Table I

step		k_+, M^{-1} s^{-1}	k_-, M^{-1} s^{-1}	ref
1	$Br^- + BrO_3^- \rightleftharpoons HOBr + HBrO_2$	$2.1[H^+]^2$	10^5	8
2	$Br^- + HBrO_2 \rightleftharpoons 2HOBr$	$2 \times 10^9[H^+]$	5×10^{-5}	8
3	$HBrO_2 + BrO_3^- \rightleftharpoons 2BrO_2$	$1 \times 10^4[H^+]$	2×10^7	8
4	$BrO_2 + Ce^{3+} \rightleftharpoons HBrO_2 + Ce^{4+}$	$6.5 \times 10^5[H^+]$	2.4×10^7	8
5	$BrO_3^- + Ce^{3+} \rightleftharpoons BrO_2 + Ce^{4+}$	$1.3 \times 10^{-4}[H^+]$	9.1	8
6	$2HBrO_2 \rightleftharpoons BrO_3^- + HOBr$	4×10^8	$2.1 \times 10^{-10}[H^+]$	9
7	$HOBr + Br^- \rightarrow Br^-$	$6.55 \times 10^7[H^+][MA]$		10
8	$Ce^{4+} + RH \rightarrow Ce^{3+} + R\cdot$	1.0		8
9	$2R\cdot \rightarrow RH + ROH$	9.9×10^8		8
10	$ROH + BrO_3^- \rightarrow Br^-$	5.0		
11	$Ce^{4+} + ROH \rightarrow Ce^{3+}$	2.13		8

Table II. Comparison of the Measured and Simulated Period Times and SBPPs^a

[MA], M	[Ce^{4+}], M	time of one oscillation, s		SBPP, s	
		measured	simulated	measured	simulated
0.10	0.001	66	67.2	16	11
0.10	0.0005	66	65.5	18	14
0.20	0.001	48	46.2	7.5	7
0.50	0.001	31	37.1	3	4

^{a} [BrO$_3^-$] = 0.06 M; [H$_2$SO$_4$] = 1.0 M.

1.0 M H$_2$SO$_4$, 0.01 M ^{82}BrMA, 0.01 AgNO$_3$, and 0.002 M Ce^{4+}. Bromide ion produced during the BZ reaction was precipitated as AgBr. The reaction was allowed to proceed until all of the silver ion was converted to AgBr (about 10-15 min). The latter was separated by filtration, dissolved in a KCN solution, and diluted to a given volume. The activity of both this solution and that of the filtrate was measured on a well-type γ-scintillator.

If bromide is produced from BrMA then the AgBr should be active, if bromate is the source, either directly or undirectly, of bromide, then the AgBr should be inactive. Three parallels each of two runs gave the following results: 6.5% and 7.3%, respectively, of the total activity appeared in AgBr and 93.5% and 92.7%, respectively, was found in the filtrate.

We did not find bromine atom exchange between BrMA and bromate ion.

Our results clearly show that in reacting BZ systems the source of bromide ion is predominantly bromate ion. This recognition prompts us to modify the chemical mechanism. As shown below, we have bromide ion being generated in a reaction between bromate ion and an oxidation product of malonic acid (ROH). The stoichiometry thus obtained agrees with the most favorable stoichiometry ($f = 1$) of the Oregonator.

The reacting BZ system is simulated by the mechanistic steps and rate constants in Table I. The value of k_{10} proposed by us seems to be reasonable for a reaction between bromate ion and a loosened alcoholic hydroxyl group. The rate-determining step is the direct attack of bromate ion on HOCH<.[11] (We are aware of that there are other possible reaction routes for the regeneration of bromide ion. We shall analyze these in the forthcoming publication. In the computational studies we intend to use not only the "high" but also the "low" sets of rate constants.[12])

Data presented in Table II show that not only the experimental period time but also the slow bromide production period (SBPP) can be simulated. Figure 1 shows the simulated bromide concentration and redox potential vs. time curves.

Since in the proposed mechanistic model bromide ion is generated not in a reaction between M$^{(n+1)+}$ (e.g., Ce^{4+}) and an organic bromo compound, it seems to be applicable to BZ systems
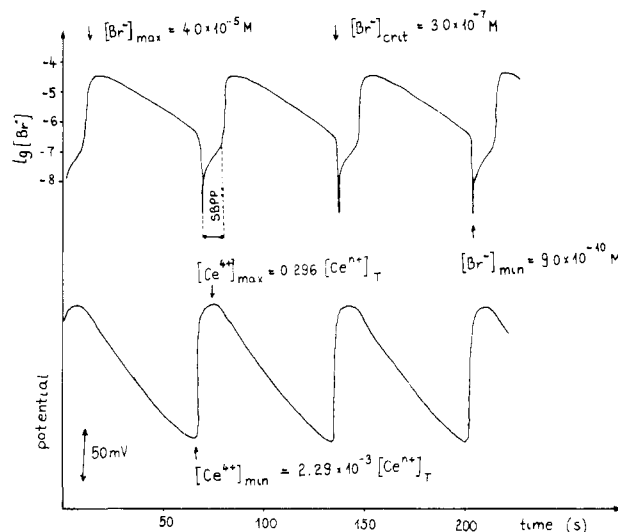

