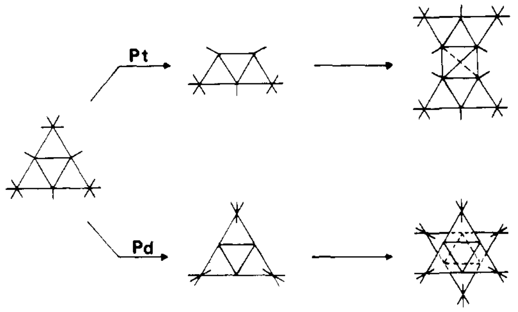
Scheme I



$[Fe_3Pt_3(CO)_{15}]^-$ clusters have been found to be isostructural, and an ORTEP view of the latter is shown in Figure 1. In both cases the structure is based on an equilateral triangle of platinum atoms which is bridged on each edge by an $Fe(CO)_4$ group. The overall idealized symmetry may be assumed to be D_{3h}. However, in both compounds the six metal atoms are not exactly coplanar, owing to a tilting of the $Fe(CO)_4$ groups above or below the triplatinum plane, with out-of-plane displacements ranging from 0.1 to 0.6 Å.[7]

A comparison among the individual molecular parameters of $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_3Pt_3(CO)_{15}]^-$ (Table I) shows in the latter a significant shortening (0.1 Å) of the average Pt–Pt bond, which suggests that the highest occupied molecular orbital involves primarily platinum atomic orbitals and is antibonding with respect to the Pt_3 triangle.[8] This unprecedented metallic array may seem unexpected for an 86 valence electron cluster such as $[Fe_3Pt_3(CO)_{15}]^{2-}$[9] and probably results from the tendency to planar coordination of platinum and the higher ligand requirement of iron. When considering the $Fe(CO)_4$ group as a bulky analogue of an edge-bridging carbonyl group, the $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion may be reformulated as $\{Pt_3(CO)_3[\mu\text{-}Fe(CO)_4]_3\}^{2-}$ and viewed as a stabilized analogue of $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$.[2] The existence of a paramagnetic species such as $\{Pt_3(CO)_3[\mu\text{-}Fe(CO)_4]_3\}^-$ may be then ascribed to the presence of axial carbonyls, which hinders dimerization along the pseudo-C_3 axis to give a species formally corresponding to $[Pt_6(CO)_{12}]^{2-}$.[2]

The decanuclear $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion presents a structure of overall idealized D_{2d} symmetry (Figure 2), which is strictly related to that of $[Fe_3Pt_3(CO)_{15}]^-$ and $[Fe_3Pt_3(CO)_{15}]^{2-}$ and may be thought to derive from the former by loss of an $Fe(CO)_4$ group and orthogonal condensation along the pseudo-C_2 axis of two resulting trapezoidal $[Fe_2Pt_3(CO)_{11}]^-$ units to give rise to a tetrahedral core of platinum atoms,[11] such as indicated in Scheme I.

Scheme I suggests also a possible mechanism of formation for the previously reported $[Fe_6Pd_6(CO)_{24}]^{4-}$ and $[Fe_6Pd_6(CO)_{24}H]^{3-}$[1] and accounts for the nonexistence of Fe–Pd species analogous to the Fe–Pt clusters reported here. Thus, a hypothetical $[Fe_3Pd_3(CO)_{15}]^{2-}$ species, analogous to $[Fe_3Pt_3(CO)_{15}]^{2-}$, would loose easily the three terminal carbonyl groups bonded to the palladium atoms, owing to the well-known reluctance of palladium to bind carbon monoxide.[2,12] Once the steric limit has been removed, two of the resulting unsaturated $[Fe_3Pd_3(CO)_{12}]^{2-}$ units may condense along the C_3 axis in a staggered conformation to give the structure found in the $[Fe_6Pd_6(CO)_{24}H]^{3-}$ trianion.[13]

