Hindawi
Heteroatom Chemistry
Volume 2019, Article ID 2596405, 10 pages
https://doi.org/10.1155/2019/2596405

Research Article

[4+2] versus [2+2] Homodimerization in P(V) Derivatives of 2,4-Disubstituted Phospholes

Guillaume Bousrez,[1] Emmanuel Nicolas,[2] Agathe Martinez,[1] Sylviane Chevreux,[1] and Florian Jaroschik[1]

[1]*Institut de Chimie Moléculaire de Reims, Université de Reims Champagne-Ardenne, BP 1039, 51687 Reims, France*
[2]*NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*

Correspondence should be addressed to Florian Jaroschik; florian.jaroschik@enscm.fr

Received 30 November 2018; Accepted 7 February 2019; Published 1 April 2019

Academic Editor: Mariateresa Giustiniano

Phosphole P(V) derivatives are interesting building blocks for various applications from ligand synthesis to material sciences. We herein describe the preparation and characterisation of new 2,4-disubstituted oxo-, thiooxo-, and selenooxophospholes. The nature of the substituents on the phosphole ring determines the reactivity of these compounds towards homodimerization reactions. Aryl and trimethylsilyl substituted oxophospholes undergo selective [4+2] dimerization, whereas, for thiooxo- and selenooxophospholes, light-induced, selective [2+2] head-to-head dimerization occurs in the case of aryl substituents. DFT calculations provide some insights on these differences in reactivity.

1. Introduction

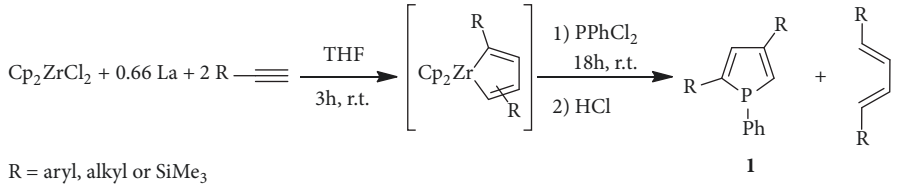
Phospholes have found widespread interest in many areas, including catalysis, material sciences, and biological applications, due to the ready modification of their electronic, steric, and physicochemical properties and their different coordination modes to metals [1–14]. Among the various possibilities, changing the substituents or the substitution pattern on the phosphole ring or on the phosphorus atom can modify the stability and the aromaticity of these heterocycles [15–17]. A major change is often induced by oxidation of the weakly aromatic P(III) compounds to non- or anti-aromatic P(V) derivatives employing oxygen/peroxides, sulphur, or selenium [18]. In material sciences and biological applications, the P(V) phospholes are mainly employed [8–14], whereas for catalysis and coordination chemistry purposes the P(III) heterocycles act as phosphine ligands or cyclopentadienyl analogues, or a combination of both [4–7].

Some years ago, we reported the synthesis of a series of 2,4-disubstituted phospholes **1** through a highly selective transformation of a mixture of 2,4- and 2,5-disubstituted zirconacyclopentadienes (Scheme 1) [19]. In this reaction, the addition of $PPhCl_2$ led only to the formation of phospholes **1**; no other regioisomer was observed. Quenching the reaction mixture with HCl yielded the 1,4-disubstituted 1,3-butadienes, which could be readily separated from **1**. This methodology was successfully applied to aryl, alkyl, and trimethylsilyl groups on the phosphole ring.

We herein show that the oxidation of some of these heterocycles to the corresponding oxo-, thiooxo-, and selenooxophospholes can lead to various reactivity behaviours with respect to homodimerization processes, i.e., [4+2] or [2+2] cycloaddition reactions.

2. Materials and Methods

2.1. General Considerations. Dichloromethane was collected under argon from a PURSOLV MD-3 (Innovative Technologie Inc.) solvent purification unit. *m*-chloroperbenzoic acid, sulphur, and selenium were purchased from Aldrich or Alfa Aesar. Phospholes **1a-d** were prepared according to the literature procedure [19]. ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P, and ^{77}Se NMR spectra were recorded in $CDCl_3$, unless specified, on a 500 MHz Bruker Avance III spectrometer equipped with a BBFO+ probe. Chemical shifts are reported in delta (δ) units,



Scheme 1: Selective formation of 2,4-disubstituted phospholes **1**.

expressed in parts per million (ppm). High resolution ESI-MS spectra were recorded on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. High resolution EI-MS spectra were obtained on a GCT-TOFmass spectrometer (Micromass, Manchester, UK) with EI source. Single crystals of **6d** were coated in Paratone-N oil and mounted on a loop. Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ= 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. The crystal structure was solved using SIR 97 and refined using Shelx 2016 [20, 21]. DFT calculations were performed using the Gaussian09 suite of software (full details are provided in the SI (available here)).

*2.2. General Procedure for the Synthesis of Oxophospholes **2** and the [4+2] Dimers **3**.* In a flask equipped with a magnetic stir bar, phosphole **1a-c** (5 mmol), dichloromethane (5 mL), and *m*-chloroperbenzoic acid (mCPBA) (6 mmol) were introduced. After stirring for 5 minutes at room temperature, the solution was filtered and the solvent evaporated under reduced pressure. The ^{31}P NMR spectrum ($CDCl_3$) of the crude residue showed complete conversion of starting phosphole and formation of oxophospholes **2a-c** and several nonidentified by-products. After a given time (several hours to days) compounds **2a,b** transform to the dimers **3a,b** in solution or in the solid state.

*2.3. General Procedure for the Synthesis of Thiooxophospholes **4** and the [2+2]dimers **5**.* In a flask equipped with a magnetic stir bar, phosphole **1a-d** (5 mmol), elemental sulphur (S_8) (1 mmol), and dichloromethane (5 mL) were introduced. After stirring overnight at room temperature, the solution was filtered, and then the solvent evaporated under reduced pressure. The ^{31}P NMR spectrum ($CDCl_3$) of the crude product showed complete conversion to **4a-d**. Under the influence of natural light, compounds **4a,d** transformed to the dimers **5a,d** after several days in solution in a classical NMR tube or in the solid state.

*2.4. General Procedure for the Synthesis of Selenooxophospholes **6** and the [2+2] Dimer **7**.* In a flask equipped with a magnetic stir bar, phosphole **1a-c** (5 mmol), elemental selenium (Se) (6 mmol), and dichloromethane (5 mL) were introduced. After stirring overnight at room temperature, the solution was filtered and the solvent evaporated under reduced pressure. The ^{31}P NMR spectra ($CDCl_3$) of the crude product showed complete conversion to **6a-c**. Under the influence of natural light, compound **6a** transformed to the dimer **7a** after several days in solution in a classical NMR tube or in the solid state.

*2.4.1. 1,10-Diphenyl-2,4,6,8-tetrakis(trimethysilyl)-1,10-diphosphatricyclo[5.6.5]deca-2,6-diene-1,10-dioxide (**3b**)*

^{1}H (500 MHz, $CDCl_3$). -0.13 (s, 9H), -0.08 (s, 9H), 0.13 (s, 9H), 0.37 (s, 9H), 3.31 (d, $J_{P\text{-}H}$ = 4.5 Hz, 1H), 3.45 (s, 1H), 6.70 (d, $J_{P\text{-}H}$ = 49.0 Hz, 1H), 6.96 (d, $J_{P\text{-}H}$ = 14.0 Hz, 1H), 7.31-7.34 (m, 2H), 7.41-7.50 (m, 4H), 7.64-7.68 (m, 2H), 7.78 (dd, $J_{H\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 2H).

