, which can not be excluded (although again no indication exists for this), could lead to a charge, instead of frontier orbital, controlled reaction.
13. Jödden,K. in *Methoden der Organischen Chemie*, Thieme, Stuttgart, New York, 1982, pp. 491.
14. Schmidpeter, A.; Zwaschka, F.; Sheldrick, W.S. *Chem. Ber.* 1985, *118*, 1078.