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Diethyl (iodoethynyl)phosphonate and (iodoethynyl)diphenylphosphane oxide: crystal structures and some cycloaddition reactions

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Abstract: The title compounds are difunctionalized acetylenic building blocks, which can serve as electrophilic dienophiles and dipolarophiles in [4+2] and azide-iodoalkyne [3+2] cycloaddition reactions, which, however, require strong thermal activation. In their crystal structures, they are self-complementary tectons, which are arranged in polymeric chains maintained by very short intermolecular Csp–I···O=P halogen bonds.

Keywords: crystal structure; cycloaddition; halogen bond; iodoalkynes; PO-substituted alkynes.

1 Introduction

Acetylenes bearing both an iodo and a phosphoryl (P=O) substituent, so far unknown compounds, have attracted our interest for two reasons: the anticipated ability to form strong intermolecular I···O halogen bonds and their eventual usefulness as electrophilic dienophiles and dipolarophiles in organic synthesis.

Halogen bonds (XBs) are, by the International Union of Pure and Applied Chemistry (IUPAC) definition, the result of "a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity" [1]. In a related common description, halogen bonds are non-covalent interactions of the type R–X···Y between an electrophilic *XB donor* R–X (X = halogen) and a nucleophilic *XB acceptor* Y. In the past two decades in particular, much attention has been given to different aspects of halogen bonding, such as its theoretical description, the characterization in solution and in the solid state, as well as its increasing relevance in synthesis, crystal engineering, material chemistry and biomolecular chemistry [2–4]. The electrophilic region at the halogen atom is the so-called σ hole, a region with a positive molecular surface electrostatic potential at the halogen atom that is located at the extension of the R–X bond on the opposite side of the halogen atom [2, 5–7]. Theoretical calculations and structural data indicate that the electrophilicity (XB donor strength) of the C–Hal bond increases in the orders C–Cl < C–Br < C–I and Csp^3 < Csp^2 < Csp [8]. On the other hand, the strongly polarized P=O bond [9, 10] is one of the best XB acceptors. Thus, it can be expected that the Csp–I···O=P interaction gives rises to a very strong halogen bond. This was so far confirmed by the (few) structural data available in the Cambridge Structural Database (2013) [11] and determination of the association constants of the (4-nitrophenyl)C≡C–I···O=P(*n*-Bu)$_3$ compared to other complexes in solution [12].

In terms of synthetic methodology (iodoethynyl) phosphoryl compounds can be envisaged as useful building blocks serving as dienophiles and dipolarophiles. The chemically related diethyl (2-bromoethynyl)phosphonate has already been engaged in Ru-catalyzed [3+2] cycloadditions with a nitrone and an organoazide [13], and (2-bromoethynyl)diphenylphosphane oxide was used as a dienophile in [4+2] cycloaddition reactions [14].

2 Results and discussion

2.1 Syntheses

Ethynylphosphonate **1** was prepared from trimethylsilylacetylene following a published procedure (metalation, electrophilic phosphorylation, desilylation, see Scheme 1) [15]. Established procedures were also applied to the synthesis of phosphane oxide **4** [16–18] from TMS-C≡CH *via* ethynyldiphenylphosphane **3** [16, 17, 19]. Iodoalkynes **2** and **5** were obtained in good yields by a silver-catalyzed iodination of terminal alkynes **1** and **4** with *N*-iodosuccinimide [20]; in contrast, reactions using I_2 or ICl in the presence of various bases led to undefined product mixtures.

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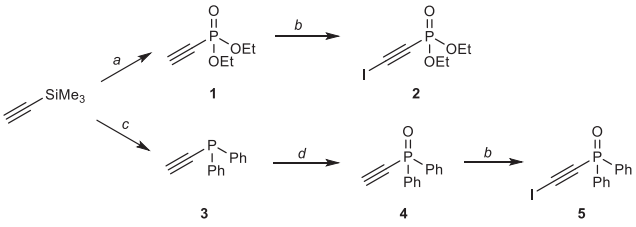


Scheme 1: Preparation of title compounds **2** and **5**. Conditions: a) 1. EtMgBr in Et_2O, TMS-acetylene in THF, r. t., 2 h; 2. $ClP(O)(OEt)_2$, THF, 0 °C, 3.5 h; 3. aq Na_2CO_3, $CHCl_3$, 30 min; 64% yield. b) NIS, $AgNO_3$ (10 mol.-%), r. t., 1 h; yield of **2**: 78%; yield of **5**: 85%. c) 1. EtMgBr, Et_2O, TMS-acetylene in THF, r .t., 2 h; 2. $ClPPh_2$, THF, –10 °C; then r. t., 3 h; 3. K_2CO_3, MeOH, r .t., 1.5 h; 92% yield. d) Aqueous H_2O_2, Et_2O, 98% yield.

2.2 Crystal structures of 2 and 5

The molecular and crystal structures of **2** and **5·CHCl$_3$** were determined by single-crystal X-ray diffraction analysis and are shown in Figures 1 and 2, respectively. As expected, both compounds are self-complementary tectons which in the solid state aggregate into infinite polymeric chains maintained by linear iodine–oxygen halogen bonds (Table 1). With iodine–oxygen distances of only 78.3 and 77.9% of the sum of van der Waals radii, these Csp–I···O=P contacts are among the shortest intermolecular iodine-oxygen contacts known so far [11]. For two 1-iodoethynyl-3,5-dinitrobenzene-pyrazine-1,4-dioxide complexes, I···O contacts of 2.673(3) and 2.734(2) Å have been reported recently [23].