^{13}C (125 MHz, $CDCl_3$). -2.2 (CH_3), -0.6 (CH_3), 0.10 (d, $J_{P\text{-}C}$ = 2.6 Hz, CH_3), 1.2 (CH_3), 46.3 (d, $J_{P\text{-}C}$ = 45.3 Hz, C), 51.7 (d, $J_{P\text{-}C}$ = 8.4 Hz, CH), 52.5 (d, $J_{P\text{-}C}$ = 60.6 Hz, CH), 53.1 (dd, $J_{P\text{-}C}$ = 15.0 Hz, $J_{P\text{-}C}$ = 15.0 Hz, C), 127.8 (d, $J_{P\text{-}C}$ = 10.3 Hz, CH), 128.3 (d, $J_{P\text{-}C}$ = 11.4 Hz, CH), 129.3 (d, $J_{P\text{-}C}$ = 83.3 Hz, C), 131.5 (d, $J_{P\text{-}C}$ = 10.1 Hz, CH), 131.5 (d, $J_{P\text{-}C}$ = 3.0 Hz, CH), 131.7 (d, $J_{P\text{-}C}$ = 2.4 Hz, CH), 134.2 (d, $J_{P\text{-}C}$ = 7.0 Hz, CH), 135.5 (d, $J_{P\text{-}C}$ = 91.0 Hz, C), 136.2 (d, $J_{P\text{-}C}$ = 61.5 Hz, C), 142.5 (d, $J_{P\text{-}C}$ = 8.5 Hz, C), 143.9 (dd, $J_{P\text{-}C}$ = 10.3 Hz, $J_{P\text{-}C}$ = 5.5 Hz, CH), 164.4 (dd, $J_{P\text{-}C}$ = 17.9 Hz, $J_{P\text{-}C}$ = 10.3 Hz, CH).

^{31}P (200 MHz, $CDCl_3$). 64.4 (d, $J_{P\text{-}P}$ = 37.0 Hz), 83.2 (d, $J_{P\text{-}P}$ = 37.0 Hz).

^{29}Si (100 MHz, $CDCl_3$). -8.3 (d, $J_{P\text{-}Si}$ = 6.4 Hz), -6.7 (dd, $J_{P\text{-}Si}$ = 15.5 Hz, $J_{P\text{-}Si}$ = 2.1 Hz), 1.8 (s), 8.1 (d, $J_{P\text{-}Si}$ = 5.5 Hz).

*2.4.2. 1,2,4-Triphenyl-thiooxophosphole (**4a**)*

^{1}H (500 MHz, Acetone-d_6). 6.85 (dd, $J_{P\text{-}H}$ = 31.0 Hz, $J_{H\text{-}H}$ = 1.5 Hz, 1H), 7.31-7.33 (m, 2H), 7.51-7.54 (m, 5H), 7.95 (dd, $J_{H\text{-}H}$ = 8.5 Hz, $J_{H\text{-}H}$ = 1.5 Hz, 1H), 7.97-7.99 (m, 3H), 8.13 (dd, $J_{P\text{-}H}$ = 40.5 Hz, $J_{H\text{-}H}$ = 1.5 Hz, 1H).

^{13}C (125 MHz, Acetone-d_6). 123.1 (d, $J_{P\text{-}C}$ = 86.1 Hz, CH), 128.0 (CH), 128.1 (d, $J_{P\text{-}C}$ = 6.4 Hz, CH), 129.6 (CH), 129.7 (C), 129.9 (CH), 130.0 (d, $J_{P\text{-}C}$ = 2.3 Hz, CH), 130.1 (d, $J_{P\text{-}C}$ = 7.5 Hz, CH), 131.3 (d, $J_{P\text{-}C}$ = 11.7 Hz, CH), 133.1 (d, $J_{P\text{-}C}$ = 3.0 Hz, CH), 133.3 (d, $J_{P\text{-}C}$ = 12.3 Hz, C), 134.9 (d, $J_{P\text{-}C}$ = 20.1 Hz, CH), 135.3 (d, $J_{P\text{-}C}$ = 16.5 Hz, C), 144.6 (d, $J_{P\text{-}C}$ = 74.0 Hz, C), 152.6 (d, $J_{P\text{-}C}$ = 17.1 Hz, C).

^{31}P (200 MHz, Acetone-d_6). 52.7 (s)

*2.4.3. 1-Phenyl-2,4-bis(trimethylsilyl)-thiooxophosphole (**4b**)*

^{1}H (500 MHz, $CDCl_3$). 0.05 (s, 9H), 0.25 (s, 9H), 6.73 (dd, J_{P-H} = 39.5 Hz, J_{H-H} = 1.0 Hz, 1H), 7.14 (dd, J_{P-H} = 48.0 Hz, J_{H-H} = 1.0 Hz, 1H), 7.40 (ddd, J_{H-H} = 7.5 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 3.0 Hz, 2H), 7.47 (ddd, J_{H-H} = 7.5 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 2.0 Hz, 1H), 7.75 (dd, J_{P-H} = 13.5 Hz, J_{H-H} = 7.0 Hz, 2H).

^{13}C (125 MHz, $CDCl_3$). -1.9 (CH_3), -0.8 (d, J_{P-C} = 1.3 Hz, CH_3), 126.6 (d, J_{P-C} = 70.1 Hz, C), 128.7 (d, J_{P-C} = 12.0 Hz, CH), 130.4 (d, J_{P-C} = 11.3 Hz, CH), 131.8 (d, J_{P-C} = 3.0 Hz, CH), 143.0 (d, J_{P-C} = 63.1 Hz, CH), 145.5 (d, J_{P-C} = 41.3 Hz, C), 150.4 (d, J_{P-C} = 18.5 Hz, CH), 158.3 (d, J_{P-C} = 11.3 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 66.1 (s)

^{29}Si (100 MHz, $CDCl_3$). -5.6 (d, J_{P-Si} = 10.9 Hz), -5.4 (d, J_{P-Si} = 7.8 Hz).

HRMS (EI) for $C_{16}H_{25}PSSi_2$: calcd. (m/z) 336.0953; found (m/z) 336.0963.

*2.4.4. 2,4-Bis(tert-butyl)-1-phenyl-thiooxophosphole (**4c**)*

^{1}H (500 MHz, $CDCl_3$). 1.14 (s, 9H), 1.21 (s, 9H), 5.83 (dd, J_{P-H} = 33.0 Hz, J_{H-H} = 1.5 Hz, 1H), 6.74 (dd, J_{P-H} = 43.5 Hz, J_{H-H} = 1.5 Hz, 1H), 7.41 (ddd, J_{H-H} = 7.5 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 3.0 Hz, 2H), 7.45-7.48 (m, 1H), 7.83 (dd, J_{P-H} = 14.0 Hz, J_{H-H} = 7.5 Hz, 2H).

^{13}C (125 MHz, $CDCl_3$). 28.3 (CH_3), 30.9 (d, J_{P-C} = 3.8 Hz, CH_3), 34.9 (d, J_{P-C} = 13.3 Hz, C), 36.4 (d, J_{P-C} = 10.5 Hz, C), 119.3 (d, J_{P-C} = 84.6 Hz, CH), 128.1 (d, J_{P-C} = 72.1 Hz, C), 128.7 (d, J_{P-C} = 12.3 Hz, CH), 130.4 (d, J_{P-C} = 11.4 Hz, CH), 131.6 (d, J_{P-C} = 3.0 Hz, CH), 133.7 (d, J_{P-C} = 26.1 Hz, CH), 155.5 (d, J_{P-C} = 66.3 Hz, C),164.1 (d, J_{P-C} = 14.8 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 51.7 (s)

HRMS (EI) for $C_{18}H_{25}PS$: calcd. (m/z) 304.1415; found (m/z) 304.1417.

*2.4.5. 2,4-Bis(4-fluorophenyl)-1-phenyl-thiooxophosphole (**4d**)*

^{1}H (500 MHz, $CDCl_3$). 6.53 (d, J_{P-H} = 30.5 Hz, 1H), 6.97 (dd, J_{H-H} = 8.5 Hz, J_{H-H} = 8.5 Hz, 2H), 7.16 (dd, J_{H-H} = 8.5 Hz, J_{H-H} = 8.5 Hz, 2H), 7.44 (ddd, J_{P-H} = 7.5 Hz, J_{H-H} = 7.5 Hz, J_{P-H} = 3.0 Hz, 2H), 7.51 (ddd, J_{P-H} = 7.5 Hz, J_{H-H} = 7.0 Hz, J_{P-H} = 1.0 Hz, 1H), 7.59 (dd, J_{P-H} = 39.5 Hz, J_{H-H} = 1.0 Hz, 1H), 7.66-7.70 (m, 4H), 7.91 (dd, J_{P-H} = 14.5 Hz, J_{H-H} = 8.0 Hz, 2H).