Figure 1. Simulation of the bromide concentration and redox potential vs. time curves by the modified chemical mechanism. The composition of the system: [BrO$_3^-$] = 0.06 M, [H$^+$] = 1.0 M, [MA] = 0.10 M, and [Ce^{4+}] = 0.001 M.

containing organic compounds other than malonic acid as well as for uncatalyzed bromate oscillators.

Synthesis of the First α-Diazo Phosphines. Phosphorus–Carbon Multiple-Bond Character of Phosphinocarbenes

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It is well established that aminonitrene,[1] sulfenylnitrene,[2] sulfinylnitrene,[3] and phosphinonitrene[4] can be regarded as diazene,

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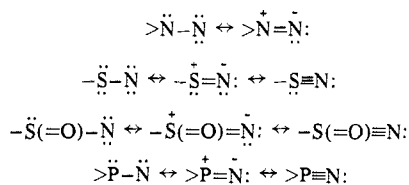(11) Adamcikova, L. Knappova, O. *Collect. Czech. Chem. Commun.* **1983**, *48*, 2335-2342.

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Communications to the Editor

thiazyne, oxathiazyne, and phosphonitrile, respectively, due to delocalization of the lone pairs

$$>\ddot{N}-\ddot{N} \leftrightarrow >\overset{+}{N}=\overset{-}{N}:$$

$$-\ddot{S}-\ddot{N} \leftrightarrow -\overset{+}{S}=\overset{-}{N}: \leftrightarrow -S\equiv N:$$

$$-\ddot{S}(=O)-\ddot{N} \leftrightarrow -\overset{+}{S}(=O)=\overset{-}{N}: \leftrightarrow -S(=O)\equiv N:$$

$$>\ddot{P}-\ddot{N} \leftrightarrow >\overset{+}{P}=\overset{-}{N}: \leftrightarrow >P\equiv N:$$

We wanted to find out if the generation of a carbenoid species next to a hereroatom, bearing both a lone pair and a vacant p or d orbital, is a general method for obtaining "triple-bonded-like" derivatives. It is reported here that λ^3-phosphinocarbenes, an entirely new type of carbene, behave as polarized λ^5-phosphaacetylenes.[5]

Diazo compounds are classical precursors of carbenes. However, although diazo-λ^5-phosphorus derivatives are well documented,[7] as far as we know, no examples of molecules possessing a diazo group bonded to a λ^3-phosphorus atom have been reported. This class of compounds, like phosphine azides, should be very unstable due to possible intermolecular reactions of the diazo moiety with the phosphorus lone pair.[8]
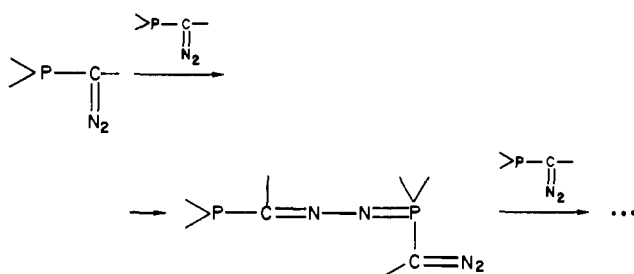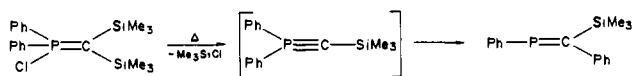

Taking into account the observed stability of phosphino azides,[4,9] we chose to prepare (trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane (1). Treatment of the lithium salt of

$$(R_2N)_2P\text{—}C(\equiv\!\!=\!\!N_2)\text{—}SiMe_3$$

1
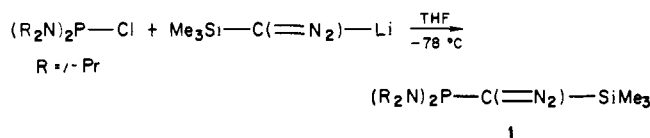
(trimethylsilyl)diazomethane[10] (26 mmol) with bis(diisopropyl-

amino)chlorophosphine[9f,11] (26 mmol) in 90 mL of THF at −78 °C produced, after workup, 1 in 85% yield. The red oily diazo compound **1** was stable enough to be purified by distillation: bp 85–90 °C (10⁻² mmHg); ³¹P NMR (C₆D₆) + 56 ppm; ¹H NMR (C₆D₆) δ 0.2 (s, 9 H, SiMe₃), 1.10 (d, J(HH) = 7 Hz, 12 H, CH₃C), 1.15 (d, J(HH) = 7 Hz, 12 H, CH₃C), 3.3 (m, 4 H, CH); IR (C₆H₆) 2010 (N₂); mass spectrum, m/e 344 (M⁺), 273 (M⁺ − i-Pr − N₂).

