Reaction of phosphaacetylenes Bu^{t}C≡P and 1-AdC≡P with $(PhSe)_2$–XeF_2: first examples of vicinal bis-selenenylation (at P and C) to form novel phosphaalkenes

Kenneth K. Laali,*[a] Wolfgang Fiedler[a,b] and Manfred Regitz[b]

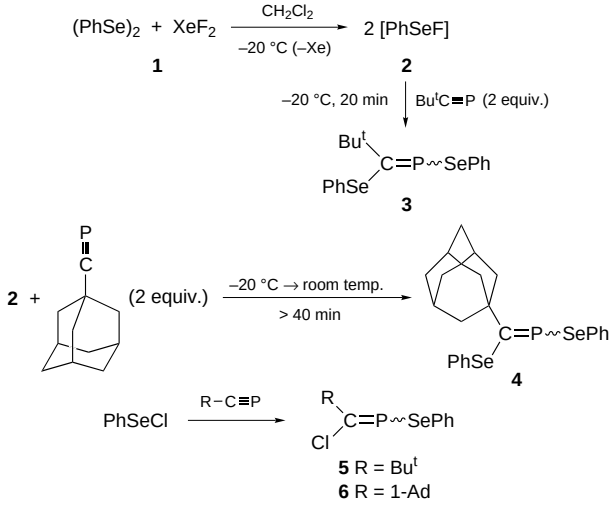
[a] *Department of Chemistry, Kent State University, Kent, OH 44242, USA*
[b] *Fachberich Chemie, Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Germany*

***tert*-Butyl- and 1-adamantyl-phosphaacetylenes (2 equiv.) react with $(PhSe)_2$–XeF_2 (→ 2 PhSeF) to give novel phosphaalkenes by vicinal bis-phenylselenenylation (at P and C), in contrast to acetylenes which undergo fluoroselenenylation.**

Whereas PhSeCl and PhSeBr are commercially available sources of selenenic electrophiles, PhSeF is too labile to be isolated. It was recently reported[1] that the system $(PhSe)_2$–XeF_2 **1** acts as an *in situ* source of PhSeF **2**, whose reaction with selected alkenes led to fluoroselenenylation (predominantly *E* alkenes). Subsequently, **1** was shown to be an efficient vicinal fluoroselenenylation reagent for alkynes.[2,3] The preferred *E* configuration of the alkene product (*trans* stereochemistry) may be traced to the intermediacy of the phenylselenirenium cation, a stable salt of which has been characterized.[4] In addition to **1**, PhSeBr·AgF in CH_2Cl_2 under sonication and PhSeCl·AgF in MeCN also serve as *in situ* sources of PhSeF for fluoroselenenylation of alkenes, alkynes and α-diazo ketones (α-diazo esters).[5]

In relation to our previous and ongoing studies of electrophilic chemistry of phosphaalkynes, ionization of phosphirenes (→ phosphirenylium cation) and electrophilic reactivity of the tetraphosphacubane skeleton,[6–9] we became interested in possible fluoroselenenylation of RC≡P, anticipating that, based on previous results on addition of protic and Lewis superacids,[6] 'PhSe$^+$' would attack at the P≡C carbon.

Under the conditions where **2** is expected to be present *via* system **1**,[2,3] Bu^{t}CP (2 equiv.) was added to the reaction mixture under argon in dry CH_2Cl_2 at −20 °C (rapid Xe loss) (Scheme 1); ^{31}P NMR monitoring of the reaction mixture indicated that following 20 min at −20 °C, only traces of Bu^{t}CP remained unreacted. The solvent was removed *in vacuo* (room temp.), the residue was taken up in $CDCl_3$ and subjected to multinuclear NMR analysis (Fig. 1). The major product (> 90% based on ^{31}P NMR integral ratios)† gives rise to a phosphorus resonance at δ 351.9 with a one-bond P/Se coupling of 319.1 Hz and a two-