^{13}C (125 MHz, $CDCl_3$). 116.1 (dd, J_{P-C} = 22.1 Hz, J_{F-C} = 22.7 Hz, CH), 121.3 (d, J_{P-C} = 86.4 Hz, CH), 127.1 (C), 127.7 (C), 128.1 (dd, J_{P-C} = 12.3 Hz, J_{F-C} = 3.5 Hz, C), 129.0 (dd, J_{P-C} = 6.8 Hz, J_{F-C} = 7.4 Hz, CH), 129.2 (d, J_{P-C} = 12.6 Hz, CH), 130.5 (d, J_{P-C} = 11.8 Hz, CH), 131.0 (dd, J_{P-C} = 6.1 Hz, J_{F-C} = 5.8 Hz, CH), 132.4 (d, J_{P-C} = 2.9 Hz, CH), 132.7 (d, J_{P-C} = 22.9 Hz, CH), 142.9 (d, J_{P-C} = 74.4 Hz, C), 150.8 (d, J_{P-C} = 17.3 Hz, C), 162.5 (d, J_{F-C} = 81.8 Hz, C), 164.5 (d, J_{F-C} = 82.8 Hz, C).

^{19}F (470 MHz, $CDCl_3$). -109.5 (s), -110.8 (s).

^{31}P (200 MHz, $CDCl_3$). 53.5 (s)

HRMS (EI) for $C_{22}H_{15}F_2PS$: calcd. (m/z) 380.0600; found (m/z) 380.0611.

*2.4.6. [2+2] Dimer of 1,2,4-triphenyl-thiooxophosphole (**5a**)*

^{1}H (600 MHz, $CDCl_3$). 4.40 (d, J_{P-H} = 21.6 Hz, 1H), 6.64 (d, J_{P-H} = 40.2 Hz, 1H), 6.97 (d, J_{H-H} = 7.2 Hz, 1H), 7.05 (dd, J_{H-H} = 7.2 Hz, J_{H-H} = 7.8 Hz, 2H), 7.10 (d, J_{H-H} = 7.2 Hz, 1H), 7.25 (dd, J_{H-H} = 6.6 Hz, J_{H-H} = 7.2 Hz, 2H), 7.32 (dd, J_{H-H} = 6.6 Hz, J_{H-H} = 7.2 Hz, 2H), 7.35-7.38 (m, 5H), 7.63-7.66 (m, 2H).

^{13}C (150 MHz, $CDCl_3$). 40.6 (dd, J_{P-C} = 64.8 Hz, J_{P-C} = 13.5 Hz, CH), 65.8 (dd, J_{P-C} = 6.0 Hz, J_{P-C} = 6.0 Hz, C), 126.9 (CH), 127.2 (CH), 127.5 (dd, J_{P-C} = 2.1 Hz, J_{P-C} = 1.9 Hz, CH), 128.1 (CH), 128.6 (CH), 128.9 (d, J_{P-C} = 6.3 Hz, CH), 128.9 (d, J_{P-C} = 2.9 Hz, CH), 129.3 (CH), 130.6 (d, J_{P-C} = 9.9 Hz, CH), 131.3 (dd, J_{P-C} = 4.9 Hz, J_{P-C} = 4.9 Hz, CH), 132.2 (d, J_{P-C} = 15.5 Hz, CH), 132.2 (CH), 132.3 (d, J_{P-C} = 2.5 Hz, CH), 133.4 (d, J_{P-C} = 19.4 Hz, CH), 134.5 (d, J_{P-C} = 13.6 Hz, C), 138.0 (CH), 137.9 (d, J_{P-C} = 7.5 Hz, C), 138.4 (d, J_{P-C} = 7.4 Hz, C), 144.6 (dd, J_{P-C} = 10.1 Hz, J_{P-C} = 9.9 Hz, CH), 151.9 (d, J_{P-C} = 14.3 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 71.2 (s)

HRMS (ESI) for $C_{44}H_{35}P_2S_2$ [M+H]: calcd. (m/z) 689.1655; found (m/z) 689.1661.

*2.4.7. [2+2] Dimer of 2,4-bis(4-fluorophenyl)-1-phenyl-thiooxophosphole (**5d**)*

^{1}H (500 MHz, $CDCl_3$). 4.40 (d, J_{P-H} = 21.0 Hz, 1H), 6.58 (d, J_{P-H} = 39.5 Hz, 1H), 6.86 (dd, J_{H-H} = 9.0 Hz, J_{F-H} = 8.5 Hz, 2H), 7.08 (dd, J_{H-H} = 9.0 Hz, J_{F-H} = 5.0 Hz, 2H), 7.17 (dd, J_{H-H} = 8.5 Hz, J_{F-H} = 8.5 Hz, 2H), 7.36 (dd, J_{H-H} = 8.0 Hz, J_{P-H} = 2.0 Hz, 2H), 7.38-7.40 (m, 3H), 7.65-7.69 (m, 2H).

^{13}C (125 MHz, $CDCl_3$). 40.9 (dd, J_{P-C} = 65.4 Hz, J_{P-C} = 14.4 Hz, CH), 65.1 (dd, J_{P-C} = 5.9 Hz, J_{P-C} = 6.0 Hz, C), 115.9 (d, J_{P-C} = 21.6 Hz, CH), 116.4 (d, J_{P-C} = 21.3 Hz, CH), 128.1 (ddd, J_{P-C} = 5.5 Hz, J_{F-C} = 5.5 Hz, J_{P-C} = 3.5 Hz, C), 128.9 (d, J_{P-C} = 7.9 Hz, CH), 129.1 (dd, J_{P-C} = 6.3 Hz, J_{P-C} = 6.3 Hz, CH), 129.3 (dd, J_{P-C} = 2.8 Hz, J_{P-C} = 2.3 Hz, CH), 129.3 (dd, J_{P-C} = 2.5 Hz, J_{P-C} = 2.5 Hz, CH), 131.1 (dd, J_{P-C} = 5.6 Hz, J_{F-C} = 6.1 Hz, CH), 132.5 (CH), 133.8 (d, J_{P-C} = 2.9 Hz, C), 137.8 (d, J_{P-C} = 72.0 Hz, C), 143.5 (dd, J_{P-C} = 12.3 Hz, J_{P-C} = 11.6 Hz, CH), 150.9 (d, J_{P-C} = 3.3 Hz, C), 161.8 (d, J_{F-C} = 97.5 Hz, C), 163.8 (d, J_{F-C} = 98.1 Hz, C).

^{19}F (470 MHz, $CDCl_3$). -111.5 (s), -113.0 (s).

^{31}P (200 MHz, $CDCl_3$). 71.2 (s)

HRMS (ESI) for $C_{44}H_{30}F_4P_2S_2$ [M+H]: calcd. (m/z) 761.1279; found (m/z) 761.1288.

*2.4.8. 1,2,4-Triphenyl-selenooxophosphole (**6a**)*

^{1}H (500 MHz, $CDCl_3$). 6.72 (dd, J_{P-H} = 32.0 Hz, J_{H-H} = 1.0 Hz, 1H), 7.29-7.34 (m, 3H), 7.45-7.47 (m, 2H), 7.48-7.52 (m, 4H), 7.73-7.75 (m, 4H), 7.77 (d, J_{P-H} = 24.0 Hz, 1H), 7.99 (dd, J_{P-H} = 14.5 Hz, J_{H-H} = 1.5 Hz, 1H), 8.01 (d, J_{P-H} = 14.5 Hz, 1H).

