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Organophosphorus Compounds. Part 151:[1] Synthesis and Reactivity of a Novel Isophosphinoline Derivative

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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Abstract—Regiospecific 1,3-dipolar cycloadditions of the carbonyl ylide **2**, generated thermally from the oxirane **1**, to the phosphaalkynes **3** furnish the polycyclic phosphaalkenes **4**. The reaction of **4a** with sulfur or gray selenium leads to the thia- or selenaphosphirane derivatives **5**. An oxidation of the phosphorus atom in **5a** can be achieved by the addition of a stoichiometric amount of sulfur and affords the thioxothiaphosphirane derivative **6**. Thermolysis of the phosphaalkenes **4a–c** gives an unexpected result: rearrangement of the ring skeleton with cleavage of the alkyl substituent at the P/C double bond to afford the isophospholine system **7** occurs. The constitution of compound **7** was deduced from its spectral data and confirmed by reactivity studies.

Introduction

Just recently, the synthetic potential of carbonyl ylide dipoles for the preparation of oxygen-containing heterocyclic systems, which has been widely used in the synthesis of natural products for a long time,[2–4] has also been exploited in the chemistry of phosphaalkynes.[5] In this way, the reactions of isomünchnones with phosphaalkynes have led to novel 1,3-oxaphosphole derivatives.[6] The carbonyl ylide dipole **2**, generated under thermal conditions from 2,3-diphenylindenone oxide (**1**), has proved in this context to be a suitable reaction partner for the phosphaalkyne **3a**.[7] Since the thus formed polycyclic phosphaalkene derivative **4a** exhibited a remarkable reactivity in initial studies, further investigations of this system were undertaken and the results are presented in the actual paper.

Results and Discussion

Synthesis of the phosphaalkenes 4a–d

Cleavage of the C–C single bond in acceptor-substituted oxiranes under thermal stress can be considered as a characteristic reaction for this class of compounds.[8] This leads to the formation of carbonyl ylide structures, as has been unambiguously demonstrated by numerous trapping reactions with suitable dipolarophiles.[9] A ring opening of this type is also observed when 2,3-diphenylindenone oxide (**1**) is warmed and leads to the dark-red carbonyl ylide dipole **2**.[10]

On thermolysis of **1** in the presence of the phosphaalkynes **3a–d** in dichloromethane as solvent the polycyclic, oxygen-bridged phosphaalkene derivatives **4a–d** are obtained through the intermediate **2** (Scheme 1). Work-up and purification by flash chromatography affords the products as light yellow solids, some of which are even analytically pure. The phosphaalkene derivatives **4a–d** can be stored for several days without the necessity for inert gas protection. This remarkable stability towards atmospheric oxygen and moisture is, on the whole, rather unusual for phosphaalkenes.[11] However, it can be easily explained in terms of the high steric shielding of the reactive phosphaalkene increment by the voluminous alkyl group and the two phenyl rings.[5]

The yields of **4a**, **4b** and **4d** obtained (52–75%) are satisfactory while that of **4c** is disappointingly low (28%).

A regiospecific reaction was observed in each case, the employed phosphaalkynes **3a–d** always attacked the carbonyl ylide dipole **2** in a non-charged controlled cycloaddition. This behavior has already been recognized as a characteristic property of this class of dipoles.[5]

The constitutions of compounds **4a–d** were unambiguously deduced from their NMR and mass spectral data. Thus, the ^{31}P NMR signals between δ=261 and δ=268 indicate the presence of a P/C double bond in the isolated products **4a–d**.[11] Further diagnostically relevant signals are found in the ^{13}C NMR spectra. Here, the two bridgehead carbon atoms C-1 and C-9 as well as the carbon atom C-10 of the P/C