In the crystal structure of **5·CHCl$_3$**, the phosphoryl oxygen atom is not only involved in an oxygen–iodine halogen bond but also in a C–H···O hydrogen bond with a chloroform solvate molecule (Figure 2).

2.3 Cycloaddition reactions

The dienophilic reactivity of alkynes **2** and **5** toward some benchmark *s-cis*-locked 1,3-dienes was tested. As the results compiled in Table 2 show, these reactions required harsh conditions and furnished the cycloaddition products in fair to good yields. Under the reaction conditions, partial decomposition of the alkyne occurred, as was indicated by the NMR-spectroscopic detection of the iodine-free alkynes HC≡C–PO(OEt)$_2$ (**1**) and HC≡C–POPh$_2$ (**4**) in the crude product mixture. A qualitative comparison with some related ethynylphosphoryl compounds shows the rather

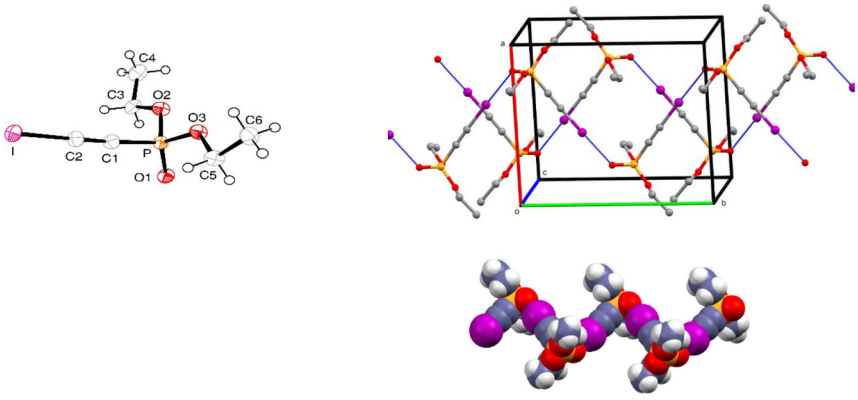


Figure 1: Solid-state molecular (left) and crystal (right) structure of **2**. Bond lengths (Å): C1–C2 1.206(7), C1–P 1.745(5), P–O1 1.463(3).

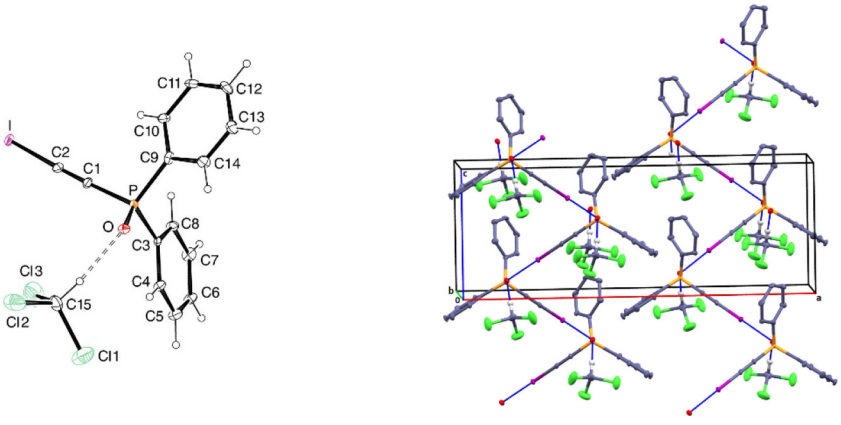


Figure 2: Solid-state molecular (left) and crystal (right) structure of **5·CHCl$_3$**. Bond lengths (Å): C1–C2 1.174(10), C1–P 1.751(7), P–O 1.487(5). Hydrogen bond: C15···O 3.050(10), C15···H15 2.12(9) A, angle C15–H···O 156(8)°.

Table 1: Geometries of (C_{sp}–)I···O halogen bond in **2** and **5·CHCl$_3$**.

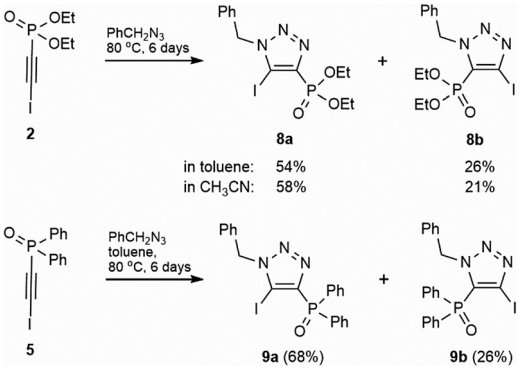
Compound	2	5·CHCl$_3$
Distances[a] (Å)		
C_{sp}–I	2.011(5)	2.030(8)
I···O	I···O1^{i} 2.742(3)	I···O^{iii} 2.727(5)
R_{XB}[b]	0.783	0.779
Angles (deg)		
C_{sp}–I···O	C2–I···O1^{i} 179.0(2)	C2–I···O^{iii} 176.9(6)
P–O···I	P–O···I^{ii} 129.5(1)	P–O···I^{iv} 124.6(3)
Torsion angle (deg)		
C1–P–O···I	48.7	65.4