^{13}C (125 MHz, $CDCl_3$). 121.8 (d, J_{P-C} = 78.3 Hz, CH), 126.9 (CH), 127.2 (d, J_{P-C} = 6.5 Hz, CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 129.2 (CH), 130.2 (CH), 131.2 (d, J_{P-C} = 12.1 Hz, CH), 131.7 (d, J_{P-C} = 12.4 Hz, C), 132.4 (d, J_{P-C} = 2.8 Hz, CH), 133.0 (d, J_{P-C} = 22.1 Hz, CH), 134.2 (d, J_{P-C} = 15.9 Hz, C), 143.7 (d, J_{P-C} = 66.8 Hz, C), 151.7 (d, J_{P-C} = 15.3 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 39.4 (J_{P-Se} = 733 Hz).

^{77}Se (96 MHz, $CDCl_3$). -397 (d, J_{Se-P} = 733 Hz).

HRMS (EI) for $C_{22}H_{17}PSe$: calcd. (m/z) 392.0233; found (m/z) 392.0230.

*2.4.9. 1-Phenyl-2,4-bis(trimethylsilyl)-selenooxophosphole (**6b**)*

^{1}H (500 MHz, $CDCl_3$). 0.08 (s, 9H), 0.26 (s, 9H), 6.82 (d, J_{P-H} = 41.0 Hz, 1H), 7.13 (dd, J_{P-H} = 47.5 Hz, J_{H-H} = 1.0 Hz, 1H), 7.40 (dt, J_{P-H} = 7.5 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 3.0 Hz, 2H), 7.46-7.49 (m, 1H), 7.76 (dd, J_{P-H} = 14.0 Hz, J_{H-H} = 1.0 Hz, 1H), 7.78 (d, J_{P-H} = 13.5 Hz, 1H).

^{13}C (125 MHz, $CDCl_3$). -1.8 (CH_3), -0.5 (CH_3), 124.8 (d, J_{P-C} = 62.6 Hz, CH), 128.8 (d, J_{P-C} = 12.1 Hz, CH), 131.0 (d, J_{P-C} = 11.8 Hz, C), 132.0 (d, J_{P-C} = 3.0 Hz, CH), 143.2 (d, J_{P-C} = 55.4 Hz, CH), 145.4 (d, J_{P-C} = 32.9 Hz, C), 150.5 (d, J_{P-C} = 16.9 Hz, CH), 158.1 (d, J_{P-C} = 9.5 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 52.0 (J_{P-Se} = 716 Hz).

^{29}Si (100 MHz, $CDCl_3$). -5.1 (d, J_{P-Si} = 20.2 Hz), -5.6 (d, J_{P-Si} = 22.1 Hz).

^{77}Se (96 MHz, $CDCl_3$). -466 (d, J_{Se-P} = 716 Hz).

HRMS (EI) for $C_{16}H_{25}PSeSi_2$: calcd. (m/z) 384.0398; found (m/z) 384.0408.

*2.4.10. 2,4-Bis(tert-butyl)-1-phenyl-selenooxophosphole (**6c**)*

^{1}H (500 MHz, $CDCl_3$). 1.16 (s, 9H), 1.21 (s, 9H), 5.89 (dd, J_{P-H} = 34.5 Hz, J_{H-H} = 1.5 Hz, 1H), 6.75 (dd, J_{P-H} = 43.0 Hz, J_{H-H} = 2.0 Hz, 1H), 7.39 (dd, J_{H-H} = 7.5 Hz, J_{P-H} = 2.5 Hz, 2H), 7.44 (dd, J_{H-H} = 7.0 Hz, J_{P-H} = 1.0 Hz, 1H), 7.83 (dd, J_{P-H} = 14.0 Hz, J_{H-H} = 7.0 Hz, 2H).

^{13}C (125 MHz, $CDCl_3$). 28.3 (CH_3), 31.2 (d, J_{P-C} = 3.8 Hz, CH_3), 34.8 (d, J_{P-C} = 12.9 Hz, C), 36.5 (d, J_{P-C} = 10.6 Hz, C), 119.4 (d, J_{P-C} = 77.1 Hz, CH), 126.0 (d, J_{P-C} = 64.3 Hz, C), 128.7 (d, J_{P-C} = 12.3 Hz, CH), 130.9 (d, J_{P-C} = 11.8 Hz, CH), 131.7 (d, J_{P-C} = 2.8 Hz, CH), 133.8 (d, J_{P-C} = 25.0 Hz, CH), 155.0 (d, J_{P-C} = 58.1 Hz, C), 164.0 (d, J_{P-C} = 13.1 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 36.9 (J_{P-Se} = 724 Hz).

^{77}Se (96 MHz, $CDCl_3$). -430 (d, J_{Se-P} = 724 Hz).

*2.4.11. [2+2] Dimer of 1,2,4-Triphenyl-selenooxophosphole (**7a**)*

^{1}H (500 MHz, $CDCl_3$). 4.55 (d, J_{P-H} = 23.0 Hz, 1H), 6.69 (d, J_{P-H} = 40.0 Hz, 1H), 7.03-7.10 (m, 2H), 7.15-7.23 (m, 5H), 7.31-7.38 (m, 5H), 7.40-7.53 (m, 10H), 7.76-7.81 (m, 2H).

^{13}C (125 MHz, $CDCl_3$). 42.5 (dd, J_{P-C} = 60.0 Hz, J_{P-C} = 15.0 Hz, CH), 67.2 (dd, J_{P-C} = 6.5 Hz, J_{P-C} = 5.0 Hz, C), 126.8 (CH), 127.2 (CH), 127.7 (CH), 128.1 (CH), 128.5 (2CH), 128.9 (d, J_{P-C} = 10.0 Hz, CH), 129.0 (d, J_{P-C} = 5.0 Hz, CH), 129.2 (d, J_{P-C} = 6.5 Hz, CH), 129.3 (d, J_{P-C} = 8.8 Hz, CH), 129.4 (2CH), 131.9 (dd, J_{P-C} = 6.5 Hz, J_{P-C} = 5.0 Hz, CH), 132.3 (CH), 133.3 (d, J_{P-C} = 25.0 Hz, C), 137.0 (C), 137.6 (C), 138.3 (CH), 144.4 (dd, J_{P-C} = 11.3 Hz, J_{P-C} = 11.3 Hz, CH), 146.2 (d, J_{P-C} = 23.8 Hz, C).

^{31}P (200 MHz, $CDCl_3$). 64.5 (J_{P-Se} = 759 Hz).

^{77}Se (96 MHz, $CDCl_3$). -385 (d, J_{Se-P} = 759 Hz).

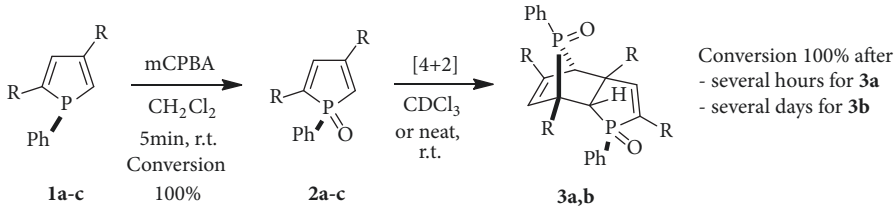
3. Results and Discussion

3.1. Oxophospholes. The reaction of phospholes **1** with *m*-chloroperbenzoic acid (mcpba) in dichloromethane at room temperature led immediately to the formation of 2,4-disubstituted oxophospholes **2** as shown by ^{31}P NMR spectroscopy (Scheme 2, Table 1). Within several hours, the aryl-substituted compound **2a** transformed to the corresponding [4+2] cycloadduct **3a** in a highly selective endo-anti fashion. For **2b** containing two trimethylsilyl groups, the dimerization took several days, whereas with the bulky tert-butyl groups in **2c** no dimerization occurred.

