

Theoretical Prediction of the Stereochemistry and Regiochemistry in Anionic Addition to Phospha-ethyne

Minh Tho Nguyen

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

The regiochemistry of anionic addition to phospha-ethyne is shown, using MO calculations, to be dependent on the nature of the nucleophile, the hydride ion leading to initial C-attack whereas the fluoride ion prefers P-addition; the latter is predicted to be stereospecific irrespective of the nucleophilic agent.

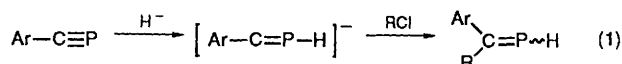
Arif and co-workers¹ studied the nucleophilic addition to aromatic phospha-ethynes in which an anion (H^- or CH_3^-) acts as the nucleophilic agent. Such a process appears to yield a carbanion intermediate which reacts further with RCl producing a phospha-alkene (equation 1). This experimental

result suggests an initial nucleophilic attack at the phosphorus end of the phospha-ethyne. However, the large steric effects in $\text{Ar-C}\equiv\text{P}$ might strongly influence the mode of addition; the stereochemical course of reaction (1) was not established.¹ In this work, we attempt to address both the regiochemistry and

Table 1. Relative energies (kcal mol⁻¹; cal = 4.184 J) of stationary points on the (H₂CP)⁻ energy surface calculated at different levels of theory.^a

Method	Basis set	HCP + H ⁻	(1) (Z)	(2) (E)	(3) (TS1)	(4) (C-adduct)	(5) (TS2)
HF	6-31++G**	0.0	-37.8	-39.9	-18.7	-60.4	9.3
MP4 ^b	6-31++G**	0.0	-32.3	-34.7	-13.6	-55.9	19.0
HF	6-311++G**	0.0	-38.5	-40.5	-19.5	-59.5	8.5
MP4SDQ	6-311++G**	0.0	-36.2	-38.3	-17.6	-56.7	14.1
ZPE ^c	6-31++G**	8.6	11.7	12.1	10.9	14.0	9.7
Estimated ^d		0.0	-31.4	-33.2	-13.7	-49.4	17.9

^a Employing HF/6-31++G** geometries given in Figure 1. ^b Including single, double, triple, and quadruple excitations. The core orbitals are frozen in MP n calculations. ^c Zero-point energies in kcal mol⁻¹ obtained from HF/6-31++G** vibrational frequencies and scaled by 0.9. ^d Estimated values including the MP4SDQ/6-311++G** energies corrected for triple-substitutions (from MP4/6-31++G**) and ZPE contributions.



the stereochemistry of the anionic 1,2-addition to phosphacetyne by means of *ab initio* MO theory.² As a simple model, we have considered the H⁻ + HC≡P and F⁻ + HC≡P reactions.

Let us first consider the H⁻ + HCP system. Of the two isomeric forms of the *P*-adduct (HC=PH⁻, Figure 1), the *E*-form (2) is calculated to be 1.8 kcal mol⁻¹ lower in energy than the *Z*-form (1) (Table 1). Both isomers are connected by the transition structure for inversion at carbon (3) (TS1). The corresponding barrier to inversion amounts to 17.7 kcal mol⁻¹ [from (1)]. The *C*-adduct (4) is found to lie 16.2 kcal mol⁻¹ below the *E*-form (2), thus being the most stable structure of the H₂CP⁻ energy surface considered (Table 1). Note that the isoelectronic HN=PH species was calculated to be about 6 and 12 kcal mol⁻¹ more stable than the triplet and singlet aminophosphinidene (H₂NP), respectively.³ Thus, regarding the anion (4) as a phosphinidene substituted by the H₂C⁻ group, a strong delocalization of the negative charge onto the vacant 3p orbital of P markedly stabilizes the singlet phosphinidene (4). Separate calculations on the CH₃⁻ + HC≡P system also show a similar energy ordering with the *C*-adduct (CH₃CH=P⁻) being more stable than the *P*-adduct (HC=PCH₃⁻) by 20 kcal mol⁻¹ at the HF/6-31++G** level.

Calculations using correlated wavefunctions show that the additions of H⁻ to both C and P of HCP are the barrier-free processes. As a consequence, the regiochemistry of the anionic addition could be determined by the relative stability of both adducts. Thus, there is a thermodynamic driving force favouring the *C*-addition forming the more stable intermediate (4). At this point, it is important to examine the interconversion between the two anionic adducts. Our calculations predict an energy barrier of 51.1 kcal mol⁻¹ (Table 1) for the HC=PH⁻ (2) → H₂C=P⁻ (4) rearrangement *via* the transition structure for 1,2-hydrogen shift (5) (TS2, Figure 1). Such a barrier height is large enough to prevent any unimolecular interconversion between both isomeric structures. In this context, the exclusive addition of H⁻ to P observed by Arif *et al.*¹ is likely to arise from a large steric effect manifested by the bulky substituents present either in the reactant (Ar-C≡P) or in the nucleophilic agent (LiHBEt₃).

