Thiophosphonium–Alkyne Cycloaddition Reactions: A Heavy Congener of the Carbonyl–Alkyne Metathesis

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ABSTRACT: While the metathesis reaction between alkynes and thiocarbonyl compounds has been thoroughly studied, the reactivity of alkynes with isoelectronic main group \( R_2E=S \) congeners is rarely reported and unknown for \( [R_2P=S]^+ \) analogues. We show that thiophosphonium ions, which are the isoelectronic phosphorus congeners to thiocarbonyl compounds, undergo \([2 + 2]\)-cycloaddition reactions with different alkynes to generate 1,2-thiaphosphete ions. The four-membered ring species are in an equilibrium state with the corresponding \( P=C−C=S \) heterodiene structure and thus undergo hetero-Diels–Alder reactions with acetonitrile. Heteroatom and substituent effects on the energy profile of the 1,2-thiaphosphete formation were elucidated by means of quantum chemical methods.

INTRODUCTION

Heavy analogues of carbonyl compounds are generally highly reactive and prone to spontaneous oligomerization owing to the energetic preference of heavy p-block elements in forming \( \sigma \) bonds instead of \( (p−p)\pi \) bonds.\(^{1−4}\) In this respect, the thiocarbonyl group \((C=S)\) is an exception, but it reacts, due to its rather weak \( C=S \) bond and the aptitude of sulfur to stabilize an adjacent charge or radical center, more easily in nucleophilic reactions and sigmatropic rearrangements than carbonyls.\(^{5}\) The carbonyl−alkyne metathesis proceeds via a four-membered oxete intermediate, which is usually directly transformed into the \( \alpha_\beta\)-unsaturated ketone,\(^{7−12}\) unless it is stabilized by strongly electron-withdrawing groups.\(^{13−15}\) Due to the lower tendency of sulfur to form double bonds, thietes are more stable than oxetes,\(^{16−21}\) and a dynamic equilibrium between the “closed” thiete and “open” \( \alpha_\beta\)-unsaturated thioketone form was observed with thiourea substituents.\(^{22,23}\) Given these differences between oxetes and thietes, we became curious to explore how the introduction of another heavy main group element would affect the stability of the four-membered ring species. Although numerous examples for heavy main group carbonyls \( R_2E=O \) and thiocarbonyls \( R_2E=S \) have been synthesized,\(^{24−34}\) the reactivity with alkynes is little developed. Stannanethiones undergo \([2 + 2]\)-cycloaddition reactions with the particularly electron-poor alkynyl dimethyl acetylenedicarbodlate in a stepwise mechanism to give 1,2-thiastannete.\(^{35,36}\) The reaction mode of stannaneselone and stannanetellone was found to be similar, but ring-opening and formation of the corresponding stannabutadiene was not observed.\(^{35,37}\) Similarly, in transition metal chemistry, the elusive zirconasulfide \([\text{Cp}^*\text{Zr=S}]\) \((\text{Cp}^* = \text{pentamethycyclopentadienyl})\) was recently trapped via \([2 + 2]\)-cycloadditions with alkynes yielding 1,2-thiazirconabutenes.\(^{38,39}\) Recently, we explored the cycloaddition reaction between oxophosphonium cations and alkynes and showed that by using strong \( \pi \)-donor substituents instead of alkyl groups at the phosphorus atom, the “closed” oxaphosphete and the “open” 1-phospha-4-oxa-butadiene get closer in energy.\(^{40}\) Enabled by our recent success in isolating the first Lewis-base-free thiophosphonium ion \([R_2P=S]^+\) \(^{41}\) we herein report on \([2 + 2]\)-cycloaddition reactions of thiophosphonium salts with alkynes, yielding 1,2-thiaphosphete cations (Scheme 1b). The first neutral \( P^{III} \) 1,2-thiaphosphete was synthesized by Kawashima and co-workers containing a \( P \)-center stabilized by the Martin ligand (Scheme 1, I).\(^{42}\) More recently, Ragogna and co-workers prepared the neutral \( P^{III} \) 1,2-thiaphosphete II via transfer of a phosphinidene sulfide intermediate to an alkyn.\(^{43}\)

RESULTS AND DISCUSSION

We began our studies by reacting thiophosphonium salts \([\text{1}] [\text{X}] \) \((X = \text{tetraakis}[3,5\text{-bis(trifluoromethyl)}\text{phenyl}]\text{borate [BArF}_{25}]^+, \text{trifluoromethanesulfonate [OTF]}^\text{ −})\) with alkynes.