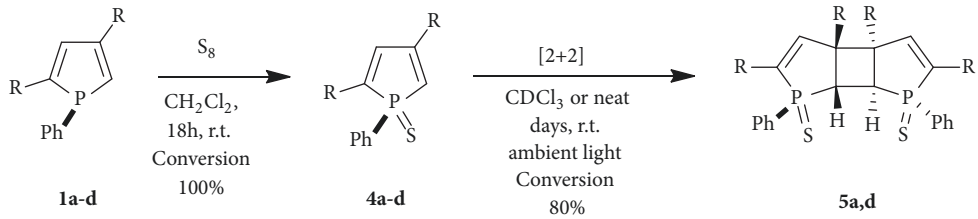
The values observed in the ^{31}P NMR spectrum for **2** and **3** are close to other values in the literature [22, 23]. The oxidation of **1a** and **1c** produced nonidentified side-products, which did not allow a full characterisation of these compounds and the dimer **3a**. In contrast, compound **3b** could be obtained as a pure product and was fully characterized by multinuclear NMR spectroscopy. In Table 2, the ^{13}C NMR data of product **3b** is compared to the previously described [4+2] dimer of 3-methylphosphole oxide **A**, which had also been characterized by X-ray diffraction analysis [22]. The good correlation of the data between compounds **3b** and **A** led us to the assumption that in our case the same endo-anti product was formed as major product.

3.2. Thiooxophospholes. The oxidation of phospholes **1** with sulfur in dichloromethane was complete after one night stirring at room temperature, as shown by ^{31}P NMR spectroscopy, yielding the corresponding thiooxophospholes **4** (Scheme 3, Table 3). In the case of aryl-substituted compounds **4a** and **4d**, a new signal appeared in the ^{31}P NMR spectrum after workup. This singlet increased steadily upon leaving the sample exposed to natural light with a concomitant decrease of the signal for **4** until nearly full conversion after several days. No other products appeared in the spectrum. The new products could be identified as [2+2] head-to-head dimers **5a** and **5d** through multinuclear NMR spectroscopy and X-ray diffraction studies for **5d**. In the case of **4b** and **4c**, no further reaction was observed. When compounds **4a** and **4d** were stored in the dark the corresponding products **5a** and **5d** did not form, whereas exposure to direct sunlight accelerated the reaction.

The ^{31}P NMR values for **4** are in agreement with literature data [24–27]. A comparison of the ^{1}H and ^{13}C NMR data of



Scheme 2: Phosphole oxidation with mcpba then [4+2] dimerization.

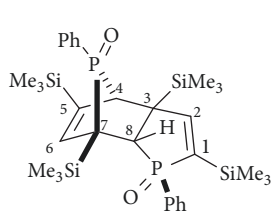


Scheme 3: Phosphole oxidation with S_8 then [2+2] dimerization.

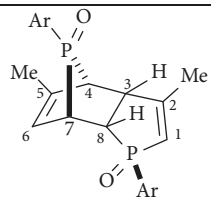
Table 1: ^{31}P NMR chemical shifts (ppm) ($CDCl_3$) of **1**, **2,** and **3**.

Entry	R	1	2	3
1	Ph (**a**)	11.3	47.8	55.8 (d, $^3J_{P\text{-}P}$ = 37.6 Hz) 76.3 (d, $^3J_{P\text{-}P}$ = 37.6 Hz)
2	Trimethylsilyl (**b**)	31.9	59.0	64.4 (d, $^3J_{P\text{-}P}$ = 37.0 Hz) 83.2 (d, $^3J_{P\text{-}P}$ = 37.0 Hz)
3	t-Butyl (**c**)	1.4	47.5	No dimer

Table 2: Comparison of ^{13}C NMR chemical shifts (ppm) ($CDCl_3$) of **3b** and **A**.



3b



A

	3b		A	
Cn	δ (ppm)	$J_{P\text{-}C}$ (Hz)	δ (ppm)	$J_{P\text{-}C}$ (Hz)
C1	135.5	91.0	130.4	103.5
C2	164.4	17.9; 10.3	154.6	24.2; 9.0
C3	53.1	15.0; 15.0	51.4	12.8; 12.8
C4	52.2	62.5	53.8	67.9
C5	142.5	8.5	134.6	11.4
C6	143.9	10.3; 5.5	122.5	12.2
C7	46.3	45.3	49.8	64.6
C8	51.7	68.8; 8.6	43.7	79.5; 15.0

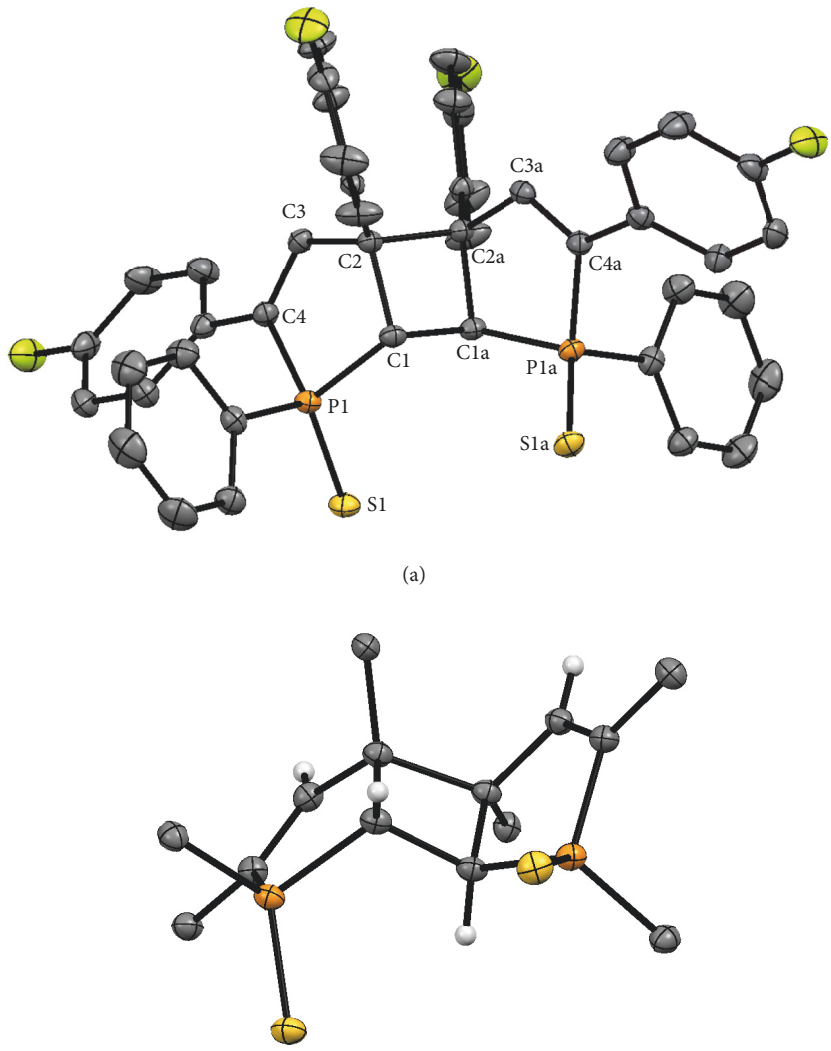


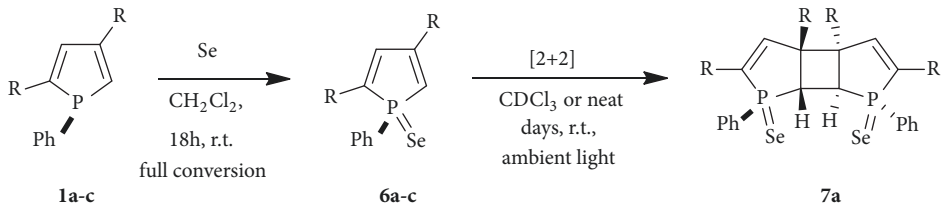
Figure 1: Molecular structure of **5d**: (a) top-view of whole molecule with 50% probability ellipsoids; hydrogens and solvent molecule omitted for clarity; (b) side-view of tricyclic [5;4;5] pattern showing the syn-anti arrangement.

Table 3: ^{31}P NMR chemical shifts (ppm) ($CDCl_3$) of **4** and **5** (*done in acetone-d_6).