Scheme 1

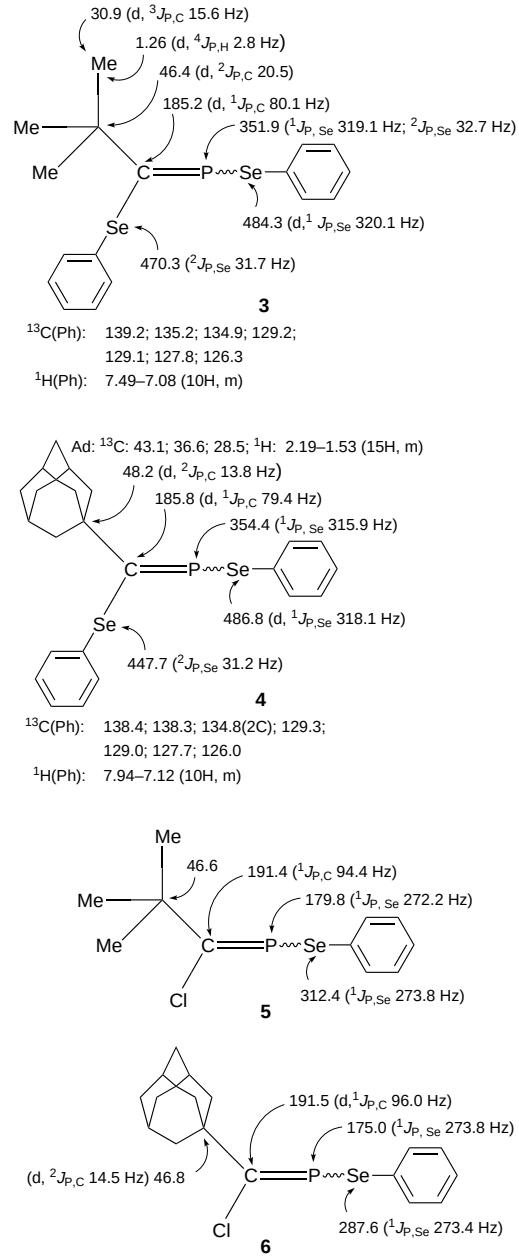


Fig. 1 Multinuclear NMR data for **3**, **4**, **5** and **6**

bond P/Se coupling of 32.7 Hz. In the ^{77}Se NMR spectrum, there are two resonances (1 : 1 ratio), one for the P–SePh moiety at δ 484.3 (one-bond P/Se coupling 320 Hz) and the other for C–SePh at δ 470.3 with a two-bond P/Se coupling of 31.7 Hz, supporting vicinal bis-selenenylation (→ **3**). Presence of an intact C=P moiety is apparant in the ^{13}C NMR spectrum *via* a distinct doublet at δ 185.2 with a one-bond P/C coupling of 80.1 Hz typical of phosphaalkenes.[10] Both *tert*-butyl carbon resonances (at δ 46.4 and 30.9) appear as doublets due to phosphorus coupling. The SePh ring carbon resonances give rise to eight resonances between δ 139.2–126.3.

Phosphaalkene **3** has a limited life-time at room temp., and prolonged reaction times gave a complex mixture, as did attempted isolation. Additional proof of the structure came from the EI-MS spectrum of a freshly prepared sample, showing the M^+ at *m/z* 412 with the appropriate isotope pattern for two Se atoms.

Attempted Se-ethylation with one and two equivalents of EtOTf, to selectively form the derived mono- and di-selenonium cation salts,[3,11] led to complex mixtures (^{31}P NMR), probably by competing C=P ethylation.

Reaction of system **1** with the more sterically crowded 1-AdC≡P was slower. After the initial addition at −20 °C, the reaction was allowed to warm to room temperature under stirring. Following an additional 40 min stirring at room temp., **4** was formed (*ca*. 75% based on ^{31}P NMR integrals; with *ca*. 25% of 1-AdC≡P remaining unreacted). Multinuclear NMR data on **4** (Fig. 1) fully agree with the suggested structure. The more shielded nature of the selenium centre (at C) in the more sterically crowded **4** as compared to **3** is noteworthy.

In the absence of XeF_2, vicinal bis-phenylselenenylation still occurs, albeit at a much slower rate. Thus $(PhSe)_2$ reacted slowly with Bu^{t}C≡P (1 equiv.) in dry CH_2Cl_2: ^{31}P NMR monitoring showed that the initial product is **3**, but its slow formation and increase over time is accompanied by extensive decomposition at room temp. Similar observations were made in experiments where only *ca.* 0.1 equiv. of XeF_2 was used. Thus although fluoroselenenylation is not the final outcome, the presence of 1 equiv. of XeF_2 is needed. The presence of 2 equiv. of RC≡P is also required, since addition of 1 equiv. of Bu^{t}C≡P to **1** under similar conditions led only to traces of **3**. The need for a 1 : 1 PhSeF–RC≡P stoichiometry (as oppossed to 1 : 0.5) coupled to the absence of the additional equivalent of RC≡P in the ^{31}P NMR is remarkable; it is tentatively rationalized by initial bis-fluoroselenenylation followed by 'elimination' (transfer fluorination of RC≡P and rapid polymerization of the resulting difluorophosphaalkene), somewhat similar to fluoroselenenylation of monosubstituted alkynes with *N*-phenylselenophthalimide–Et_3N–3HF forming vinylic diselenated compounds by HF loss.[12]