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Scheme 1. (a) Reaction of Thiocarbonyls with Alkynes, (b) Reaction of Thiophosphonium Ions with Alkynes to Give 1,2-Thiaphosphete Cations Presented in This Work, and (c) Neutral P⁺ 1,2-Thiaphosphete by Kawashima (I) and PIII 1,2-Thiaphosphete by Ragogna (II).

a) Thiocarbonyl-alkyne metathesis

b) This work

c) Known 1,2-thiaphosphetes

Heating a fluorobenzene solution containing [1][BArF24] and phenylacetylene to 120 °C gave the [2 + 2]-cycloaddition product [2a][BArF24] as a beige, moisture-sensitive solid in quantitative yield (Scheme 2). The thiaphosphete salt [2a][BArF24] shows a characteristic doublet at −36.1 ppm (J₁/₂ = 19 Hz) in the ³¹P NMR spectrum, which appears at lower frequency than that of the analogous oxaphosphete salt (−14.6 ppm).⁴⁰ P⁺ thiaphosphete I contains a pentavalent phosphorus atom and exhibits a similar ³¹P NMR chemical shift (−40.7 ppm) to [2a]+,⁴² whereas the resonance of the PIII thiaphosphete II appears at 37.5 ppm.⁴³

In order to explore possible substituent effects on the [2 + 2]-cycloaddition reaction, acetylene derivatives with electron-donating groups were reacted with thiophosphonium salt [1][BArF24] (Scheme 2 and Table 1), which gave the thiaphosphete salts [2b−e][BArF24] in excellent yields. The cycloaddition reaction with electron-rich alkynes, e.g., para-(dimethylamino)phenylacetylene (entry 3) and ethoxyacetylene (para-<ref>http://dx.doi.org/10.1021/acs.inorgchem.1c03076</ref>phenyl)acetylene (entry 4), is significantly faster than that with phenylacetylene. The electron-poor alkyne 1-ethynyl-3,5-bis-(trimethylsilyl)benzene (entry 6) reacted with [2a][BArF24] very slowly, even with prolonged heating at 180 °C. After 16 h, only 12% conversion was observed. This accelerated cycloaddition reaction between [2a][BArF24] and electron-rich alkynes can be explained by the high electrophility of the thiophosphonium cation and is contrary to the reactivity trend of neutral stannanethiophenes.⁴⁵ The same regioselectivity was observed for all [2 + 2]-cycloaddition reactions, which agrees with that of the 1,2-thiaphosphete II.⁴³

Table 1. Scope of Terminal Alkynes in [2 + 2]-Cycloaddition Reactions with Thiophosphonium Salt [1][BArF24]⁴⁴

| entry | compd. R | cond. | yield | δ(³¹P) [J₁/₂] |
|-------|---------|------|-------|-------------|
| 1     | [2a]+ Ph− | 120 °C, 16 h | 99% | −36.1 ppm [19 Hz] |
| 2     | [2b]+ p-MeO−C₆H₄ | 60 °C, 3 h | 99% | −35.2 ppm [19 Hz] |
| 3     | [2c]+ p-Me,N−C₆H₄ | 21 °C, 2 h | 99% | −32.2 ppm [20 Hz] |
| 4     | [2d]+ EtO− | 21 °C, 2 h | 99% | −35.7 ppm [15 Hz] |
| 5     | [2e]+ TsMeN− | 21 °C, 2 h | 97% | −36.4 ppm [15 Hz] |
| 6     | [2f]+ 3,5-CF₃−C₆H₄ | 180 °C, 16 h | 12%⁶ | −40.6 ppm² [18 Hz] |

⁴°The NMR data were obtained from CDCl₃ solutions. Ts = p-toluensulfonyl. ⁵°Conversion according to ³¹P NMR spectroscopy after 16 h when the reaction was stopped. ⁶NMR in fluorobenzene.

The formation of the four-membered heterocycle [2a]+ is further confirmed by the $^{13}$C{¹H} NMR spectrum, revealing a doublet at 120.3 ppm ($J_{PC} = 106$ Hz) for the phosphorus-bound carbon atom and a doublet at 153.4 ppm ($J_{PC} = 5$ Hz) of the adjacent carbon atom, which is deshielded by the sulfur atom. The ¹H NMR resonance of the thiaphosphete ring proton appears at 3.80 ppm and is significantly shifted to lower frequency compared to that of the parent thiete C₄H₄S (6.50 ppm).⁴¹ The effect can be explained by an enhanced polarization of the π bond of the thiaphosphete heterocycle, resulting from the negative hyperconjugation of π-electron density from the carbon atom into low-lying σ* orbitals of the phosphorus atom. The ³¹P NMR resonance of the thiaphosphete salt [2a][BArF24] appears at lower frequency than that of the analogous oxaphosphete salt (−14.6 ppm).⁴⁰ P⁺ thiaphosphete I contains a pentavalent phosphorus atom and exhibits a similar ³¹P NMR chemical shift (−40.7 ppm) to [2a]+,⁴² whereas the resonance of the PIII thiaphosphete II appears at 37.5 ppm.⁴³