Entry	R	**1**	**4**	**5**
1	Ph (**a**)	11.3	52.7*	71.2
2	Trimethylsilyl (**b**)	31.9	66.1	No dimer
3	t-Butyl (**c**)	1.4	51.7	No dimer
4	4-F-Ph (**d**)	11.9	53.5	71.2

compounds **1d**, **4d**, and **5d** is shown in Table 4 confirming the head-to-head dimerization of compound **4d**. Interesting observations are the changes in the coupling constants $^1J_{P\text{-}C}$ for C_α and $C_{\alpha'}$' upon oxidation from **1d** (0 and 1.8 Hz) to **4d** (86.4 and 74.0 Hz) [24]. Upon dimerization to **5d**, the $^1J_{P\text{-}C}$ for $C_{\alpha'}$' is most impacted (down to 3.3 Hz), whereas for C_α a high value remains (65.4 Hz).

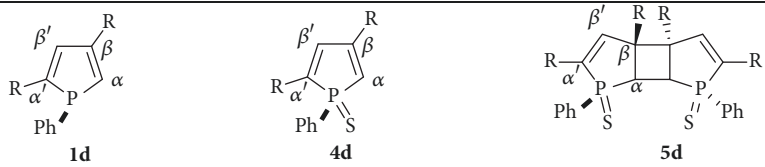
Crystals of compound **5d** suitable for X-ray diffraction studies were obtained through slow evaporation of the chloroform solvent. **5d** crystallised in the monoclinic space group C2/c with one disordered solvent molecule in the unit cell (Figure 1). The tricyclic [5;4;5] pattern shows a syn-anti arrangement with respect to the phosphole units and the substituents on the cyclobutene ring. There are only two other structurally characterised compounds with this arrangement in the literature, i.e., the dimerised helical phosphoindole oxides which have no substituents on the C1 and C2 position, reported by Marinetti and Voituriez [28]. The cyclobutane ring in **5d** is quasi-rectangular (angles C1–C2–C2a 88.32(8)° and C2–C1–C1a 90.95(8)°) with a considerable deviation



R = Ph (**a**), $SiMe_3$ (**b**), t-Bu (**c**)

Scheme 4: Phosphole oxidation with Se then [2+2] dimerization.

Table 4: Chemical shifts (ppm) and coupling constants (Hz) of **1d**, **4d,** and **5d**.



R = 4-F-C_6H_4

		^{1}H		^{13}C			
Entry	R	H_α $^2J_{P\text{-}H}$	$H_{\beta'}$ $^3J_{P\text{-}H}$	C_α $^1J_{P\text{-}C}$	$C_{\alpha'}$ $^1J_{P\text{-}C}$	C_β $^2J_{P\text{-}C}$	$C_{\beta'}$ $^2J_{P\text{-}C}$
1	**1d**	6.97 (39.0)	7.48 (12.5)	127.4 (0)	153.1 (1.8)	149.3 (7.6)	131.5 (10.1)
2	**4d**	6.53 (30.5)	7.59 (39.5)	121.3 (86.4)	142.9 (74.0)	150.8 (17.3)	132.7 (22.9)
3	**5d**	4.40 (21.0)	6.58 (39.5)	40.9 (65.4)	150.9 (3.3)	65.1 (5.9)	143.5 (12.3)

Table 5: ^{31}P and ^{77}Se NMR chemical shifts (ppm) ($CDCl_3$) and coupling constants of **6** and **7**.

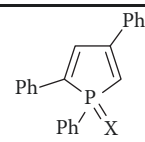
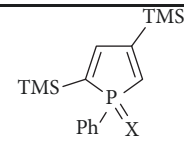
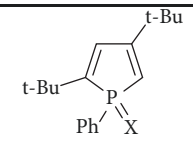
		6		**7**	
Entry	R	δ (^{31}P)	δ (^{77}Se)	δ (^{31}P)	δ (^{77}Se)
1	Ph (**a**)	39.4	-397 (d, $^1J_{Se\text{-}P}$ = 733 Hz)	64.5	-385 (d, $^1J_{Se\text{-}P}$ = 759 Hz)
2	Trimethylsilyl (**b**)	52.0	-466 (d, $^1J_{Se\text{-}P}$ = 716 Hz)		No dimer
3	t-Butyl (**c**)	36.9	-430 (d, $^1J_{Se\text{-}P}$ = 724 Hz)		No dimer

from planarity (dihedral angle C1–C2–C2a-C1a 9.1°). The biggest differences with respect to the reported structures are the bond lengths within the cyclobutane ring. Whereas C1-C2 and C1-C1a are in the expected range (1.562(2)Å and 1.547(3)Å), the C2-C2a bond (1.619(3) Å) is considerably longer, which is probably due to the adjacent phenyl groups. For the latter bond, the corresponding bond lengths in the reported nonsubstituted phosphoindole oxides are 1.563(5) Å and 1.564(18) Å [28].

3.3. Selenooxophospholes. When selenium was employed for the oxidation of phospholes **1** in dichloromethane the corresponding selenooxophospholes **6** were obtained quantitatively after 18h at room temperature (Scheme 4). The substituents on the phosphole ring influence strongly the ^{31}P NMR shifts and, in this case, also the ^{77}Se NMR values (Table 5). Leaving compound **6a** in a standard NMR tube for several days exposed to natural light led to a good but not full conversion to the [2+2] head-to-head dimer **7a** as shown by ^{31}P NMR.

It has previously been shown that the coupling constant $^1J_{Se\text{-}P}$ can provide information on the σ-donor ability of phospholes [4–7, 29–32]. According to Table 5, phosphole **1b** having the trimethylsilyl groups in positions 2 and 4 is the strongest σ-donor as **6b** has the smallest coupling constant with 716 Hz, close to the value for 1-phenyl-3,4-dimethylphosphole (713 Hz). The value for compound **6a** is smaller compared to the corresponding 1,2,5-triphenylselenooxophosphole (742 Hz) [4–7], indicating a certain influence of the position of the ring substituents on the σ-donor ability. Interestingly, the dimer **7a** has a considerably higher coupling constant with 759 Hz.

Table 6: Comparison of NICS(0) (ppm) and HOMO-LUMO gap (eV) for three disubstituted phospholes and their oxides.

X		 **a**	 **b**	 **c**
lone pair (**1**)	NICS(0)	-2.83	-3.09	-2.62
	Δ(HOMO-LUMO)	3.968	4.770	4.898
O (**2**)	NICS(0)	1.41	1.79	1.22
	Δ(HOMO-LUMO)	3.698	4.458	4.646
S (**4**)	NICS(0)	0.58	0.92	0.40
	Δ(HOMO-LUMO)	3.555	3.848	4.142
Se (**6**)	NICS(0)	0.34	0.62	0.20
	Δ(HOMO-LUMO)	3.262	3.475	3.761

3.4. DFT Calculations. In an attempt to correlate the observed reactivity of the different phosphole P(V) derivatives with their electronic properties, we carried out DFT calculations at the B3LYP-D3/6-31G(d) level of theory (see SI) to determine the HOMO-LUMO gaps and the NICS(0) values (Table 6). Phospholes **1** are often considered as weakly aromatic compounds [15–17] and this is reflected in the small negative values for the NICS(0) (-2.83, -3.09, and -2.62 ppm for **1a**, **1b**, and **1c**, respectively). In contrast, phosphole P=O compounds **2** tend towards anti-aromatic systems with positive NICS(0) values (1.41, 1.79, and 1.22 ppm for **2a**, **2b**, and **2c**, respectively), which makes them more reactive towards further dimerization reactions [18]. The steric bulk of the substituents can strongly influence these reactions. The P=S and P=Se analogues **4** and **6** are best described as non-aromatic or slightly anti-aromatic (NICS values ranging from 0.20 to 0.92 ppm for **4a-c** and **5a-c**) and they are more stable towards dimerization. However, the aryl-substituted yellow compounds **4a** and **4d** can absorb visible light and undergo [2+2] reactions, in agreement with the calculated HOMO-LUMO gaps (3.555 and 3.541 eV, respectively; see SI for **4d**). The colourless compounds **4b** and **4c** show no reactivity, which is also in good agreement with the calculations (HOMO-LUMO gaps of 3.848 and 4.142 eV, respectively). Neither phospholes **1** nor phosphole oxides **2** undergo [2+2] dimerisation under ambient conditions in agreement with the too large HOMO-LUMO gaps, all above 3.698 eV. It is worthwhile noting that for all computed P(V) compounds the HOMO corresponds to the π system, with a contribution of the O, S, or Se atom, while the LUMO corresponds to the π^* system. Single-electron excitation is thus consistent with the visible-light-induced [2+2] dimerization that is observed.