With regard to the *P*-addition, although no transition structure can be located, extensive exploration on the HC=PH⁻ energy surface (at the HF/6-31++G** level) shows that the *cis*-addition (A) [yielding the *Z*-ion (1)] is favoured over the *trans*-addition (B) [giving the *E*-ion (2)]. For

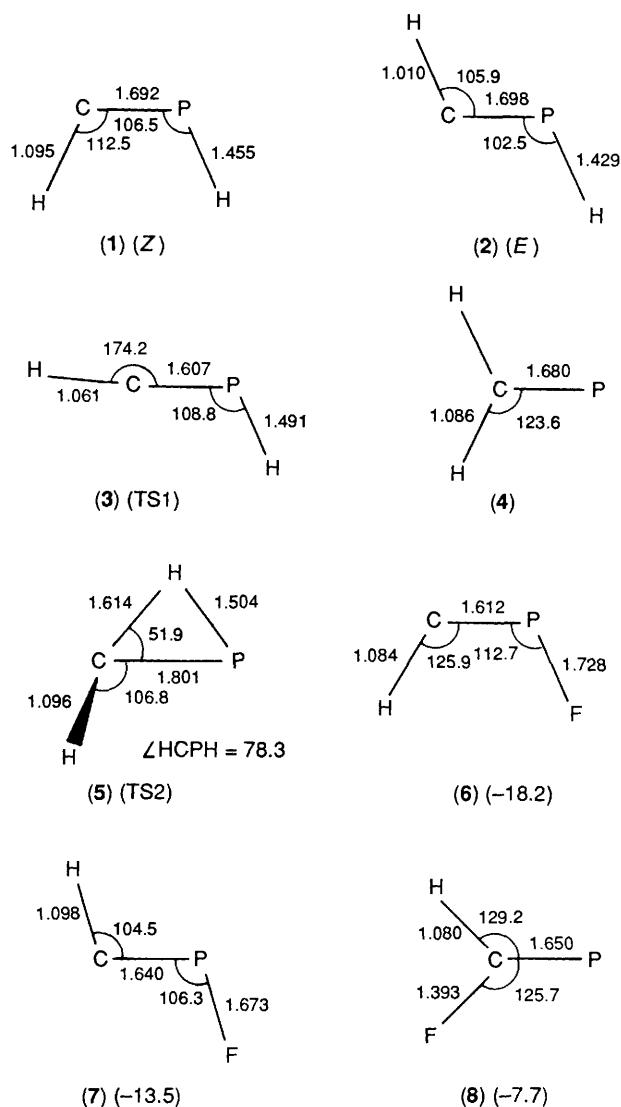
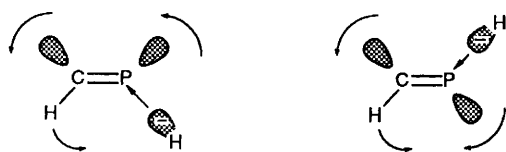


Figure 1. Structures were located and characterized (by harmonic vibrational wavenumbers) at the Hartree-Fock level with the 6-31++G** basis set. Bond lengths are given in Å and bond angles in degrees. For the (H₂CP)⁻ system: (1), (2), and (4) are minima while (3) and (5) are transition structures. Geometry of HCP is: CH 1.06 and CP 1.516 Å. For the (HCFP)⁻ system: (6), (7), and (8) are minima. For the latter, in parentheses are the relative energies, i kcal/mol with respect to the separated F⁻ + HCl species, obtained from single-point calculations at the MP2/6-311++G** + ZPE level.

(A) *cis* - addition(B) *trans* - addition

instance, even at large $P \cdots H$ distances ($\geq 2.5 \text{ \AA}$), the approach of H^- to P induces a strong bending of the HCP moiety ($\angle HCP \sim 120^\circ$) and the $(HCPH^-)$ supersystem goes downhill to the *Z*-form (A). The corresponding *E*-form (B) is found to be *repulsive* with respect to the separated $H^- + HCP$ system in that region of the potential energy surface. Because the *Z*-*E* isomerization is not quite a facile process (see above), the less stable *Z*-form of the anionic adduct, once formed, may undergo further reactions (for example, protonation yielding a *Z*-phospha-alkene). In other words, the *anionic addition to phospho-ethyne is predicted to be stereospecific* (or at least strongly stereoselective). Such a behaviour can be rationalized in terms of a concerted motion of electron pairs in the same direction as illustrated in (A) and (B).⁴

We now turn to the $F^- + HCP$ system [Figure 1, structures (6), (7), and (8)]. The fluorine atom exerts a dramatic effect

on the relative stability between isomeric anions. The *Z*-form (6) turns out to be the most stable of the three minima located, the *C*-adduct (8) being the least stable form. Additions of F^- to both C and P of HCP are again barrier-free. Therefore, when the fluoride anion is employed as the nucleophilic agent, the *cis*-addition to phosphorus of phospho-ethyne is overall preferred and becomes the predominating mode of addition. In this case, the anionic addition is both regioselective and stereospecific.

The author is a Research Associate of the National Fund for Scientific Research, Belgium.

Received, 11th December 1989; Com. 9/05267D

References

- 1 A. M. Arif, A. R. Barron, A. H. Cowley, and S. W. Hall, *J. Chem. Soc., Chem. Commun.*, 1988, 171.
- 2 J. S. Binkley, R. A. Whiteside, K. Raghavachari, D. J. DeFrees, H. B. Schlegel, M. J. Frisch, E. M. Fluder, and J. A. Pople, Gaussian-82, Carnegie-Mellon University, 1983.
- 3 K. Ito and S. Nagase, *Chem. Phys. Lett.*, 1986, **126**, 531.
- 4 M. T. Nguyen, A. F. Hegarty, M. Sana, and G. Leroy, *J. Am. Chem. Soc.*, 1985, **107**, 4141.