Computational Studies

We performed DLPNO−CCSD(T)/def2-TZVPP calculations using the simplified thiophosphonium cation [(RMe)₂PS]⁺, which contains methyl groups at the imidazole N atoms instead of the bulky Dipp substituents. Three different model reactions involving phenyl-
acyclic structure. The rather low transition state with ethoxyacetylene implies that the reaction is thermoneutral for the oxaphosphete system. Remarkably, the ethoxy substituent is most effective in facilitating the ring-opening reaction, leading to a C=S platform in hetero-Diels-Alder reactions. In fact, dissolving [(RMe)2PS]+ (RMe = 1,3-dimethylimidazolin-2-ylidenamino) in acetonitrile precipitates within 5 min (Scheme 3).

### [4 + 2]-HETERO-DIELS–ALDER REACTIONS

The low energy barrier of 12.9 kcal/mol for the ring-opening reaction of [2d] suggests the possibility of employing the acyclic P=C–C=S platform in hetero-Diels–Alder reactions. In fact, dissolving [2d][BArF4] in acetonitrile gave a clear solution from which the [2 + 4] cycloaddition product [3d][BArF4] precipitates within 5 min (Scheme 3).

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**Figure 1.** Solid-state structure of [2a][BArF4] (left) and [2d][BArF4] (right). Hydrogen atoms (except H1), solvent molecules, and the BArF4 anions are omitted for clarity. Ellipsoids are drawn at 50% probability. Dipp groups are shown in wireframe. Selected bond lengths [Å] and angles [°]: [2a][BArF4]: P–S 2.15(1), C1–C2 1.79(2), C1–C2 1.349(3), P–C1 1.768(2), N1–P 1.576(2), N4–P 1.571(2), S–C2 73.6(1), S–C2–C1 107.17(14), C2–C1–P 98.93(14), C1–P–S 80.28(7). [2d][BArF4]: P–S 2.1665(6), C1–C2 1.765(2), C1–C2 1.376(2), P–C1 1.816(2), N1–P 1.5735(14), N4–P 1.6742(13), C2–O 1.327(2), P–S–C2 72.62(6), S–C2–C1 112.03(13), C2–C1–P 93.81(12), C1–P–S 81.52(6).

**Figure 2.** DLPNO–CCSD(T)/def2-TZVPP results including corrections to Gibbs free energy for different reactions of [(RMe)2PS]+ (RMe = 1,3-dimethylimidazolin-2-ylidenamino) with the corresponding alkyne (see legend). Separated reactants (SR) have been used as a reference.

**Figure 3.** DLPNO–CCSD(T)/def2-TZVPP results including corrections to Gibbs free energy for ring-opening reactions of model oxo- and thiophosphites (RMe = 1,3-dimethylimidazolin-2-ylidenamino). The closed forms (CF) have been used as a reference.
Scheme 3. [4 + 2]-Cycloaddition Reactions of [2a][BARF24] and [2d][BARF24] with Acetonitrile*

\[ \text{[2a]}^+; R = \text{Ph} \\
\text{[2d]}^+; R = \text{OEt} \\
\text{[3a]}^+; R = \text{Ph} \\
\text{[3d]}^+; R = \text{OEt} \\
\text{[4 + 2]-hetero-Diels-Alder} \\
\text{NEC-CH2} \]

* [BARF24]+ anions are omitted.

The formation of the six-membered thiazaphosphinine ring in [3d]⁺ is confirmed by the deshielded doublet of the S–C–N carbon atom at 164.6 ppm (\(^{7}J_{CP} = 6\) Hz) in the \(^{13}\)C NMR spectrum. The \(^{31}\)P resonance (−22.2 ppm) appears at higher frequency compared to the precursor [2d]⁺ (−35.7 ppm). The thiaphosphete salt [2a][BARF24] shows no reaction with acetonitrile below 60 °C and only very slow conversion at 100 °C. Heating the mixture to 170 °C for 16 h gave [3a][BARF24] in quantitative yield. The \(^{31}\)P NMR resonance of the heterocycle appears at −34.0 ppm. The reaction conditions for the ring expansion reactions indicate that ring-opening of the thiaphosphetates is required prior to the hetero-Diels–Alder reactions, which, in agreement with the computational results, is more easily accessible for [2d]⁺ than for [2a]⁺. The analogous ring expansion reaction with oxaphosphetes proceeds at lower temperature than that with thiaphosphetes, which again is consistent with the energy barrier of the electrocyclic ring-opening reaction.