[a]Symmetry codes, **2**: (i) 1 – *x*, 0.5 + *y*, 0.5 – *z*; (ii) 1 – *x*, –0.5 + *y*, 0.5 – *z*; **5·CHCl$_3$**: (iii) 0.5 – *x*, 0.5 + *y*, –0.5 + *z*; (iv) 0.5 – *x*, –0.5 + *y*, 0.5 + *z*.
[b]$R_{XB} = (d_{IO}/(r_{vdW}(I) + r_{vdW}(O))$ [21]; van der Waals radii r_{vdW} [22]: I 1.98, O 1.52 Å (XB = halogen bond).

low dienophilic reactivity of the two iodoethynylphosphoryl compounds: **2**, **5** < BrC≡C–P(O)R$_2$ (R = OEt [24], Ph [14]) < HC≡C–PO(OEt)$_2$ [25] < CF$_2$X–C≡C–PO(OEt)$_2$ (X = F, H) [26, 27]. The low reactivity of **2** and **5** is not unexpected, since a) both substituents attached to the C,C triple bond are sterically quite demanding and b) the iodo substituent hardly contributes to the electronic activation in terms of lowering the LUMO of the C≡C bond.

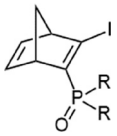
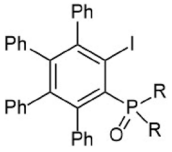
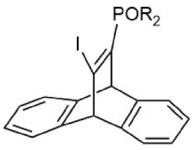
The classical thermal 1,3-dipolar cycloaddition (Huisgen reaction) of alkynes and organoazides often yields mixtures of regioisomeric 1,2,3-triazoles. Considering the only moderate reactivity of their internal acetylenic bond, it was not surprising that [3+2] cycloaddition reactions of alkynes **2** and **5** using benzyl azide as the 1,3-dipole also require strong thermal activation (Scheme 2) and reaction times of several days (complete conversion according to ^{31}P NMR monitoring). With both alkynes, a mixture of the two regioisomers of triazoles **8** and **9**, respectively, was obtained and could be separated chromatographically. The 5-iodo-1,2,3-triazoles **8a** and **9a** were formed as the major regioisomers. Their constitution was assigned based on HMBC NMR spectra, which showed a PhC*H*$_2$/*C*I correlation signal that was absent in the minor regioisomer.

Analogous results have been reported for the uncatalyzed cycloaddition of 2-phenylethyl azide and



Schema 2: Synthesis of 1,2,3-triazoles **8** and **9**.

Table 2: [4+2] Cycloaddition reactions of alkynes **2** and **5**.[a]

Diene	Product	R = OMe (6)		R = Ph (7)	
		Conditions	Yield (%)	Conditions	Yield (%)
cyclopentadiene		100 °C, 20 h	65 (**6a**)	100 °C, 22 h	68 (**7a**)
tetraphenyl-cyclopentadienone		125 °C, 10 d	75 (**6b**)	125 °C, 4 d	83 (**7b**)
anthracene		125 °C, 11 d	77 (**6c**)	125 °C, 13 d	56 (**7c**)

[a]The reactions were carried out in anhydrous toluene, using an excess of the diene component.

$BrC{\equiv}C{-}PO(OEt)_2$, whereas a Ru(II)-catalyzed variation at room temperature furnished the 5-bromo isomer regioselectively [13]. Cu(I)-catalyzed azide–iodoalkyne cycloadditions in the presence of accelerating ligands yielded 4-iodo-1,2,3-triazoles under mild conditions and with high regioselectivity [28]. We expect that these catalytic approaches will also be applicable to the triazole syntheses shown in Scheme 2.

3 Conclusion

This study has uncovered two interesting aspects of easily synthesized iodoethynyl-phosphonates and -phosphanoxides. Their ability to form strong intermolecular iodine–oxygen halogen bonds is the basis for the formation of infinite chains in the crystal lattice. Furthermore, they represent so far untapped building blocks for organic synthesis, as we have shown herein with selected examples of Diels–Alder and azide-alkyne cycloadditions, which afforded unsaturated carbocycles or 1,2,3-triazoles with adjacent iodine and phosphoryl substituents. Further research can foucus on catalytic variations of the [3+2] cycloaddition of suitable 1,3-dipoles and on synthetic opportunities offered by the Csp–I bond in the alkynes themselves and the Csp^2–I bond in the derived products.

4 Experimental section

4.1 General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 (^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz; ^{31}P: 161.98 MHz) and Avance 500 spectrometers (^{1}H: 500.14 MHz, ^{13}C: 125.76 MHz). Chemical shifts (δ) are reported in ppm. For ^{1}H and ^{13}C spectra, the solvent signal was used as an internal standard [$\delta^{H}(CHCl_3)$ = 7.26 ppm, $\delta^{C}(CDCl_3)$ = 77.16 ppm]; for ^{31}P spectra, external H_3PO_4 served as standard (δ = 0.00 ppm). The ^{13}C and ^{31}P NMR spectra were recorded in the proton-decoupled mode. IR spectra: Bruker Vector 22 FT-IR; wavenumbers (cm^{-1}) and relative intensities (s = strong, m = medium, w = weak) are given. Elemental analyses: elementar vario MICRO cube. Mass spectra: Finnigan MAT SSQ-7000 (CI, 100 eV) and Bruker solariX (HRMS-ESI, DCTB as matrix). Melting points were determined with a Büchi Melting Point B-540 apparatus; the heating rate was 2 K min^{-1}. Column chromatography: silica gel 0.063–0.200 mm, Macherey–Nagel.