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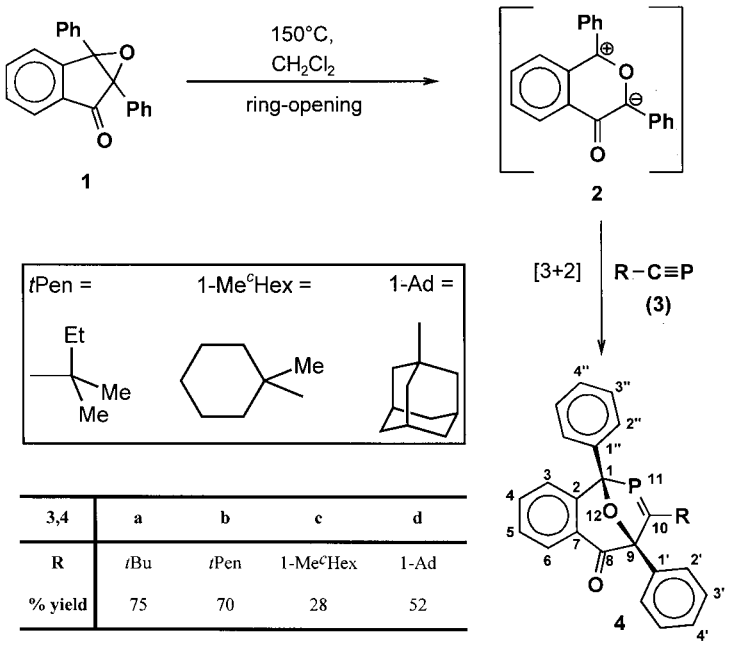
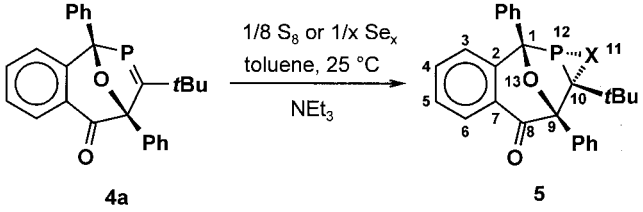


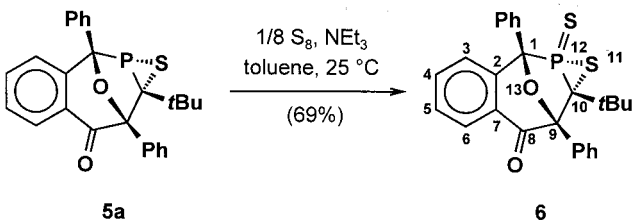
3,4	a	b	c	d
R	*t*Bu	*t*Pen	1-Me^{c}Hex	1-Ad
% yield	75	70	28	52

Scheme 1.

double bond give rise to three characteristic signals that differ only slightly among the newly prepared compounds **4a–d** and thus demonstrate the identical regiochemistries.

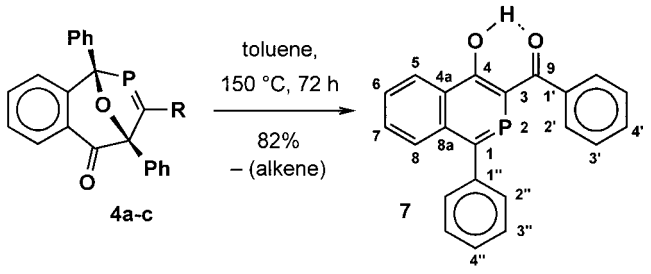
The signals of the carbon atom C-10 with chemical shifts between δ=210 and δ=214 are in the typical region for phosphaalkenes. The measured $^1J_{C,P}$ coupling constants are on average 45 Hz. The signals of the bridgehead carbon atoms C-1 and C-9 are also of major importance for the exact structural elucidation of the cycloaddition products **4a–d** with their chemical shifts between δ=94.4 and δ=94.8 and δ=97.6 and δ=98.2, respectively. As a result of the neighboring carbonyl group the carbon atoms C-9 are assigned to the more strongly downfield shifted signals. However, in all the products these signals show a doublet splitting of on average 9 Hz which corresponds to a $^2J_{C,P}$ coupling. When the signals of the bridgehead carbon atoms C-1 are considered an appreciably larger doublet splitting of on average 38 Hz is seen which is obviously caused by a $^1J_{C,P}$ coupling. Thus, it is possible to determine the constitutions of the phosphaalkenes **4a–d** on the basis of these data.





5	a	b
X	S	Se
% yield	57	59

Scheme 2.



Scheme 3.