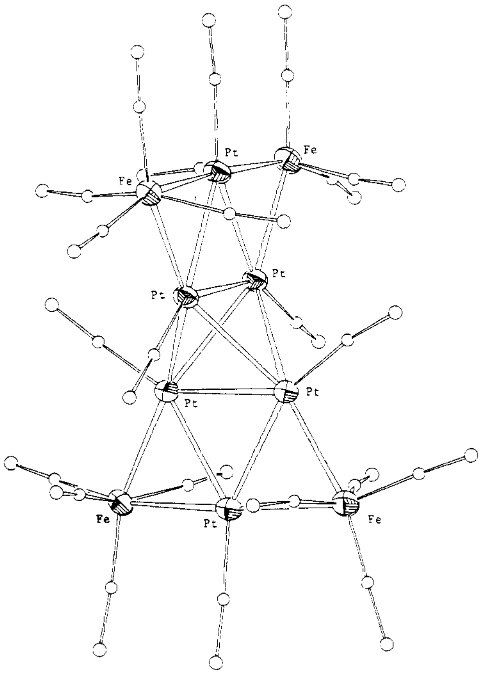


Figure 2. ORTEP view of the $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion.

Acknowledgment. We acknowledge the late Professor P. Chini, whose interest and helpful suggestions have been a continuous stimulus for carrying out this work.

Supplementary Material Available: Listings of the thermal and positional parameters of $[N(C_4H_9)_4]_2[Fe_3Pt_3(CO)_{15}]$ (Table II), $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$ (Table III), and $[N(CH_3)_3CH_2Ph]_2[Fe_4Pt_6(CO)_{22}]$ (Table IV) (6 pages). Ordering information is given on any current masthead page.

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Evidence against Phosphacylium Cation Participation in Nucleophilic Displacement at Tetracoordinated Phosphorus

Sir:

Information concerning the mechanistic aspects of organophosphorus chemistry has during its development been subject to interpretation based on analogy to hydrocarbon mechanisms. This can be especially noted in the chemistry of carboxylic acid esters and phosphoric acid esters. That carboxylates can undergo nucleophilic displacement via a tetrahedral intermediate was supported by the synthesis of orthoformates and orthocarbonates.[1]

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(5) Crystal data follow. $[N(C_4H_9)_4]_2[Fe_3Pt_3(CO)_{15}]$: $M_r = 1657.9$; monoclinic; space group $P2_1/c$; $a = 14.24$ (1), $b = 19.18$ (2), $c = 22.41$ (2) Å; $\beta = 96.4$ (1)°; $V = 6082$ Å^3; $D_c = 1.81$ g/cm^3 for $Z = 4$. The current R for 3042 independent reflections having $I \geq 3\sigma(I)$ is 0.052. $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$: $M_r = 1323.1$; triclinic; space group $P\bar{1}$ (after refinement); $a = 17.327$ (6), $b = 10.722$ (4), $c = 18.854$ (6) Å; $\alpha = 96.25$ (3), $\beta = 90.37$ (3), $\gamma = 93.99$ (4)°; $V = 3473$ Å^3; $D_c = 2.53$ g/cm^3 for $Z = 4$. The current R for 4614 independent reflections having $\sigma(I) \leq 0.30I$ is 0.046. $[N(CH_3)_3CH_2Ph]_2[Fe_4Pt_6(CO)_{22}]$: $M_r = 2310.6$; monoclinic; space group C_c (after refinement); $a = 13.228$ (4), $b = 42.022$ (13), $c = 12.896$ (6) Å; $\beta = 124.68$ (3)°; $V = 5895$ Å^3; $D_c = 2.60$ g/cm^3 for $Z = 4$. The current R for 3394 independent reflections having $I \geq 3\sigma(I)$ is 0.046. Intensity data were collected on a BASIC diffractometer with graphite-monochromatized Mo Kα radiation up to $2\theta = 50°$ and corrected for absorption by the numerical integration method. The structures have been solved by standard Patterson and Fourier methods and refined by block-matrix least squares to the current R's.

(6) For distances and bond angles see supplementary material.

(7) The freedom of the $Fe(CO)_4$ groups is well documented by the two independent molecules found in the unit cell of $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$, which show different out-of-plane displacements of the iron atoms, although all the other individual molecular parameters are strictly equivalent.

(8) Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032–41.

(9) With the exception of $[Pt_6(CO)_{12}]^{2-}$, all the other 86 valence electron hexanuclear carbonyl clusters present an octahedral metal skeleton.[10]

(10) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285–344.

(11) The idealized symmetry of the Pt_4 core is D_{2d} (see Table I).