4.2 Syntheses of iodoalkynes 2 and 5

4.2.1 Diethyl ethynylphosphonate (1)

The compound was prepared by a published procedure [15] from TMS-acetylene (7.36 g, 75.0 mmol) and ethyl chlorophosphate (10.83 mL, 75 mmol); an oil was obtained (7.75 g, 48 mmol, 64% yield). The NMR data agreed with literature values [29].

4.2.2 Diethyl (2-iodoethynyl)phosphonate (2)

To a solution of alkyne **1** (7.75 g, 48 mmol) in dry acetone (100 mL) was added *N*-iodosuccinimide (10.79 g, 48 mmol) followed by $AgNO_3$ (81 mg, 0.48 mmol). The mixture was stirred for 1 h under protection from light, then rapidly passed over a column filled with silica gel (200 g) and the product, which remained in the starting zone, was eluted with EtOAc. The product was isolated as a colorless solid (10.80 g, 37.5 mmol, 78% yield), m. p. 50 °C. – IR (KBr): $\tilde{\nu}$ = 2119 (s), 1239 (s), 1158 (m), 1104 (m), 1020 (s), 829 (s) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (td, J = 7.1 and 0.7 Hz, 6H), 4.10–4.22 (m, 4H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 16.18 (d, $^3J_{PC}$ = 7.1 Hz, CH_3), 26.23 (d, $^2J_{PC}$ = 45.9 Hz, C-2), 63.65 (d, $^2J_{PC}$ = 5.6 Hz, $POCH_2$), 87.04 (d, $^1J_{PC}$ = 287.6 Hz, C-1). – ^{31}P NMR ($CDCl_3$): δ = –8.68. – Anal. calcd. for $C_6H_{10}IO_3P$ (288.02): C 25.02, H 3.50; found C 24.96, H 3.49.

4.2.3 Ethynyl-diphenylphosphane (3)

The synthesis was carried by analogy to lit. [16, 19] from HC≡CMgBr (7.36 g, 75 mmol) in THF (200 mL) and chorodiphenylphosphane (13.23 g, 60 mmol). The residual oil was purified by column chromatography (230 g of silica gel, eluent EtOAc, R_f = 0.75) to obtain **2** as a colorless oil, which gradually crystallized yielding a powder (11.61 g, 55 mmol, 92% yield), m. p. 35 °C. The spectroscopic data agreed with literature data [19].

4.2.4 Ethynyl-diphenylphosphane oxide (4)

A solution of ethynylphosphane **3** (11.61 g, 55 mmol) in Et_2O (250 mL) was cooled at 0 °C and aqueous H_2O_2 (30%, 30 mL) diluted with 70 mL of water was slowly added. After stirring for 4 h, the mixture was extracted with satd. aqueous $Na_2S_2O_3$ (30 mL), the organic phase was collected and the aqueous phase extracted with 2 × 40 mL of $CHCl_3$. The combined organic phases were dried ($MgSO_4$), concentrated and the residue was submitted to column

chromatography over silica gel (200 g, EtOAc as eluent, R_f = 0.3). The product was obtained as a colorless solid (14.06 g, 54 mmol, 98% yield), m. p. 57 °C. The spectroscopic data agreed with published values [30].

4.2.5 (2-Iodoethynyl)diphenylphosphane oxide (5)

To a solution of 4 (14.06 g, 54 mmol) in anhyd acetone (100 mL) were added *N*-iodosuccinimide (12.15 g, 54 mmol) and $AgNO_3$ (82 mg, 0.54 mmol). The mixture was stirred for 1 h under protection from light, followed by work-up as described in Section 4.2.2. Colorless microcrystalline solid (11.95 g, 46 mmol, 85% yield), m. p. 144 °C. – IR (KBr): $\tilde{\nu}$ = 2105 (s), 1437 (m), 1182 (s), 1122 (m), 1100 (m), 795 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.46–7.55 (m, 6H), 7.78–7.83 (m, 4H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 32.57 (d, $^2J_{PC}$ = 21.4 Hz, C-2), 91.34 (d, $^1J_{PC}$ = 156.1 Hz, C-1), 128.82 (d, J_{PC} = 13.6 Hz), 131.11 (d, J_{PC} = 11.3 Hz), 132.51 (d, J_{PC} = 12.2 Hz), 132.57 (d, J_{PC} = 2.9 Hz). – ^{31}P NMR ($CDCl_3$): δ = 8.88. – Anal. calcd. for $C_{14}H_{10}IOP$ (352.11): C 47.76, H 2.86; found C 47.65, H 2.90.

4.2.6 [4+2] cycloadditions; general procedure

A thick-walled Schlenk tube equipped with a screw cap was purged with argon, anhydrous toluene (4 mL), alkyne **2** (or **5**) and a diene were added, and the mixture was heated at 100–125 °C, until the reaction was complete (monitoring by TLC or ^{31}P NMR). The solution was brought to r. t., the solvent was evaporated and the residue was subjected to column chromatography (30–45 g of silica gel, EtOAc as eluent). The isolated product was dried *in vacuo*.