Reactivity of the phosphaalkene 4a towards chalcogens

On reaction of the phosphaalkene **4a** with an equimolar amount of sulfur or gray selenium at room temperature the polycyclic compounds **5a**,**b** are obtained in high selectivities (Scheme 2). Although the reactions do proceed at room temperature, the addition of triethylamine to the reaction mixture is essential in order to avoid excessively long reaction times.

When the thiaphosphirane **5a** is treated with a further equivalent of sulfur, selective formation of the thioxothiaphosphirane **6** occurs. Compound **6** is also obtained when the phosphaalkene **4a** is allowed to react with 2 equiv. of sulfur; **5a** can be detected as an intermediate by ^{31}P NMR spectroscopy in the latter reaction.

The ^{31}P NMR spectra of products **5a**,**b** exhibit signals at $\delta=-65.0$ and $\delta=-41.1$, i.e. in the typical region for the currently known thia- and selenaphosphiranes and thus support the proposed structures.[12,13] Further evidence for these structures is provided by the ^{13}C NMR spectra which no longer contain the characteristic signal for the phosphaalkene carbon atom of the starting material **4a** at $\delta=212.5$. In its place the spectrum of compound **5a** contains a new signal at $\delta=73.2$ which, on account of its $^{1}J_{C,P}$ coupling constant of 43.8 Hz, can be assigned to the carbon atom C-10.

From the stereochemical point of view, the described syntheses of **5a**,**b** could furnish two diastereomers that differ in the position of the sulfur or selenium atom, respectively, relative to the oxygen bridge. However, as can be seen already from the respective ^{31}P NMR spectra, only one diastereomer is formed in each case. Analysis of the configurations requires a detailed discussion of the $^{2}J_{C,P}$ coupling constants: in general, $^{2}J_{C,P}$ coupling constants show a pronounced dependence on the relative positions of the respective carbon atom to the free electron pair at the phosphorus atom.[14–16] If they are in a *syn*-orientation the $^{2}J_{C,P}$ coupling constants reach relatively large values whereas with an *anti*-orientation only small values are achieved. In the case of compound **5a**, therefore, the doublet splittings of the signals for the quaternary carbon of the *tert*-butyl substituents and for the *ipso*-carbon atom C-1″ of the phenyl substituents at C-1 would be decisive. In the present case, $^{2}J_{C,P}$ coupling constants of 7.2 and 17.7 Hz were measured for these signals. From this it can be deduced that not only the *tert*-butyl substituent at C-10 but also the phenyl group at C-1 must be in approximately *syn*-relationships to the free electron pair at the phosphorus atom. This means that the approach of the sulfur atom to the P/C double bond in **4a** must have occurred from the side of the molecule opposite the oxygen bridge and this defines the structure of **5a**. Since compound **5a** occurs as an intermediate in the formation of **6**, the stereochemistry of **6** can also be deduced on the basis of this discussion.

The ^{31}P NMR spectrum of **6** shows a typical resonance at $\delta=21.5$ for a compound with a $\lambda^5\sigma^4$-phosphorus atom.[17] Thus, compound **6** well complements the series of known thioxothiaphosphiranes exhibiting signals with similar chemical shifts in their ^{31}P NMR spectra.[18–21]

In the ^{31}P NMR spectrum of the newly synthesized selenaphosphirane **5b** an additional $^{1}J_{P,Se}$ coupling constant of 125 Hz is also observed and can be considered to be of a magnitude typical for this class of compounds.[13] As expected the ^{13}C NMR spectrum of **5b** is closely analogous to that of **5a**. Similar to the case for compound **5a**, an analysis of the $^{2}J_{C,P}$ coupling constants allows the unequivocal determination of the configurations at C-10 and P-12. As expected, the directions of attack of selenium and sulfur at the P/C double bond are the same.