3.5. Discussion

3.5.1. [4+2] Dimerization. The propensity of phosphole derivatives to undergo [4+2] homodimerization reactions has been a long-standing research issue and the selectivity of such transformations has been investigated by synthetic and theoretical means [1, 33–35]. It concerns mainly, but not exclusively, phosphole oxides and metal-coordinated phospholes [22, 23, 36]. The steric bulk and the position of the substituents play an important role. Whereas 3,4-disubstituted phospholes are prone to homodimerization, 2,5-disubstituted phospholes are stable towards this reaction. The latter can nevertheless react under more stringent conditions with other dienophiles [37]. In our case, the 2,4-disubstituted phosphole oxides are just borderline: with aryl groups and the bulky, but flexible trimethylsilyl groups homodimerization occurs, albeit slowly, whereas the bulky t-butyl group prevents this reaction. A very good regioselectivity with the formation of mainly one [4+2] dimer, the endo-anti isomer, is observed.

3.5.2. [2+2] Dimerization. Until recently, thermal or light-induced [2+2] dimerization reactions were mainly restricted to phosphole derivatives coordinated to metals [38–41]. In 2012, Marinetti and Voituriez reported the first metal-free, head-to-head [2+2] photocyclizations with nonsubstituted helical phosphoindole oxides [28]. More recently, a helical phosphinamide substituted in the C2 position was examined, providing the head to tail [2+2] dimer in solution under sunlight. Furthermore, the reaction took also place in the solid state under sunlight or X-ray radiation [42]. In our case, the 2,4-disubstituted thiooxo- and selenooxophospholes **4a, 4d** and **6a** are the first examples for phosphole P=S and P=Se derivatives to undergo metal-free head-to-head [2+2] homodimerization reactions, despite the presence of substituents in the C2 position. These transformations are highly regio- and stereoselective, yielding a single isomer. The aryl groups have a crucial role in this case, as they allow the absorption of visible light by the phosphole moiety and, as can be seen from the DFT calculations, they lower the HOMO-LUMO gaps just under the threshold for visible light energy, so that [2+2] dimerization can occur. In contrast, trimethylsilyl or t-butyl substituted phospholes **4b,c** and **5b,c** do not absorb in the visible light region and, in most cases, have too wide HOMO-LUMO gaps for visible light mediated reactions. These findings open the way to further light-driven transformations of phosphole P(V) derivatives.

4. Conclusions

We have shown that P(V) derivatives of 2,4-disubstituted phospholes have intriguing properties with respect to [4+2] and [2+2] homodimerization reactions, which are highly dependent on (a) the heteroatom on phosphorus (O vs S, Se) and (b) the substituents on the phosphole ring (aryl vs. trimethylsilyl vs. t-butyl). Their reactivity and their properties lie in-between the corresponding 2,5- and 3,4-disubstituted phospholes, as, for example, shown with the $^{1}J_{PSe}$ coupling constants. Particularly, the light-driven [2+2] photocyclization requires further in-depth studies to explore its full potential towards other derivatization reactions. Further transformations of the new [2+2] dimers (reduction of the P=S bond and chiral resolution) could provide the platform for a new family of chiral ligands for asymmetric catalysis.

Data Availability

The NMR spectra, X-ray data, and computed structures used to support the findings of this study are included within the supplementary information file(s).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This research was funded by the Région Champagne-Ardenne, France (PhD scholarship for Guillaume Bousrez), by the CNRS, and by the Université de Reims Champagne-Ardenne. The authors thank the CNRS, the Université de Reims, and the Région Champagne-Ardenne for financial support and CINES (Project DARI A0040806494) and the platform PlAneT for technical support. They are also grateful to Dr. Norbert Hoffman for helpful discussions regarding the photocyclization reaction. The assistance of Mrs. Carine Machado and Dr. Dominique Harakat (mass spectrometry) is acknowledged.

Supplementary Materials

Multinuclear NMR spectra are provided for compounds detailed in the experimental section and X-ray data for compound **5d** (CCDC 1882024). Full computational details, XYZ coordinates, and parameters used for the DFT calculations are provided. *(Supplementary Materials)*

References

[1] F. Mathey, "The organic chemistry of phospholes," *Chemical Reviews*, vol. 88, no. 2, pp. 429–453, 1988.

[2] D. Carmichael, "Chapter 7: Phospholes," in *Phosphorus (III) Ligands in Homogeneous Catalysis: Design and Synthesis*, P. Kamer and P. W. N. M. van Leeuwen, Eds., pp. 267–286, Wiley VCH, 2012.

[3] Y. Matano and H. Imahori, "Phosphole-containing calixpyrroles, calixphyrins, and porphyrins: synthesis and coordination chemistry," *Accounts of Chemical Research*, vol. 42, no. 8, pp. 1193–1204, 2009.

[4] L. Kollar and G. Keglevich, "*P*-Heterocycles as ligands in homogeneous catalytic reactions," *Chemical Reviews*, vol. 110, no. 7, pp. 4257–4302, 2010.

[5] K. Fourmy, D. H. Nguyen, O. Dechy-Cabaret, and M. Gouygou, "Phosphole-based ligands in catalysis," *Catalysis Science & Technology*, vol. 5, no. 9, pp. 4289–4323, 2015.

[6] P. Le Floch, "Phosphaalkene, phospholyl and phosphinine ligands: new tools in coordination chemistry and catalysis," *Coordination Chemistry Reviews*, vol. 250, no. 5-6, pp. 627–681, 2006.

[7] M. Ogasawara, Y.-Y. Tseng, M. Uryu et al., "Molybdenum-catalyzed enantioselective synthesis of planar-chiral (η^5-phosphacyclopentadienyl)manganese(I) complexes and application in asymmetric catalysis," *Organometallics*, vol. 36, no. 20, pp. 4061–4069, 2017.

[8] S. Urig, K. Fritz-Wolf, R. Réau et al., "Undressing of phosphine gold(I) complexes as irreversible inhibitors of human disulfide reductases," *Angewandte Chemie International Edition*, vol. 45, no. 12, pp. 1881–1886, 2006.

[9] M. Arribat, E. Rémond, S. Clément, A. V. D. Lee, and F. Cavelier, "Phospholyl(borane) amino acids and peptides: stereoselective synthesis and fluorescent properties with large stokes shift," *Journal of the American Chemical Society*, vol. 140, no. 3, pp. 1028–1034, 2018.

[10] T. Baumgartner and R. Réau, "Organophosphorus π-conjugated materials," *Chemical Reviews*, vol. 106, no. 1, pp. 4681–4727, 2006.

[11] M. P. Duffy, W. Delaunay, P.-A. Bouit, and M. Hissler, "π-Conjugated phospholes and their incorporation into devices: components with a great deal of potential," *Chemical Society Reviews*, vol. 45, no. 19, pp. 5296–5310, 2016.

[12] A. Saito, T. Miyajima, M. Nakashima et al., "Acenaphtho[1,2-c]phosphole *P*-oxide: a phosphole-naphthalene π-conjugated system with high electron mobility," *Chemistry - A European Journal*, vol. 15, no. 46, pp. 10000–10004, 2009.

[13] D. Joly, D. Tondelier, V. Deborde et al., "White organic light-emitting diodes based on quench-resistant fluorescent organophosphorus dopants," *Advanced Functional Materials*, vol. 22, no. 4, pp. 567–576, 2012.