4.2.6.1 Diethyl (3-iodobicyclo[2.2.1]hepta-2,5-dien-2-yl) phosphonate (6a)

Prepared from **2** (400 mg, 1.39 mmol) and cyclopentadiene (0.25 mL, 2.8 mmol); 100 °C/20 h. Brownish oil (320 mg, 0.90 mmol, 65% yield). – IR (KBr): $\tilde{\nu}$ = 1295 (m), 1247 (s), 1162 (m), 1023 (s), 966 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.32 (dt, J = 5.0, 7.0 Hz, 6H, CH_3), 2.02 (dd, J = 6.7, 1.5 Hz, 1H, 7-H^A), 2.27 (d, ^2J = 6.7 Hz, 1H, 7-H^B), 3.89 (broadened, 1H, CH), 3.96 (broadened, 1H, CH), 3.98–4.11 (m, 4H, OCH_2), 6.82–6.87 (m, 2H, 5,6-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 16.50 (d, $J_{P,C}$ = 6.3 Hz, CH_3), 55.51 (d, $J_{P,C}$ = 11.2 Hz, CH), 61.99 and 62.14 (two d, $J_{P,C}$ = 5.2 Hz, OCH_2), 66.56 (d, $J_{P,C}$ = 14.7 Hz, CH), 72.99 (d, $J_{P,C}$ = 5.5 Hz, C-7), 122.84 (d, $J_{P,C}$ = 9.2 Hz, CI), 140.54 (d, $J_{P,C}$ = 2.3 Hz, CH_{olef}), 142.44 (d, $J_{P,C}$ = 0.9 Hz, CH_{olef}), 146.07 (d, $^1J_{P,C}$ = 207.1 Hz, C-1). – ^{31}P NMR ($CDCl_3$): δ = 14.59. – Anal. calcd. for $C_{11}H_{16}IO_3P$ (354.12): C 37.31, H 4.55; found C 37.17, H 4.51.

4.2.6.2 Diethyl (2-iodo-3,4,5,6-tetraphenyl)benzenephosphonate (6b)

Prepared from alkyne **2** (200 mg, 0.52 mmol) and tetraphenyl-cyclopentadienone (423 mg, 1.1 mmol); 125 °C, 10 days. R_f = 0.71 ($CHCl_3$-EtOAc 3:1). The product obtained after column chromatography was washed with cold MeOH and *n*-pentane. Colorless solid (250 mg, 0.39 mmol, 75% yield), m. p. 174 °C. – IR (KBr): ν = 1247 (m), 1056 (s), 1023 (s), 965 (m), 699 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 3.66 (m_c, 2H, OCH_2), 3.98 (m_c, 2H, OCH_2), 6.59–6.77 (m, 10H), 6.98–7.21 (m, 10H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 16.21 (d, $J_{P,C}$ = 6.7 Hz, CH_3), 62.02 (d, $J_{P,C}$ = 6.5 Hz, OCH_2), 105.99 (d, $^2J_{P,C}$ = 7.4 Hz, CI), 125.73 (d, $J_{P,C}$ = 30.3 Hz), 126.67 (d, $J_{P,C}$ = 4.9 Hz), 126.77 (d, $J_{P,C}$ = 46.6 Hz), 126.82 (s), 127.12 (d, $J_{P,C}$ = 84.8 Hz), 130.49 (s), 130.58 (d, $J_{P,C}$ = 63.3 Hz); further signals between 131.72 and 148.42, see the Supporting Information (available online). – ^{31}P NMR ($CDCl_3$): δ = 15.62. – MS (CI): m/z = 644 $[M+H]^+$. – Anal. calcd. for $C_{34}H_{30}IO_3P$ (644.49): C 63.66, H 4.69; found C 63.63, H 4.65.

4.2.6.3 Diethyl {16-iodotetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,9(14),10,12,15-heptaen-15-yl}phosphonate (6c)

Prepared from alkyne **2** (200 mg, 0.52 mmol) and anthracene (356 mg, 2 mmol); 125 °C, 12 days. Purification by two subsequent column chromatography runs (1.60 g of silica gel, cyclohexane-$CHCl_3$ (1:1) as eluent; 2.60 g of silica gel, EtOAc-*n*-hexane (1:1), R_f = 0.43). The obtained colorless solid was washed with pentane and dried *in vacuo*. Yield: 190 mg (0.40 mmol, 77%) of a colorless solid, m. p. 117 °C. – IR (KBr): $\tilde{\nu}$ = 1257 (s), 1061 (m), 1016 (s), 966 (m) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (td, J ~ 8, 5 Hz, 6H, CH_3), 3.78–3.88 (m_c, 2H, OCH_2), 3.92–4.03 (m_c, 2H, OCH_2), 5.54 (d, J = 4.3 Hz, 1H, $CH_{bridgehead}$), 5.62 (d, J = 9.0 Hz, 1H, $CH_{bridgehead}$), 6.99–7.06 (m, 4H), 7.32–7.38 (m, 4H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 16.28 (d, $J_{P,C}$ = 6.7 Hz, CH_3), 55.69 (d, $J_{P,C}$ = 9.1 Hz, $CH_{bridgehead}$), 62.29 (d, $J_{P,C}$ = 4.8 Hz, OCH_2), 68.80 (d, $J_{P,C}$ = 12.5 Hz, $CH_{bridgehead}$), 118.36 (d, $^2J_{P,C}$ = 7.0 Hz, CI), 123.37, 123.73, 125.33, 125.87, 142.98 (d, $J_{P,C}$ = 3.0 Hz, C_{Ar}), 143.06 (d, $J_{P,C}$ = 2.5 Hz, C_{Ar}), 143.09 (d, $J_{P,C}$ = 196.4 Hz, P–C). – ^{31}P NMR ($CDCl_3$): δ = 13.65. – MS (CI): m/z = 467 $[M+H]^+$. – Anal. calcd. for $C_{20}H_{20}IO_3P$ (466.26): C 51.52, H 4.32; found C 51.17, H 4.38.