Thermolysis of the phosphaalkenes 4a–c

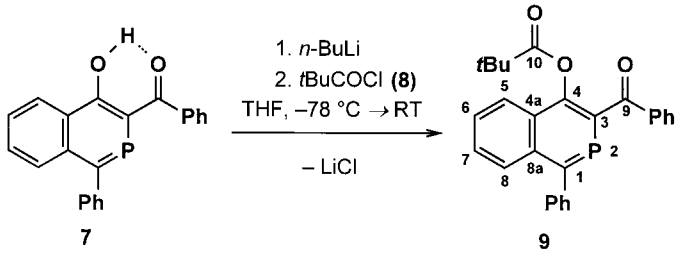
When the polycyclic phosphaalkenes **4a**–**c** are heated for 72 h at 150°C, the highly selective formation of a single new compound giving a signal at $\delta=197.4$ is observed by ^{31}P NMR spectroscopy. The formation of this new compound is strongly dependent on the solvent used. The synthesis proceeds best in toluene, less efficiently in THF, while in dichloromethane only a very low conversion is observed. The new compound was purified by flash chromatography and then obtained in the form of an analytically pure, bright yellow solid in a yield of up to 82%. Evaluation of the analytical data leads to the sole conclusion that the product must be the isophosphinoline derivative **7** shown (Scheme 3).

A remarkable feature of this conversion of the phosphaalkenes **4a**–**c** into the isophosphinoline **7** is the complete loss of the alkyl substituents present on the original P/C double bond of **4a**–**c**; the mechanism for this reaction cannot as yet be satisfactorily rationalized.

Compound **7** also exhibits a remarkable stability to atmospheric oxygen. Apparently, the complete substitution of the phosphorus-containing ring of the structure has a stabilizing effect on compound **7**. The unsubstituted isophosphinoline skeleton was described by *Bickelhaupt* as being extremely reactive and very sensitive to hydrolysis.[22]

The isophosphinoline derivative **7** described here is the first member of this class of compounds to be isolated in pure form. Although the synthesis of two further 4-hydroxyisophosphinolines was reported by Dötz in 1993, these compounds, however, could not be separated from accompanying products present in the reaction mixture.[23]

The ^{31}P NMR spectrum provides the first useful information for the structural elucidation of compound **7**. Thus, the phosphorus chemical shift of $\delta=197.4$ is in the typical



Scheme 4.

range for a phosphorus-containing aromatic system.[24] The ^{1}H NMR spectrum contains a signal for the hydroxy proton at δ=15.6. This dramatic low field shift is a convincing indication for its incorporation in an intramolecular, chelating hydrogen bond.[25] A similar situation is found in the enol form of acetylacetone with a signal at δ=15.4.[26] The IR spectrum of **7** also provides evidence for the presence of a hydrogen bond. Thus, a very broad band of weak intensity is observed in the region between 2300 and 3200 cm^{-1} which is typical for systems of this type.[26] In addition, the IR spectrum no longer contains any characteristic absorptions for a carbonyl group but instead only a broad band at 1601 cm^{-1}.

The ^{13}C NMR spectrum of the isophosphinoline **7** contains a signal for the carbon atom C-1 at δ=203.8, the corresponding $^1J_{C,P}$ coupling constant of 32.9 Hz is relatively small. The carbon atoms C-3 and C-4 give rise to further characteristic signals at δ=140.9 and δ=164.9.

A mechanistic rationalization for the formation of the isophosphinoline **7** upon thermolysis of the phosphaalkenes **4a–c** is difficult, especially since no intermediates can be detected or identified by ^{31}P NMR spectroscopy. Various experimental findings, however, are suggestive of a radical course for these reactions.