When a benzene solution of **1** was irradiated, at room temperature, at λ = 300 nm, for 8 h, in the presence of an excess of trimethylchlorosilane, dimethylamine, or dimethyl sulfoxide, release of nitrogen was observed and products **2**, **3**, or **4** were obtained in near quantitative yield.[12]
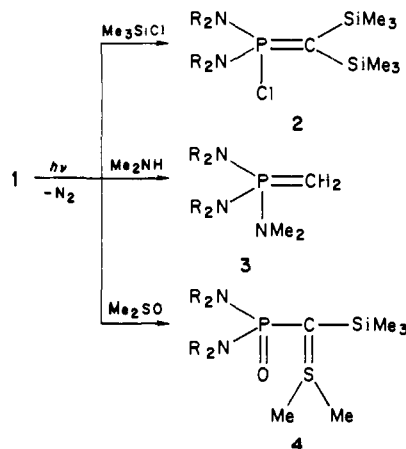
On the other hand (i) no trapping reactions occurred[13] in the presence of dimethylbutadiene, cyclohexene, or dimethylsulfur which are well-known to react with carbenes;[14] (ii) although α-silyl and α-phosphoryl diazo derivatives rearrange into reactive silaethylenes[15] and tricoordinated pentavalent phosphorus intermediates,[7] respectively, diazo phopshine **1** does not undergo 1,2-migration of a substituent from silicon or phosphorus to the carbene center.

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(12) **2**: ³¹P NMR (C₆H₆) δ +72.2; ¹H NMR (C₆D₆) δ 0.35 (S-like, 18 H, SiMe₃), 1.2 (d, J(HH) = 7 Hz, 24 H, CCH₃), 4.3 (sept-like, J(HH) = 7 Hz, 4 H, CH); mass spectrum, m/e 424 (M⁺). **3**: ³¹P NMR (C₆H₆) δ + 59.2; ¹H NMR (CDCl₃) δ 1.15 (d, J(HH) = 7 Hz, 24 H, CCH₃), 2.15 (d, J(PH) = 13 Hz, 2 H, CH₂), 2.65 (d, J(PH) = 10 Hz, 6 H, NMe₂), 3.50 (m, 4 H, CH); mass spectrum, m/e 289 (M⁺). **4**: mp 143–145 °C; ³¹P NMR (C₆D₆) δ +44.8; ¹H NMR (CDCl₃) δ 0.1 (s, 9 H, SiMe₃), 1.2 (d, J(HH) = 7 Hz, 12 H, CH₃C), 1.25 (d, J(HH) = 7 Hz, 12 H, CH₃C), 2.6 (s, 6 H, CH₃S), 3.8 (sept-d, J(HH) = 7, J(PH) = 7 Hz, 4 H, CH); IR (KBr) 1200 (P=O); mass spectrum, m/e 394 (M⁺). **8**: ³¹P NMR (CDCl₃) δ +33.2; ¹H NMR (CDCl₃) δ 1.2 (d, J(HH) = 7 Hz, 12 H, CCH₃), 1.3 (d, J(HH) = 7 Hz, 12 H, CCH₃), 1.5 (d, J(PH) = 15 Hz, 3 H, PCH₃), 3.5 (m, 4 H, CH); IR (neat) 1200 (P=O); mass spectrum, m/e 262 (M⁺). **10**: ³¹P NMR (C₆H₆) δ + 48.8; ¹H NMR (C₆D₆) δ 0.95 (d, J(HH) = 7 Hz), 12 H, CCH₃), 1.05 (d, J(HH) = 7 Hz, 12 H, CCH₃), 2.7 (d, J(PH) = 20 Hz, 1 H, CHN₂), 3.2 (m, 4 H, CH); IR (C₆H₆) 2030 (N₂); mass spectrum, m/e 272 (M⁺), 244 (M−N₂). **11**: mp 105 °C; ³¹P NMR (C₆H₆) δ +29.5; ¹H NMR (C₆D₆) δ 1.0 (d, J(HH) = 7 Hz, 12 H, CCH₃), 1.15 (d, J(HH) = 7 Hz, 12 H, CCH₃), 3.4 (sept-like, J(HH) = 7 Hz, 4 H, CH); mass spectrum, m/e 257 (M⁺).