4.2.6.4 2-(Diphenylphosphoryl)-3-iodobicyclo[2.2.1] hepta-2,5-diene (7a)

Prepared from alkyne **5** (500 mg, 1.42 mmol) and cyclopentadiene (180 mg, 2.8 mmol); 100 °C, 22 h. R_f = 0.46 (EtOAc). Colorless solid (400 mg, 0.96 mmol, 68% yield), m. p. 98 °C. – IR (KBr): $\tilde{\nu}$ = 1437 (s), 1295 (m), 1184 (s), 1118 (s), 1019 (m), 723 (s) cm^{-1}. – ^1H NMR ($CDCl_3$,

500 MHz): δ = 1.89/2.26 (AB system, $^2J_{HH}$ = 6.7 Hz, 2H, 7-H_2), 3.77 and 3.84 (2 s, 2H, 1,4-H), 6.60 (dd, J = 5.0, 2.9 Hz, 1H, CH_{olefin}), 6.74 (dd, J = 4.8, 3.2 Hz, 1H, CH_{olefin}), 7.33–7.40 (m, 4H, CH_{Ph}), 7.40–7.46 (m, 2H, CH_{Ph}), 7.52–7.58 (m, 4H, CH_{Ph}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 55.65 (d, $J_{P,C}$ = 10.1 Hz, C-1 or C-4), 67.47 (d, $J_{P,C}$ = 10.2, C-4 or C-1), 72.53 (d, $J_{P,C}$ = 4.3 Hz, C-7), 122.76 (d, $^2J_{P,C}$ = 6.0 Hz, CI), 128.53 (d, $J_{P,C}$ = 3.5 Hz, CH_{Ph}), 128.63 (d, $J_{P,C}$ = 3.4 Hz, CH_{Ph}), 130.76 (d, $J_{P,C}$ = 65.0 Hz, C_{Ph}), 131.19 (d, $J_{P,C}$ = 43.0 Hz, C_{Ph}), 131.77 (d, $J_{P,C}$ = 7.1 Hz, CH_{Ph}), 131.85 (d, $J_{P,C}$ = 7.3 Hz, CH_{Ph}), 132.00 (d, $J_{P,C}$ = 3.0 Hz, CH_{Ph}), 132.02 (d, $J_{P,C}$ = 3.0 Hz, CH_{Ph}), 140.10 (d, $J_{P,C}$ = 1.9 Hz, CH_{Ph}), 142.25 (d, $J_{P,C}$ = 0.6 Hz, CH_{Ph}), 148.21 (d, $^1J_{P,C}$ = 112.4 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = 25.20. – Anal. calcd. for $C_{19}H_{16}IOP$ (418.21): C 54.57, H 3.86; found C 54.80, H 3.87.

4.2.6.5 1-(Diphenylphosphoryl)-2-iodo-3,4,5,6-tetraphenylbenzene (7b)

Prepared from alkyne **5** (300 mg, 0.85 mmol) and tetraphenyl-cyclopentadienone (610 mg, 1.5 mmol); 125 °C, four days. R_f = 0.50 ($CHCl_3$-EtOAc (3:1)). Colorless solid (500 mg, 0.71 mmol, 83% yield), m. p. 299 °C. – IR (KBr): $\tilde{\nu}$ = 1489 (m), 1437 (s), 1371 (m), 1168 (s), 1104 (m), 1072 (m), 1022 (m), 762 (m) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.52–6.85 (m, 15H), 6.99–7.03 (m, 2H), 7.07–7.25 (m, 9H), 7.51–7.58 (m, 4H). – $^{13}C\{^1H\}$ NMR: see the Supporting Information. – ^{31}P NMR ($CDCl_3$): δ = 31.70. – HRMS (ESI): m/z = 708.1078; calcd. for $[M+H]^+$: 708.1079. – Anal. calcd. for $C_{42}H_{30}IO_3P$ (708.58): C 71.19, H 4.27; found C 71.21, H 4.30.

4.2.6.6 15-(Diphenylphosphoryl)-16-iodotetracyclo[6.6.2.0^{2,7}.8^{9,14}]hexadeca-2,4,6,9(14),10,12,15-heptaene (7c)