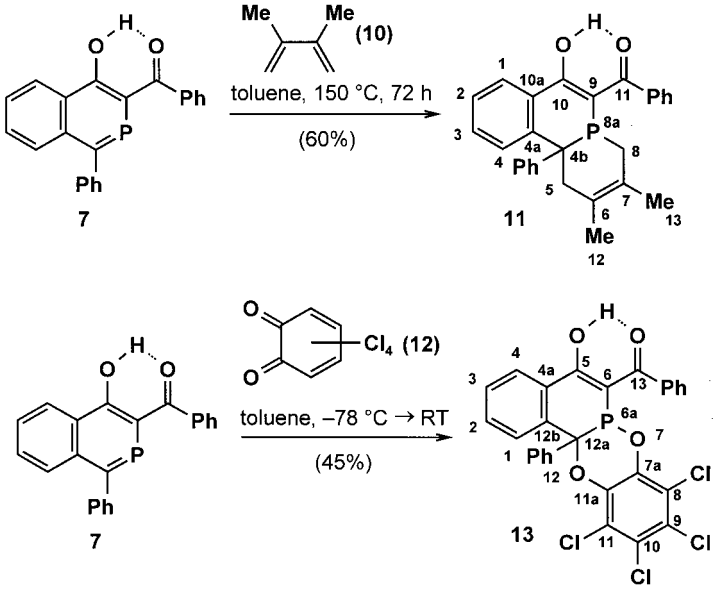
Thus, the formation of the isophosphinoline **7** proceeds preferentially in toluene as solvent. Non-polar solvents such as toluene are known to favor homolytic bond cleaving processes leading to radicals.[27] In addition, it is not possible to achieve an ionic ring opening of the polycyclic system **4a** by addition of electrophiles to the oxygen bridge.

As a first working hypothesis, we can formulate a cleavage of the alkyl substituents by way of the corresponding tertiary alkyl radical which is stabilized by formation of the corresponding alkene. The formal transfer of hydrogen from the detached alkyl residue also offers an elegant explanation for the formation of the hydroxy group. However, this mode of reaction is not possible for the adamantyl-substituted derivative **4d** since *Bredt's rule* forbids the creation of a C/C double bond in the adamantane skeleton. When the thermolysis of the derivative **4d** is carried out under the respective reaction conditions the formation of the isophosphinoline **7** is indeed not observed, instead the phosphaalkene **4d** decomposes in an unspecific manner.

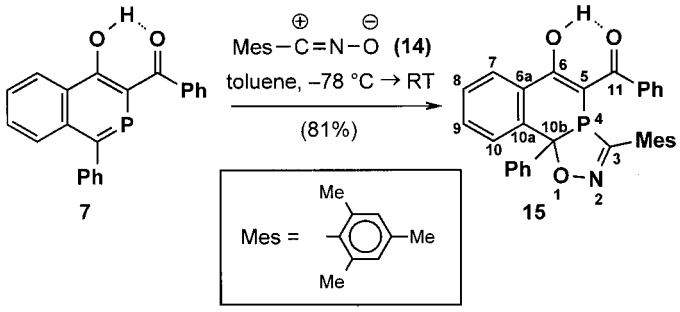
Reactivity of the isophosphinoline 7

Esterification. The chemical confirmation of the presence of the hydroxy group in **7** is provided by deprotonation with *n*-butyllithium and subsequent reaction with the acid chloride **8**. The ester **9** (Scheme 4) is formed in this manner.

The esterification of **7** is evident from the ^{1}H NMR spectra



Scheme 5.



Scheme 6.

of the product **9** in which the signal for the hydroxy proton is no longer present. Instead the spectrum of **9** contains a signal for the newly introduced alkyl group. The ^{31}P NMR signal of the newly prepared compound **9** is, as expected, relatively similar and, in comparison to the starting material **7**, shows a slight shift to higher field. As a result of the absence of the intramolecular hydrogen bond in **9** a typical carbonyl band at around 1700 cm^{-1} is now visible in the IR spectra. Also, the characteristic ^{13}C NMR chemical shifts of the carbon atoms C-1, C-3, C-4 in compound **9** show only minor differences to those of the starting material **7**.

[4+2] Cycloaddition. According to our current knowledge, phosphinine derivatives can only act as dienophiles in [4+2] cycloaddition reactions with 2,3-dimethylbutadiene **10** to give satisfactory yields of products when the phosphorus atom has been complexed with a transition metal fragment prior to the reaction.[28] The isophosphinoline derivative **7**, on the other hand, reacts completely with the diene **10** on heating at 150°C. Chromatographic work-up furnishes the cycloaddition product **11** as a light yellow solid in 60% yield (Scheme 5).