(13) According to the ³¹P NMR, besides numerous products, a major species (δ³¹P)-41) was formed, in the absence of trapping agents or in the presence of dimethylbutadiene, cyclohexene, or dimethylsulfur. However, because of the extreme instability of this compound (may be the four-membered ring dimer of **5**), we have not been able to characterize it.

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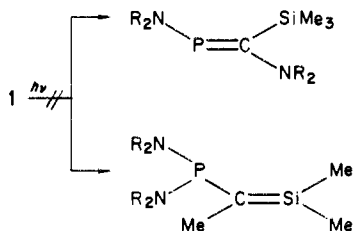
This lack of typical carbene reactivity and the nature of products **2**-**4** must be explained. The presence of an electron-rich phosphorus atom adjacent to an electron-deficient carbon suggests that delocalization of phosphine nonbonded electron pair would complete the octet of carbon and produce a dipolar species. Moreover, like phosphorus ylides, some back-bonding of the carbon electron with the phosphorus d orbital could also contribute to decrease the charge separation.

$$>\!\ddot{P}\!-\!\ddot{C}\!-\;\leftrightarrow\;>\!\overset{+}{P}\!=\!\ddot{C}\!-\;\leftrightarrow\;>\!P\!\equiv\!C\!-$$
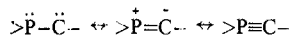
Thus, it is reasonable to postulate that λ^5-phosphorus compounds **2** and **3** result from 1,2-addition of the trapping agents to the phosphorus–carbon multiple bond of a "phosphorus vinyl ylide–phosphaacetylene" intermediate **5**.
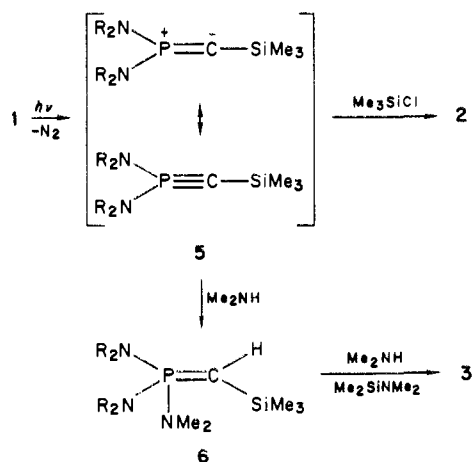

The subsequent cleavage of the carbon–silicon bond in **6** was confirmed by the action of dimethylamine on the phosphorus ylide **7**.[16]
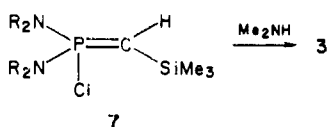
In the same way, mild hydrolysis of **2** led to the oxide of methylbis(diisopropylamino)phosphorane **8**.[12]
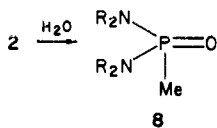

Formation of sulfur ylide **4** can be rationalized by a 2 + 2 cycloaddition leading to a four-membered cyclic phosphorus ylide **9** followed by ring opening.[17]
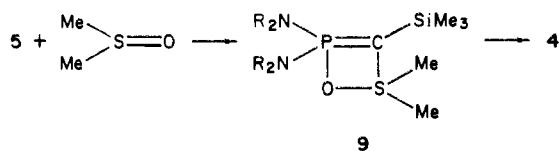
The choice of the trapping agents was limited by the lack of reactivity of **5** with nonpolar reagents and by the great lability of the silicon–carbon bond in the starting material **1**. Indeed a stoichiometric amount of water or methanol readily gives rise to the formation of a new diazo product **10** in 90% yield.[12]
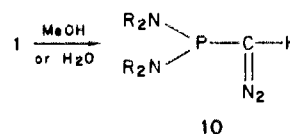
In marked contrast with **1**, [bis(diisopropylamino)phosphino]diazomethane (**10**) is thermally unstable and rearranged under attempted distillation to give the unexpected bis(diisopropylamino)phosphinenitrile **11**[12] in 30% yield, most probably via an intermolecular reaction.
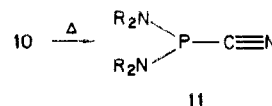
New Chromia Pillared Clay Catalysts

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Pillared clays are members of the smectite family of 2:1 layered silicates in which the gallery cations are robust species capable of preventing the collapse of the interlayer region upon dehydration. These intercalation compounds allow a rational approach to the design of new families of microporous solids because the pores formed between the gallery cations can be systematically regulated by varying the cation size, shape, and spacing. Several types of cations have been used as pillaring agents, including alkylammonium ions,[1-3] metal chelates,[4-6] and polyoxymetal cations.[7-13] Clays pillared by certain polyoxycations are of particular importance, because they can be converted upon dehydration and dehydroxylation to intercalates containing molecular-size oxide aggregates and protons which impart catalytically

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