(12) Nyholm, R. S. *Proc. Chem. Soc. London* **1961**, 273.

(13) In Scheme I the carbonyl groups bridging the Fe–Pd interlayer bonds and the $FePd_2$ triangular faces found in $[Fe_6Pd_6(CO)_{12}(\mu\text{-}CO)_6(\mu_3\text{-}CO)_6H]^{3-}$ are arbitrarily assigned only to the iron atoms for the sake of clarity.

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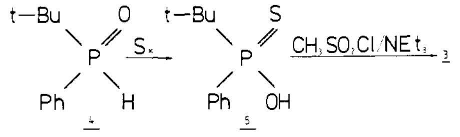
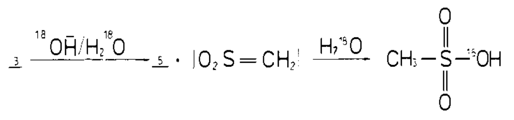
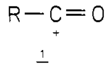
Scheme I



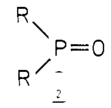
Scheme II



In a similar fashion the intervention of a five-coordinate intermediate during nucleophilic displacement of a phosphate ester was supported by the synthesis of pentaoxyphosphoranes.[2] Carboxylic acid esters can also undergo nucleophilic displacement via a dissociative mechanism involving intermediacy of an acylium cation[3] **1**; thus the analogous "phosphacylium" cation **2** is still a subject of search.



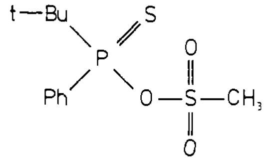
1



2

The participation of the phosphacylium cation during nucleophilic substitution at four-coordinate phosphorus is a problem that has been undertaken by only a few investigators.[4-11] The probability of formation of such an intermediate through a dissociative mechanism has usually been regarded to be very low. Only Haake et al. found evidence for its participation in the hydrolysis of chlorophosphinates[8] and phosphinamides.[9]

During the past few years we have investigated the synthesis and stereochemistry of mixed phosphorus–sulfonic anhydrides, and some of our results involve the problem under discussion. The mixed anhydride **3** seemed to us ideally suited for this investigation.



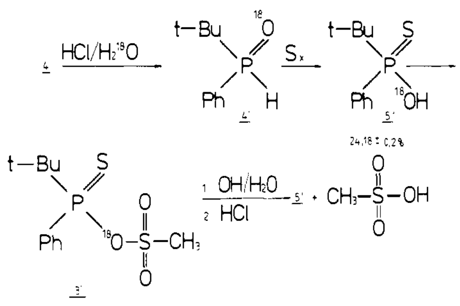
3

Leaving-group characteristics, electronic effects, and steric effects should promote the involvement of a dissociative mechanism during nucleophilic displacement at the tetracoordinate phosphorus center. The synthesis of **3** is shown in Scheme I. We have worked out conditions in which only the phosphorus atom of **3** is attacked by the nucleophilic reagent and in which the sulfonyl group is the center of attack.

The alkaline hydrolysis of **3** can be considered a β-elimination reaction involving the formation of a sulfene intermediate.[12] Only the S–O bond is cleaved, leaving the P–O bond intact. This conclusion is supported by the data obtained when this reaction was carried out in $H_2{}^{18}O$, unambiguously showing the absence of ^{18}O incorporation in the thiophosphoric acid product **5** (Scheme II).

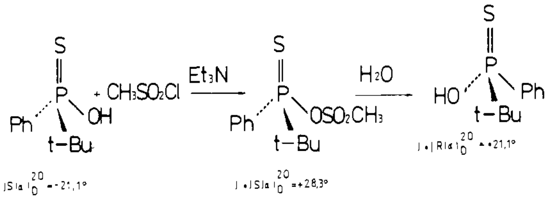
The same reaction was carried out with ^{18}O incorporated into the substrate **3**, as shown in Scheme III. Isotopic enrichment in this case was observed to remain exclusively on the phosphorus product while the isolated methanesulfonic acid showed no significant enrichment above natural-abundance ^{18}O. A small decrease in ^{18}O enrichment occurs during the neutralization of the sodium salt of the thioacid with HCl in its isolation.