The ^{31}P NMR signal of the cycloaddition product **11** at $\delta=-49.5$ by itself is rather characteristic for a cycloaddition product from dimethylbutadiene and an alkyl- or aryl-substituted phosphaalkene.[29] Further confirmation for the proposed structure is provided by the ^{1}H NMR spectrum. The signal for the bridging hydrogen atom is seen at $\delta=17.8$, and the diastereotopic protons at C-5 and C-8 give rise to three complex multiplets between $\delta=1.90$ and $\delta=2.87$. As in the starting material **7** typical carbonyl absorptions cannot be seen in the IR spectrum of **11** on account of the hydrogen bond to the benzoyl substituent at C-9, instead only a broad absorption at 1600 cm^{-1} is present. In the ^{13}C NMR spectrum, the signal at $\delta=42.2$ can be attributed to the carbon atom C-4b; the differentiation from the methylene carbon atoms C-5 and C-8 is unambiguously achieved by means of a ^{13}C-DEPT experiment. In this respect, however, the very small $^{1}J_{C,P}$ coupling constant of merely 3.9 Hz to the quaternary carbon atom is worthy of note.

The constitution of the polycyclic compound **11** was also confirmed by X-ray crystallography. However, the quality of the data set obtained does not allow a detailed discussion of bond lengths and angles.

When the heterodiene **12** is used as the [4+2] cycloaddition partner for the isophosphinoline **7**, complete conversion to the polycyclic compound **13** occurs under appreciably milder conditions. After recrystallization of the crude product from dichloromethane/*n*-pentane the addition product **13** is obtained as an analytically pure, light yellow solid (Scheme 5).

The mass spectrum of the obtained product provides decisive evidence for its constitution: the observed isotope distribution of the molecular ion peak resulting from the halogen substitution is exactly simulated by the usual methods.[5] The ^{31}P NMR spectrum of compound **13** also shows an appropriate signal at $\delta=76.9$. In the ^{13}C NMR spectrum the structurally relevant signals for C-5, C-6, and C-12a are closely analogous to those in the spectrum of **11**.

[3+2] Cycloaddition. The isophospholine **7** reacts with mesityl nitrile oxide **14**, also under very mild conditions, in a 1,3-dipolar cycloaddition to furnish the oxazaphospholine **15**. The product **15** is isolated after column chromatographic work-up in 81% yield as a yellow solid that is not sensitive to atmospheric oxygen or moisture (Scheme 6).

The directions of addition and thus the constitution of **15** is unambiguously derived from an analysis of the ^{13}C NMR spectrum. The decisive finding here is the signal for the carbon atom C-3 at $\delta=160.2$. It appears as a doublet with a coupling constant of 49.4 Hz which is indisputable evidence for the occurrence of a $^{1}J_{C,P}$ coupling. The chemical shifts of the signals for the carbon atoms C-5 and C-6 are, as expected, very similar to those of the corresponding atoms in compounds **11** and **13**. The ^{1}H NMR spectrum of compound **15** is of particular interest. Besides the characteristic signal for the proton of the chelating hydrogen bond at $\delta=18.3$, three different signals, two of which are markedly broadened, are observed for the methyl groups of the mesityl substituent. The fact that the *ortho*-methyl groups are no longer chemically equivalent is indicative of a hindered rotation. This assumption is impressively confirmed by ^{1}H NMR spectra recorded at various temperatures. From these measurements a coalescence temperature of 333 K was determined which corresponds to an energy of 69.9 kJ/mol for the barrier to rotation.[30]

Conclusion

Not only the novel phosphaalkenes **4** but also the isophosphinoline **7** obtained by thermolysis from **4a–c** exhibit a

surprising and diverse reactivity. The formation of **7**, in particular, poses a number of as yet unresolved mechanistic questions. Further investigations with this objective are at present in progress.

Experimental

General

All experiments were carried out under argon (purity>99.998%) in previously evacuated and baked Schlenk vessels. When the reaction mixture had to be heated to temperatures above the boiling point of the solvent, special pressure Schlenk tubes (glass tubes, 3×5 cm^2, wall thickness 2 mm) with screw-threaded Teflon stoppers and Teflon stopcocks were used. The solvents were dried by standard procedures, distilled and stored under argon until used. Melting points were determined on a Mettler FP61 apparatus (heating rate 2°C min^{-1}) and are uncorrected. NMR spectra were recorded on Bruker WP200 and AMX400 instruments. Chemical shifts for ^1H and ^{13}C are reported in ppm relative to the solvent as internal standard; the chemical shifts for ^{31}P are expressed relative to external 85% orthophosphoric acid. Elemental analyses were performed on a Perkin–Elmer Analyser 2400. IR spectra were measured on a Perkin–Elmer 16 PC FT-IR spectrophotometer and mass spectra were recorded on a Finnigan MAT90 spectrometer. Compounds **1**[31] and **3**[32] were prepared according to published methods.