Prepared from alkyne **5** (400 mg, 1.14 mmol) and anthracene (445 mg, 5.5 mmol); 125 °C, 13 days. Purification by repeated column chromatography (1. silica gel (100 g), $CHCl_3$-EtOAc (3:1), R_f = 0.49); 2.50 g of silica gel, $CHCl_3$-cyclohexane (1:1), R_f = 0.10). Colorless solid (340 mg, 0.64 mmol, 56% yield), m. p. 176 °C. – IR (KBr): $\tilde{\nu}$ = 1195 (s), 1117 (s), 1102 (m), 749 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.18 (d, J = 8.7 Hz, 1H, $H_{bridgehead}$), 5.56 (d, J = 3.0 Hz, 1H, $H_{bridgehead}$), 6.97–7.04 (m, 6H), 7.35–7.57 (m, 12H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 56.21 (d, $J_{P,C}$ = 10.0 Hz, $CH_{bridgehead}$), 69.53 (d, $J_{P,C}$ = 8.6 Hz, $CH_{bridgehead}$), 119.00 (d, $^2J_{P,C}$ = 4.4 Hz, CI), 123.33, 123.63, 125.25, 125.67, 128.69 (d, $J_{P,C}$ = 12.5 Hz), 130.91 (d, $^1J_{P,C}$ = 108.0 Hz, PC_{Ph}), 132.06 (d, $J_{P,C}$ = 10.3 Hz), 132.23 (d, $J_{P,C}$ = 2.7 Hz), 142.56 (d, $J_{P,C}$ = 2.7 Hz), 143.18 (d, $J_{P,C}$ = 1.9 Hz), 144.82 (d, $^1J_{P,C}$ = 103.7 Hz, PC=). – ^{31}P NMR ($CDCl_3$): δ = 29.54. – MS (CI): m/z = 531 $[M+H]^+$. – Anal. calcd. for $C_{28}H_{20}IOP$ (530.35): C 63.41, H 3.80; found C 63.06, H 3.87.

4.3 [3+2] Cycloaddition reactions

4.3.1 Diethyl (1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl) phosphonate (8a) and diethyl (1-benzyl-4-iodo-1*H*-1,2,3-triazol-5-yl)phosphonate (8b)

A thick-walled Schlenk tube fitted with a screw cap was purged with argon and charged with a solution of benzyl azide (533 mg, 4.0 mmol) and alkyne **2** (1.00 g, 3.47 mmol) in anhydrous acetonitrile (6 mL). After heating at 80 °C for six days, the reaction mixture was brought to r. t., the solvent was evaporated, and the residue was subjected to column chromatography (silica gel (150 g), elution with EtOAc-cyclohexane (1:1) to furnish **8b** (R_f = 0.56) and **8a** (R_f = 0.15).

Isomer **8a**: yellowish solid (780 mg, 1.85 mmol, 54% yield), m. p. 71 °C. – IR (KBr): $\tilde{\nu}$ = 2117 (s), 1456 (s), 1392 (m), 1261 (s), 1200 (s), 1160 (s), 1103 (s), 1017 (s), 796 (m), 724 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.37 (td, J = 7.1, 0.5 Hz, 6H, CH_3), 4.17–4.31 (m, 4H, OCH_2), 5.65 (s, 2 H, PhCH_2), 7.27–7.38 (m, 5 H, CH_{Ph}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz): δ = 16.38 (d, J_{PC} = 6.6 Hz, CH_3), 54.43 (s, PhCH_2), 63.44 (d, J_{PC} = 5.8 Hz, OCH_2), 86.24 (d, $^2J_{PC}$ = 34.0 Hz, CI); 128.07, 128.85, 129.08 (3 s, CH_{Ph}); 133.71 (s, C_{Ph}), 142.54 (d, $^1J_{PC}$ = 242.6 Hz, PC=). – ^{31}P NMR ($CDCl_3$): δ = 5.66. – HRMS ((+)-ESI): m/z = 443.9944; calcd. 443.9950 $[M+Na]^+$. – Anal. calcd. for $C_{13}H_{17}IN_3O_3P$ (421.1): C 37.07, H 4.07, N 9.98; found C 37.08, H 4.11, *N* 10.00.

Isomer **8b**: yellowish very viscous oil (380 mg, 0.90 mmol, 26% yield). – IR (KBr): $\tilde{\nu}$ = 1456 (s), 1261 (s), 1200 (s), 1160 (s), 1103 (s), 1021 (s), 796 (s), 724 (s), 696 (m) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (td, J = 7.1, 0.6 Hz, 6H, CH_3), 3.83–4.04 (m, 4H, OCH_2), 5.96 (s, 2H, PhCH_2), 7.28–7.39 (m, 5H, H_{Ph}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 16.12 (d, J_{PC} = 6.7 Hz, CH_3), 54.68 (s, PhCH_2), 63.63 (d, J = 5.4 Hz, CH_2), 96.81 (d, $^2J_{PC}$ = 19.5 Hz, CI), 128.37 (s, C_{Ph}), 128.63 (s, C_{Ph}), 128.77 (s, C_{Ph}), 128.97 (d, $^1J_{PC}$ = 220.3 Hz, PC=), 135.22 (s, C_{Ph}). – ^{31}P NMR ($CDCl_3$): δ = 12.38. – HRMS ((+)-ESI): m/z = 443.9944, calcd. 443.9950 $[M+Na]^+$. – Anal. calcd. for $C_{13}H_{17}IN_3O_3P$ (421.1): C 37.07, H 4.07, N 9.98; found C 37.06, H 4.13, N 9.92.

4.3.2 1-Benzyl-4-(diphenylphosphoryl)-5-iodo-1*H*-1,2,3-triazole (9a) and 1-benzyl-5-(diphenylphosphoryl)-4-iodo-1*H*-1,2,3-triazole (9b)

A thick-walled Schlenk tube fitted with a screw cap was purged with argon and charged with a solution of benzyl azide (100 mg, 0.8 mmol) and alkyne **5** (200 mg, 0.57 mmol) in anhydrous acetonitrile (4 mL). After heating at 80 °C for

nine days, the reaction mixture was brought to r. t., the solvent was evaporated, and the residue was subjected to column chromatography (silica gel (30 g), elution with $CHCl_3$-EtOAc (3:1) to furnish **9b** (R_f = 0.71) and **9a** (R_f = 0.26).