Scheme III[a]

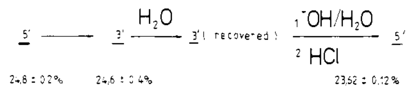


[a] ^{18}O enrichment shown below the formulas.

Scheme IV



Scheme V



When optically active **3** is used (obtained from the resolution of racemic **5** by α-phenylethylamine and the subsequent reaction of optically pure **5** with methanesulfonyl chloride–triethylamine), complete retention of configuration is observed in the product **5**. In contrast, under conditions of spontaneous hydrolysis in 2:8 acetone–water (v/v) complete inversion of configuration is observed in the product **5** (Scheme IV). The fact that the absolute value of the optical rotation remains unchanged (only the sign changed) confirms the high optical purity of the starting anhydride **3** and is a new example of Walden inversion in phosphorus chemistry.

The ^{18}O-labeled anhydride **3'** was subjected to the same reaction conditions in an attempt to observe scrambling of the isotope and hence gather evidence for the participation of a dissociative mechanism. After 50% of the substrate **3'** reacted, the substrate was separated from products by column chromatography. The recovered substrate was treated in a similar fashion as **3'** in Scheme III with identical results, that is, almost identical ^{18}O enrichment in the isolated acid as in substrate **3'** used initially for the hydrolysis experiment (Scheme V). If an ion pair is involved during the reaction, even as an intimate ion pair, it can be assumed that the position of ^{18}O should equilibrate among the three oxygens of the anion. Since this is not observed, it is believed the solvolysis of the anhydride **3** under conditions of spontaneous hydrolysis involves a concerted mechanism involving nucleophilic attack at phosphorus.

This result is even more remarkable considering that kinetic studies indicate a large sensitivity of the hydrolysis of **3** on the ionizing power *Y* of the solvent[13] [*m* (Grunwald–Winstein constant) = 0.86]. Thus the mechanistic criteria used in carbon chemistry are not fulfilled in the chemistry of tetracoordinated phosphorus.

It seems likely that the transition state in the hydrolysis of **3** is relatively polar but that the phosphacylium cation **2** is certainly not an intermediate even under the favorable conditions for its formation presented here.

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Dissociation of the Ethylene Cation: Mechanism of Energy Randomization

Sir:

We wish to discuss the validity of statistical theories of unimolecular dissociation under conditions which correspond to photochemical excitation at very low pressures. We have determined[1] by ab initio calculations the reaction paths of the ethylene cation for its two low-energy dissociations (reactions 1 and 2).

$$C_2H_4^+ \rightarrow C_2H_3^+ + H \qquad (AP = 13.22\ eV)^2 \qquad (1)$$

$$C_2H_4^+ \rightarrow C_2H_2^+ + H_2 \qquad (AP = 13.14\ eV)^2 \qquad (2)$$

Since the threshold energies[2] of these two reactions fall within the second band of the photoelectron spectrum of ethylene, we investigated in detail the dissociation mechanisms of the ground ($\tilde{X}\ ^2B_{3u}$) and first excited ($\tilde{A}\ ^2B_{3g}$) states of $C_2H_4^+$. (Higher electronic states were shown[1] to undergo facile radiationless conversion to the ground state by internal rotation.)

Calculations were done with a simple Dunning (3s2p) GTO basis set either at the open-shell SCF level or with intermediate configuration[3] MOs and a relatively small CI (200–500 CSF). Point calculations were done for the most important structures with and without polarization functions ($3d_c$ and $2p_H$) added to the AO basis set and with larger CI matrices ($\simeq$2500 CSF). Results are given in Figure 1. Details of the calculation will be published elsewhere.[1]

The reaction path of process 2 was found to consist of a sequence of several steps connected by several bottlenecks. Some of these steps are adiabatic and therefore can be studied by conventional statistical theory (RRKM[4,5] or QET[6]). Others involve nonadiabatic interaction and thus require an extension of these theories.

What we wish to point out here is that the presence of all these bottlenecks compels the system to fulfill various requirements and hence compels it to visit a large fraction of phase space. Therefore, the more complicated the reaction path, the more likely it is for a statistical theory to be valid.