10-Alkyl-1,9-diphenyl-12-oxa-11-phosphatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-ones (4a–d). Solutions of equimolar amounts of oxirane **1** and the phosphaalkynes **3a–d** in 15 ml CH_2Cl_2 were heated for 18 h at 150°C under 5 bar Ar overpressure. After evaporation of the solvent the residue was dissolved in 5 ml of CH_2Cl_2 and subjected to flash chromatography on silica gel 60 with an *n*-pentane/ether mixture (80:1) to furnish the products as pale yellow solids.

10-*tert*-Butyl-1,9-diphenyl-12-oxa-11-phosphatricyclo[7.2.1.0^{2,7}] dodeca-2,4,6,10-tetraen-8-one (4a). From 2000 mg oxirane (**1**, 6.70 mmol) and 670 mg phosphaalkyne (**3a**, 6.70 mmol), yield: 2000 mg (75%), mp 96°C; ^{31}P NMR ($CDCl_3$): δ=261.4 (s); ^1H NMR ($CDCl_3$): δ=1.04 (d, 9H, $^4J_{H,P}$=1.2 Hz, C(C*H*$_3$)$_3$), 6.81–8.09 (m, 14H, aryl-H); ^{13}C NMR ($CDCl_3$): δ=32.9 (d, $^3J_{C,P}$=13.0 Hz, C(*C*H$_3$)$_3$), 37.2 (d, $^2J_{C,P}$=13.0 Hz, *C*(CH$_3$)$_3$), 94.4 (d, $^1J_{C,P}$=37.8 Hz, C-1), 98.0 (d, $^2J_{C,P}$=8.9 Hz, C-9), 122.8 (s), 127.7 (s), 127.9 (s), 128.00 (s), 128.03 (s), 128.1 (s), 128.3 (s), 128.6 (s), 129.0 (s), 132.4 (s), aryl-C, 126.7 (s), 148.3 (s), C-2 and C-7, 138.5 (d, $^3J_{C,P}$=4.0 Hz, C-1′), 139.9 (d, $^2J_{C,P}$=10.4 Hz, C-1″), 189.6 (d, $^3J_{C,P}$=10.4 Hz, C-8), 212.5 (d, $^1J_{C,P}$=45.0 Hz, C-10); IR (CCl_4): $\tilde{\nu}$=2962 (s, CH), 1698 (vs, C=O), 1594 (s), 1492 (m), 1448 (w), 1446 (s), 1364 (m), 1280 (s), 1200 (s), 1184 (m), 1060 (m), 1027 (s), 836 (s); MS (EI, 70 eV): *m/z* (%)=398 (5.6) $[M]^+$, 342 (2.8) $[M-C_4H_8]^+$, 105 (37.6) $[Ph\text{-}CO]^+$, 77 (16.6) $[C_6H_5]^+$, 57 (47.0) $[C_4H_9]^+$; $C_{26}H_{23}O_2P$ (398.43 g/mol): calcd C 78.39, H 5.78; found C 77.50, H 5.75.