Single-crystal XRD studies of [3a][BARF24] and [3d][BARF24] revealed planar thiazaphosphinine rings (sum of angles: 720°) flanked by the bulky substituents at the phosphorus atom (Figure 4). Both structures have very similar geometrical parameters. The C–N bonds ([3a]⁺: 1.268 Å, [3d]⁺: 1.264 Å) and the C–C bonds ([3a]⁺: 1.338 Å, [3d]⁺: 1.336 Å) of the six-membered rings are in the range of double bonds. The hexagonal shape of the heterocycles is significantly distorted due to the small bond angles centered around the sulfur ([3a]⁺: 105°, [3d]⁺: 104°) and phosphorus ([3a]⁺: 107°, [3d]⁺: 108°) atoms.

CONCLUSIONS

The P=S double bond of a Lewis-base-free thio phosphonium ion undergoes [2 + 2]-cycloadditions with terminal alkynes to generate thiaphosphate cations [2a−f]⁺. The four-membered rings undergo electrocyclic ring-opening reactions to the acyclic 1-phospha-4-thia-butadiene structure, which was used to generate the six-membered heterocycles [3a]⁺ and [3d]⁺ via [4 + 2]-hetero-Diels–Alder reactions. Quantum chemical calculations reveal that electron-donating substituents at the alkyne facilitate both the [2 + 2]-cycloaddition reaction and the ring-opening reaction, while an increasing number of heavy atoms generally stabilizes the four-membered ring structure.

The presented heavy congener of a thietoketone–alkyne metathesis is an appealing example for the diagonal relationship between carbon and phosphorus in the periodic table. The great potential of the \(R_P^+\) fragment to act in a thermoneutral fashion in bond metathesis reactions is indicated by the ring-opening reaction of the ethoxy substituted oxaphosphete. Further studies into this direction will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02076.

Synthetic procedures, NMR spectra, mass spectrometry data, crystallographic data, and computational details (PDF)

Accession Codes

CCDC 2094371–2094374 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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REFERENCES

(1) Jutzi, P. New Element-Carbon (p-p) Bonds. Angew. Chem., Int. Ed. Engl. 1975, 14 (4), 232–245.

(2) Mulliken, R. S. Structures of the Halogen Molecules and the Strength of Single Bonds 1. J. Am. Chem. Soc. 1937, 59 (4), 884–887.

(3) Mulliken, R. S. Overlap Integrals and Chemical Binding 1. J. Am. Chem. Soc. 1948, 70 (6), 2140–2145.

(4) Page, P. C. B. Organosulfur Chemistry I: Topics in Current Chemistry; Springer, 1999; Vol. 204.

(5) Becker, M. R.; Watson, R. B.; Schindler, C. S. Beyond olefins: new metathesis directions for synthesis. Chem. Soc. Rev. 2018, 47 (21), 7867–7881.

(6) Bos, H. J. T.; Arens, J. F. Addition of carbonyl compounds to alkynes under the influence of boron trifluoride. React. Chem. Pays-Bas 1963, 82 (9), 845–858.

(7) Martin, P. C.; Shevlin, P. B. Oxetene: synthesis and energetics of electrocyclic ring opening. J. Am. Chem. Soc. 1980, 102 (16), 5429–5430.

(8) Middleton, W. J. The Isolation of a Cyclic Intermediate in the Ketene—Alkoxycarbonylation Reaction. J. Org. Chem. 1965, 30 (4), 1307.

(9) Obin, M.; Pons, J.-M.; Parrain, J.-L.; Rajzmann, M. Experimental evidence for a [2 + 2] mechanism in the Lewis acid-promoted formation of α,β-unsaturated esters from ethoxycarbonyl and alkylides. Synthesis and characterisation of α,β-oxoethyoxetenes. Chem. Commun. 1998, 16, 1619–1620.

(10) Oblin, M.; Rajzmann, M.; Pons, J.-M. 2-H-Methoxoxye: a reactive intermediate en route to methyl acrylate from methoxycarbonyl and formaldehyde under BF3 catalysis. An ab initio HF and DFT study. Tetrahedron 2001, 57 (15), 3099–3104.