Consider (Figure 1) the fate of a molecular ion created in the $\tilde{A}\ ^2B_{3g}$ state with an energy higher than 13.22 eV. Initially, the Franck–Condon principle allows the ion to receive energy in three vibrational modes:[7] ν_1 (sym CH stretch), ν_2 (CC stretch), and ν_3 (CH_2 scis). The potential-energy surfaces are such that high barriers exist in every direction except along the stretching motion of a single CH bond. This corresponds to the excitation of a *local* CH stretching mode, i.e., a linear combination of *four* CH normal modes: ν_1, ν_5, ν_9, and ν_{11}. Production of $C_2H_3^+$ fragments is thus accounted for. However, the potential-energy surface of the $\tilde{A}\ ^2A'$ state is crossed (at point C of Figure 1) by that of the ground state ($\tilde{X}\ ^2A''$ for these nuclear configurations) which correlates with a higher asymptote. Thus, at the crossing point C, the system has to decide between heading toward the asymptote of channel 1 or cascading to the ground state $\tilde{X}$. The crossing point C is in fact a conical intersection[8] and the competition is controlled by the amount of internal energy which goes into internal torsion. The larger the angle of twist, the more likely the internal conversion to the ground state, as shown by our calculations of the nonadiabatic coupling matrix element.[1] Hence, energy must flow into the torsional vibration ν_4 for reaction 2 to proceed. We find that energy barriers prevent direct dissociation of ground state $\tilde{X}$ in its usual $CH_2CH_2^+$ conformation according to reaction 2, either by 1,2 or by 1,1 elimination. Its only possibility is to undergo a hydrogen shift (via a hydrogen-bridged structure already considered[9] by Dewar and Rzepa) and to isomerize to the ethylidene structure CH_3CH^+ (^2E state in the C_{3v} point group). This requires excitation of CH bending modes (ν_3, ν_6, ν_{10}, and ν_{12}). In order to proceed further and give rise to reaction 2 by 1,1 hydrogen elimination, the system must leave the $^2A''$ state and switch to the $^2A'$ surface. This is possible if doubly degenerate skeletal vibrations of the CH_3CH^+ structure are excited, because in the degenerate ^2E state the system experiences nonadiabatic interaction (Jahn–Teller effect). Finally, our calculations indicate the presence of a very low ($\simeq$0.13 eV) energy barrier for the last step (at point M of Figure 1), but it was also observed that the more accurate the calculations, the smaller the barrier. Hence, the barrier might very well not exist at all.

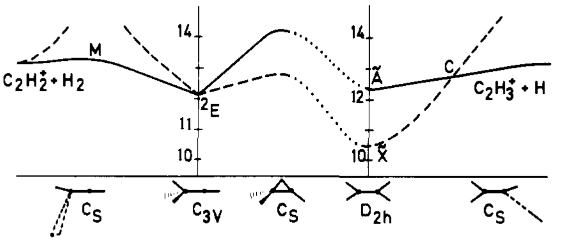

Figure 1. Folding-screen representation of the reaction paths of $C_2H_4^+$. Solid lines, $^2A'$ states; dashed lines, $^2A''$ states; dotted lines, no symmetry at all. Energy scale in eV.

In summary, we see that experimentally observed reactions in $C_2H_4^+$ can occur only if energy is redistributed among many molecular normal modes. Something approaching energy randomization comes about naturally, first, as a result of the multistep nature of the reaction path, and secondly as a result of the presence of nonadiabatic processes. The latter factor is particularly interesting and reveals novel aspects on the problem of intramolecular energy transfer. Dissociation of the ethylene cation should be amenable to statistical treatment.

Reactions 1 and 2 have previously been studied by the quasi-equilibrium theory of mass spectra[6] with some success.[10] However, this theory usually assumes fast electronic relaxation to the ground state. This is indeed the case for the upper electronic states $\tilde{B}$ and $\tilde{C}$ as a result of internal rotation[1] but not for state $\tilde{A}$, because the conical intersection between states $\tilde{X}$ and $\tilde{A}$ (point C of Figure 1) acts like a railway switch: electronic relaxation and dissociation take place with comparable rates. Therefore, the success of these calculations must be considered as somewhat fortuitous.

The present discussion of energy randomization raises a number of questions which deserve further consideration.

(1) How general is our explanation? Detailed calculations of

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