Isomer **9a**: yellowish solid (190 mg, 0.39 mmol, 68% yield), m. p. 175 °C. – IR (KBr): $\tilde{\nu}$ = 1436 (s), 1409 (m), 1221 (m), 1189 (s), 1120 (m), 1028 (w), 785 (m), 727 (s), 696 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.65 (s, 2H, PhCH_2), 7.27–7.38 (m, 5H, CH_{Bn}), 7.44–7.58 (m, 6 H, CH_{Ph}), 7.81–7.88 (m, 4 H, CH_{Ph}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 54.05 (s, PhCH$_2$). 86.52 (d, $^2J_{P,C}$ = 24.7 Hz, CI); signals between 128.01 and 133.67, see the Supporting Information; 143.96 (d, $^1J_{P,C}$ = 136.5 Hz, PC=). – ^{31}P NMR ($CDCl_3$): δ = 17.56. – MS: (CI): m/z = 486 $[M+H]^+$. – Anal. calcd. for $C_{21}H_{17}IN_3OP$ (485.27): C 51.98, H 3.53, N 8.66; found C 51.70, H 3.68, N 8.38.

Isomer **9b**: yellowish solid (70 mg, 0.14 mmol, 26% yield), m. p. 168 °C. – IR (KBr): $\tilde{\nu}$ = 1435 (s), 1037 (m), 1290 (m), 1229 (m), 1200 (s), 1143 (m), 1119 (s), 1002 (m), 749 (m), 724 (s), 689 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.15 (s, 2H, PhCH_2), 6.98–7.16 (m, 5H, CH_{Bn}), 7.38–7.44 (m, 4H, CH_{Ph}), 7.48–7.59 (m, 6H, CH_{Ph}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 55.02 (s, PhCH$_2$), 97.46 (d, $^2J_{P,C}$ = 16.0 Hz, CI); several signals between 128.23 and 129.73, see the Supporting Information; 130.47 (d, $^1J_{P,C}$ = 110.4 Hz, PC=); 132.29 (d, $J_{P,C}$ = 10.9 Hz, CH_{Ph}), 133.17 (d, $J_{P,C}$ = 2.9 Hz, CH_{Ph}), 134.60 (s, i-C_{Bn}). – ^{31}P NMR ($CDCl_3$): δ = 19.82. – MS: (CI): m/z = 486 $[M+H]^+$. – Anal. calcd. for $C_{21}H_{17}IN_3OP$ (485.27): C 51.98, H 3.53, N 8.66; found C 51.78, H 3.47, N 8.55.

Table 3: Crystal structure data for **2** and **5·CHCl$_3$**.

	2	**5·CHCl$_3$**
Formula	$C_6H_{10}IO_3P$	$C_{14}H_{10}IOP \times CHCl_3$
M_r	288.01	471.46
Cryst. size, mm^3	0.21 × 0.18 × 0.08	0.22 × 0.18 × 0.15
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a, Å	10.3741(7)	22.2610(7)
b, Å	12.0407(4)	9.6471(4)
c, Å	8.0624(5)	8.4199(3)
β, deg	98.319(6)	90
V, Å^3	996.5(1)	1808.2(1)
Z	4	4
D_{calcd}, g cm^{-3}	1.920	1.732
μ(Mo$K\alpha$), mm^{-1}	3.34	2.30
F(000), e	552	912
Temperature, K	150(2)	150(2)
hkl range	$-12 \le h \le +12$, $-15 \le k \le +15$, $-8 \le l \le +10$	$-26 \le h \le +27$, $-6 \le k \le +12$, $-7 \le l \le +10$
θ range, deg	3.06–26.37	3.03–26.37
Refl. measured	7443	5572
Refl. unique/R_{int}	2030/0.0540	3033/0.0361
Param. refined	102	194
$R(F)/wR(F^2)$[a] [$I > 2\sigma(I)$]	0.0358/0.0543	0.0329/0.0706
$R(F)/wR(F^2)$[a] (all refl.)	0.0658/0.0766	0.0399/0.0760
GoF (F^2)[a]	1.080	1.034
Flack parameter x	–	−0.020(36)
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.26/−0.76	0.93/−1.02

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$; GoF = $[\Sigma w(|F_o| - |F|_c)^2/(N_{obs}-N_{param})]^{1/2}$.

4.4 X-ray structure determinations

Single crystals were obtained from Et_2O (**2**) or by diffusion crystallization from $CHCl_3$-*n*-pentane (**5·CHCl$_3$**). The data collection was performed on an Oxford Diffraction diffractometer (SuperNova, Dual Source, Atlas CCD) using MoKα radiation. Software for structure solution and refinement: SHELXS-97 [31] and SHELXL-2014/16 [32]; molecule plots: ORTEP-3 [33] and MERCURY [34]. Further details are provided in Tables 1 and 3.

CCDC 1992727 (**2**) and 1992728 (**5·CHCl$_3$**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/getstructures.

5 Supporting information

NMR spectra (^1H, ^{13}C, ^{31}P) of synthesized compounds are given as Supplementary Material available online (DOI: 10.1515/znb-2020-0047).

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