[14] T. Baumgartner, "Insights on the design and electron-acceptor properties of conjugated organophosphorus materials," *Accounts of Chemical Research*, vol. 47, no. 5, pp. 1613–1622, 2014.

[15] L. Nyulászi, "Aromaticity of phosphorus heterocycles," *Chemical Reviews*, vol. 101, no. 5, pp. 1229–1246, 2001.

[16] L. Nyulászi and Z. Benkö, "Aromatic phosphorus heterocycles," *Topics in Heterocyclic Chemistry*, vol. 19, pp. 27–81, 2009.

[17] G. Keglevich, Z. Böcskei, G. M. Keserü, K. Újszászy, and L. D. Quin, "1-(2,4,6-tri-tert-butylphenyl)-3-methylphosphole: a phosphole with a significantly flattened phosphorus pyramid having pronounced characteristics of aromaticity," *Journal of the American Chemical Society*, vol. 119, no. 22, pp. 5095–5099, 1997.

[18] Z. Mucsi and G. Keglevich, "Why are phosphole oxides unstable? The phenomenon of antiaromaticity as a destabilizing factor," *European Journal of Organic Chemistry*, no. 28, pp. 4765–4771, 2007.

[19] G. Bousrez, F. Jaroschik, A. Martinez et al., "Reactivity differences between 2,4- and 2,5-disubstituted zirconacyclopentadienes: a highly selective and general approach to 2,4-disubstituted phospholes," *Dalton Transactions*, vol. 42, no. 30, pp. 10997–11004, 2013.

[20] G. M. Sheldrick, "Crystal structure refinement with SHELXL," *Acta Crystallographica Section C*, vol. 71, no. 1, pp. 3–8, 2015.

[21] A. Altomare, M. C. Burla, M. Camalli et al., "SIR97: a new tool for crystal structure determination and refinement," *Journal of Applied Crystallography*, vol. 32, no. 1, pp. 115–119, 1999.

[22] G. Keglevich, L. Toke, Z. Böcskei, and V. Harmat, "Steric hindrance in the synthesis and properties of the dimer of 1-(2,4,6-tri-tert-butylphenyl)phosphole 1-oxide," *Heteroatom Chemistry*, vol. 8, no. 6, pp. 527–531, 1997.

[23] G. Keglevich, T. Chuluunbaatar, B. Dajka, B.-A. Namkhainyambuu, K. Ludányi, and L. Tóke, "Competitive [4+2] cycloadditions in equimolar mixtures of 1-arylphosphole oxides," *Heteroatom Chemistry*, vol. 12, no. 7, pp. 633–635, 2001.

[24] D. Klintuch, K. Krekic, C. Bruhn, Z. Benkć, and R. Pietschnig, "A rational synthetic approach to 2,5-diphenyl-β-silyl phospholes," *European Journal of Inorganic Chemistry*, vol. 2016, no. 5, pp. 718–725, 2016.

[25] J. Hydrio, M. Gouygou, F. Dallemer, J.-C. Daran, and G. G. A. Balavoine, "Convenient route for the preparation of unsymmetrical phospholes via zirconacyclopentadienes," *Journal of Organometallic Chemistry*, vol. 595, no. 2, pp. 261–267, 2000.

[26] Y. Matano, A. Saito, T. Fukushima et al., "Fusion of phosphole and 1,1′-biacenaphthene: Phosphorus(V)-containing extended π-systems with high electron affinity and electron mobility," *Angewandte Chemie International Edition*, vol. 50, no. 35, pp. 8016–8020, 2011.

[27] O. Fadhel, Z. Benkö, M. Gras et al., "3,4-Dithiaphosphole and 3,3′,4,4′-tetrathia-1,1′-biphosphole π-conjugated systems: S makes the impact," *Chemistry - A European Journal*, vol. 16, no. 37, pp. 11340–11356, 2010.

[28] K. Yavari, P. Retailleau, A. Voituriez, and A. Marinetti, "Heterohelicenes with embedded P-chiral 1H-phosphindole or dibenzophosphole units: diastereoselective photochemical synthesis and structural characterization," *Chemistry - A European Journal*, vol. 19, no. 30, pp. 9939–9947, 2013.

[29] M. Kumaravel, J. T. Mague, and M. S. Balakrishna, "Chalcogenide derivatives of 1,2,5-triphenyl-1H-phosphole: structure and photophysical properties," *Tetrahedron Letters*, vol. 55, no. 18, pp. 2957–2961, 2014.

[30] A. Oukhrib, L. Bonnafoux, A. Panossian et al., "Novel C1-symmetric dibenzophosphole ligands: application in hydroformylation reactions," *Tetrahedron*, vol. 70, no. 7, pp. 1431–1436, 2014.

[31] D. Miesel, A. Hildebrandt, M. Korb, P. J. Low, and H. Lang, "Synthesis and (spectro)electrochemical behavior of 2,5-diferrocenyl-1-phenyl-1 H-phosphole," *Organometallics*, vol. 32, no. 10, pp. 2993–3002, 2013.

[32] K. Eichele, R. E. Wasylishen, J. M. Kessler, L. Solujić, and J. H. Nelson, "Phosphorus chemical shift tensors of phosphole derivatives determined by 31P NMR spectroscopy of powder samples," *Inorganic Chemistry*, vol. 35, no. 13, pp. 3904–3912, 1996.

[33] G. M. Keseru and G. Keglevich, "Stereospecific cyclodimerization of 1-methylphosphole 1-oxide: a theoretical study," *Journal of Organometallic Chemistry*, vol. 586, no. 2, pp. 166–170, 1999.

[34] T. C. Dinadayalane and G. N. Sastry, "Density functional theory study on dimerizations of phospholes," *Organometallics*, vol. 22, no. 26, pp. 5526–5533, 2003.

[35] S. Bhai, K. Jana, and B. Ganguly, "Probing the structural and electronic effects on the origin of π-facial stereoselectivity in 1-methylphosphole 1-oxide cycloadditions and cyclodimerization," *ACS Omega*, vol. 3, no. 9, pp. 10945–10952, 2018.

[36] C. C. Santini, J. Fischer, F. Mathey, and A. Mitschler, "Phosphole [2+2] and [4+2] dimerizations around metal carbonyl moieties, structure and chemistry of a new type of exo [4+2] dimers," *Journal of the American Chemical Society*, vol. 102, no. 18, pp. 5809–5815, 1980.

[37] T. Möller, P. Wonneberger, N. Kretzschmar, and E. Hey-Hawkins, "P-chiral phosphorus heterocycles: a straightforward synthesis," *Chemical Communications*, vol. 50, no. 44, pp. 5826–5828, 2014.

[38] T. J. Barton and A. J. Nelson, "Heterocyclopentadiene photochemistry," *Tetrahedron Letters*, vol. 10, no. 57, pp. 5037–5040, 1969.

[39] M. P. Duffy, Y. Lin, L. Y. Ting, and F. Mathey, "Intramolecular [4+2] versus [2+2] cycloadditions in P-X-P-linked biphospholes (X = O, S)," *New Journal of Chemistry*, vol. 35, no. 10, pp. 2001–2003, 2011.

[40] W. L. Wilson, J. Fischer, R. E. Wasylishen et al., "Thermal coupling reactions of 1-phenyl-3,4-dimethylphosphole within the coordination sphere of Palladium(II)," *Inorganic Chemistry*, vol. 35, no. 6, pp. 1486–1496, 1996.

[41] H.-L. Ji, J. H. Nelson, A. DeCian et al., "[2+2] Photocycloadditions of $[(\eta^5\text{-}C_5H_5)$ Ru(DMPP) $_2$L]PF_6 complexes," *Journal of Organometallic Chemistry*, vol. 529, no. 1-2, pp. 395–408, 1997.

[42] C. S. Demmer, P. Aillard, J. Febvay, P. Retailleau, A. Voituriez, and A. Marinetti, "Photochemical [2+2] cyclization of helical phosphinamides in solution and in the solid state," *ChemPhotoChem*, vol. 1, no. 12, pp. 535–538, 2017.