For comparison, we examined the reactions of Bu^{t}C≡P and 1-AdC≡P with PhSeCl (1 equiv.) in CH_2Cl_2 (Scheme 1). Dropwise addition of a solution of PhSeCl (CH_2Cl_2) to a cold solution of Bu^{t}C≡P (CH_2Cl_2) at dry ice–acetone temperature (over 30 min) followed by slow warming to room temp. and removal of solvent *in vacuo* gave the chloroselenenylation product **5** (70–80% in independent reactions). Under comparable conditions, chloroselenenylation of 1-AdC≡P was slower (→ **6**; *ca*. 60%). These reactions demonstrate that 'PhSe$^+$' attacks at phosphorus, not carbon.‡ Whereas the phosphorus and carbon environments in the phosphaalkene unit and the one-bond P/Se couplings are very similar for **5** and **6**, the selenium chemical shifts vary by almost 25 ppm. Observation of minor amounts of $(PhSe)_2$ ($\delta_{^{77}Se}$ 460.8) in both cases suggests possible intervention by a radical process.§

The observed bis-selenenylations with the $(PhSe)_2$–XeF_2 system points to a different addition mechanism for 'PhSeF' compared to PhSeCl towards the P≡C triple bond. Moreover, although PhSeCl effects chloroselenenylation, its regiochemistry is opposite to protonation and Lewis acid complexation reactions of RC≡P.[6]

The stereochemistry in **3** and **4** has not been unambiguously established, but the magnitude of $^2J_{C,P}$ is a good indicator of a synperiplanar relationship between the R group and the lone-pair at phosphorus (*syn* addition).[10,13]

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Footnotes and References

* E-mail: klaali@kentvm.kent.edu

† Fluorinated minor products: ^{31}P NMR: −30.2 (q, *J* 1014.3 Hz), −34.4 (quint, *J* 1013.4 Hz), −142.6 (quint, *J* 710.9 Hz); ^{19}F NMR: −45.3 (dd, *J* 1013.5 and 9 Hz), −72.7 (d, *J* 713.5 Hz). In addition, there is a minor side-product (*ca.* 5%) in the phosphaalkene region; ^{31}P NMR: 256.6 ($^1J_{P,Se}$ 227.3, $^1J_{P,Se}$ 280.4 Hz).

‡ A byproduct is present (10–30% in independent reactions); ^{31}P NMR: δ 157.3 with two types of one-bond P/Se couplings at 317.7 and 195.6 Hz, with no indication of an intact P=C unit.

§ In the selenium NMR spectra, as well as $(PhSe)_2$ being present in both reactions ($\delta_{^{77}Se}$ 460.8), in the Bu^{t}CP reaction there is unreacted PhSeCl ($\delta_{^{77}Se}$ 446.5) and small peaks at $\delta_{^{77}Se}$ 449.8 and 451.4. In 1-AdC≡P reaction there are two peaks at $\delta_{^{77}Se}$ 426.7 and 424.9 (in 1 : 1 ratio with 100 Hz separation, a $^1J_{P,Se}$?)

1 K. Uneyama and M. Kanai, *Tetrahedron Lett.*, 1990, **31**, 3583.
2 H. Poleschner, M. Heydenreich, K. Spindler and G. Haufe, *Synthesis*, 1994, 1043.
3 H. Poleschner, M. Heydenreich and U. Schilde, *Leibigs. Ann.*, 1996, 1187.
4 G. H. Schmid and D. G. Garrett, *Tetrahedron Lett.*, 1975, 3991.
5 S. Tomoda and Y. Usuki, *Chem. Lett.*, 1989, 1235; Y. Usuki, M. Iwaoka and S. Tomoda, *Chem. Lett.*, 1992, 1507; Y. Usuki, M. Iwaoka and S. Tomoda, *J. Chem. Soc., Chem. Commun.*, 1992, 1148; J. R. McCarthy, D. P. Mathews and C. L. Barney, *Tetrahedron Lett.*, 1990, **31**, 973.
6 K. K. Laali, B. Geissler, M. Regitz and J. J. Houser, *J. Org. Chem.*, 1995, **60**, 6362.
7 K. K. Laali, B. Geissler, O. Wager, J. Hoffmann, R. Armbrust, W. Eisfeld and M. Regitz, *J. Am. Chem. Soc.*, 1994, **116**, 9407.
8 K. K. Laali, B. Geissler, M. Regitz and J. J. Houser, *J. Org. Chem.*, 1995, **60**, 47.
9 K. K. Laali, M. Regitz, M. Birkel, P. J. Stang and C. M. Crittell, *J. Org. Chem.*, 1993, **58**, 4105.
10 K. Karaghiosoff, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, p. 463f.
11 K. Laali, H. Y. Chen and R. J. Gerzina, *J. Org. Chem.*, 1987, **52**, 4126.
12 C. Saluzzo, G. Alvernhe and D. Anker, *Tetrahedron Lett.*, 1990, **31**, 2127.
13 T. W. Mackewitz, PhD Dissertation, Kaiserslautern, 1996.

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