(11) Vieregge, H.; Schmidt, H. M.; Renema, J.; Bos, H. J. T.; Arens, J. F. Chemistry of acetylenic ethers 84: Addition of aldehydes, ketones, esters and amides to 1-alkynyl ethers under the influence of Lewis acids; direct formation of α,β-unsaturated esters. React. Chem. Pays-Bas 1966, 85 (9), 929–951.

(12) Sagesh, S.; Habibi, A. K. Triphenylphosphine-Catalyzed Synthesis of Stable, Functionalized 2H-Oxetes. Phosphorus, Sulfur Silicon Relat. Elem. 2005, 180 (11), 2451–2456.

(13) Fan, H.; Wang, X.; Zhao, J.; Li, X.; Gao, J.; Zhu, S. Synthesis of trifluormethyl substituted oxetenes by the reaction of acetylenedi-
Crystal Structure of a Kinetically Stabilized Silanethione. J. Am. Chem. Soc. 1994, 116 (25), 11578–11579.

(35) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Gotò, M. Formation and reactions of stannanethiones and stannaneselenoles. Organometallics 1993, 12 (7), 2573–2583.

(36) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. The first stable 1,2-thiastannetane and 1,2-selenastannetane: their syntheses and crystal structures. J. Chem. Soc., Chem. Commun. 1993, 4, 407–409.

(37) Tajima, T.; Takeda, N.; Sasamori, T.; Tokitoh, N. A Kinetically Stabilized Stannanetellone, a Tin–Tellurium Double-Bonded Compound. Organometallics 2006, 25 (15), 3552–3553.

(38) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. Generation of the highly reactive intermediates Cp^2Zr-O and Cp^2Zr:S: trapping reactions with alkynes, nitriles, and dative ligands. Organometallics 1992, 11 (2), 761–777.

(39) Kortman, G. D.; Orr, M. J.; Hull, K. L. Synthesis and Reactivity of Diazocyclohexanes: Development of a Zirconium–Oxo-Mediated Alkyme–Aldehyde Coupling Reaction. Organometallics 2015, 34 (6), 1013–1016.

(40) Löwe, P.; Feltl, M.; Wünsche, M. A.; Wilm, L. F. B.; Diermann, F. OXophosphonium-Alkyl Cyloaddition Reactions: Reversible Formation of 1,2-Oxaphosphates and Six-membered Phosphorus Heterocycles. J. Am. Chem. Soc. 2020, 142 (11), 9818–9826.

(41) Löwe, P.; Witteler, T.; Diermann, F. Lewis base-free thiophosphonium ion: a cationic sulfur atom transfer reagent. Chem. Commun. 2021, 57 (41), 5043–5046.

(42) Kawashima, T.; Iijima, T.; Kikuchi, H.; Okazaki, R. Synthesis of the First Stable Pentaco-Ordinate 1,2-Thiaphosphetene. Phosphorus Sulphur Silicon Relat. Elem. 1995, 99 (1), 149–152.

(43) Graham, C. M.; Macdonald, C. L. B.; Boyle, P. D.; Wisner, J. A.; Bagogna, P. J. Addressing the Nature of Phosphinidene Sulfides A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair sparse maps. J. Chem. Phys. 2016, 144 (2), 743–749.

(44) Dittmer, D. C.; Chang, P. L. F.; Davis, F. A.; Iwamani, M.; Stamos, I.; Takahashi, K. Derivatives of thiacyclobutene (thiete). VI. Natural orbital based local coupled cluster method. J. Chem. Phys. 2005, 7 (18), 3297–3305.

(45) Reilinger, C.; Neese, F. An efficient and near linear scaling pair natural orbital based local coupled cluster method. J. Chem. Phys. 2013, 138 (3), 34106.

(46) Reilinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. Sparse maps—A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory. J. Chem. Phys. 2016, 144 (2), 24109.

(47) Reilinger, C.; Sandhofer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. J. Chem. Phys. 2013, 139 (15), 134101.

(48) Saitow, M.; Becker, U.; Reilinger, C.; Valeev, E. F.; Neese, F. A new near-linear scaling, efficient and accurate, open-shell domain-based local pair natural orbital coupled cluster singles and doubles theory. J. Chem. Phys. 2017, 146 (16), 164105.

(49) Saitow, M.; Neese, F. Accurate spin-densities based on the domain-based local pair-natural orbital-coupled-cluster theory. J. Chem. Phys. 2018, 149 (3), 34104.

(50) Eichhorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. Theor. Chem. Acta. 1997, 97, 119–124.

(51) Eichhorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. Theor. Chem. Acta. 1997, 97, 119–124.