10-(1,1-Dimethylpropyl)-1,9-diphenyl-12-oxa-11-phosphatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (4b). From 1000 mg oxirane (**1**, 3.35 mmol) and 3.35 mmol phosphaalkyne **3b**, yield: 983 mg (70%), mp 93°C; ^{31}P NMR (C_6D_6): δ=267.2 (s); ^1H NMR (C_6D_6): δ=0.55 (pt, 3H, $^3J_{H,H}$=7.4 Hz, –C(CH$_3$)(CH$_3$)CHHC*H*$_3$), 0.89 (d, 3H, $^4J_{H,P}$=1.0 Hz, –C(C*H*$_3$)(CH$_3$)CHHCH$_3$), 1.11 (s, 3H, –C(CH$_3$)(C*H*$_3$)CHHCH$_3$), 1.10–1.19 (m, 1H, –C(CH$_3$)(CH$_3$)C*H*HCH$_3$), 1.37–1.46 (m, 1H, –C(CH$_3$)(CH$_3$)CH*H*CH$_3$), 6.69–8.83 (m, 14H, aryl-*H*); ^{13}C NMR (C_6D_6): δ=8.7 (d, $^4J_{C,P}$=1.2 Hz, –C(CH$_3$)(CH$_3$)CHH*C*H$_3$), 30.3 (d, $^3J_{C,P}$=13.7 Hz, –C(*C*H$_3$)(CH$_3$)CHHCH$_3$), 30.7 (d, $^3J_{C,P}$=14.5 Hz, –C(CH$_3$)(*C*H$_3$)CHHCH$_3$), 35.9 (d, $^3J_{C,P}$=9.6 Hz, –C(CH$_3$)(CH$_3$)*C*HHCH$_3$), 43.1 (d, $^2J_{C,P}$=10.8 Hz, –*C*(CH$_3$)(CH$_3$)CHHCH$_3$), 94.7 (d, $^1J_{C,P}$=38.2 Hz, C-1), 98.2 (d, $^2J_{C,P}$=8.8 Hz, C-9), 122.7 (d, $J_{C,P}$=1.2 Hz), 127.6 (s), 127.9 (s), 128.0 (s), 128.1 (s), 128.2 (s), 128.5 (s), 128.7 (s), 129.0 (s), 132.2 (s), aryl-*C*, 126.8 (s), 148.4 (d, $J_{C,P}$=2.8 Hz), C-2 and C-7, 138.7 (d, $^3J_{C,P}$=4.4 Hz, C-1′), 140.2 (d, $^2J_{C,P}$=10.8 Hz, C-1″), 189.2 (d, $^3J_{C,P}$=10.0 Hz, C-8,), 210.5 (d, $^1J_{C,P}$=46.8 Hz, C-10); IR (CH_2Cl_2): $\tilde{\nu}$=2966 (m, CH), 1698 (vs, CO), 1594 (s), 1201 (m), 1026 (m), 836 (w); MS (EI, 70 eV): *m/z* (%)=412 (70.3) $[M]^+$, 397 (5.7) $[M-Me]^+$, 383 (13.0) $[M-Et]^+$, 342 (31.0) $[M-C_5H_{10}]^+$, 105 (100.0) $[PhCO]^+$, 77 (41.0) $[Ph]^+$, 71 (4.3) $[C_5H_{11}]^+$; $C_{27}H_{25}O_2P$ (412.37 g/mol): calcd C 78.62, H 6.11; found C 78.22, H 6.30.

10-(1-Methylcyclohexyl)-1,9-diphenyl-12-oxa-11-phosphatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (4c). From 1000 mg oxirane (**1**, 3.35 mmol) and 3.35 mmol phosphaalkyne **3c**, yield: 415 mg (28%), mp 102°C; ^{31}P NMR ($CDCl_3$): δ=268.5 (s); ^1H NMR ($CDCl_3$): δ=0.74 (s, 3H, –C*H*$_3$), 1.05–1.60 (m, 10H, alkyl-*H*), 6.81–8.21 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=22.1 (d, $^4J_{C,P}$=2.9 Hz), 22.3 (s, $^4J_{C,P}$=2.4 Hz), 25.5 (d, $^3J_{C,P}$=9.2 Hz), 25.6 (s), 39.4 (d, $^3J_{C,P}$=13.8 Hz), 41.2 (d, $^3J_{C,P}$=15.7 Hz), 43.4 (d, $^2J_{C,P}$=9.5 Hz), alkyl-*C*, 94.5 (d, $^1J_{C,P}$=38.1 Hz, C-1), 97.8 (d, $^2J_{C,P}$=9.5 Hz, C-9), 122.8 (s), 127.6 (s), 127.8 (s), 128.0 (s), 128.1 (s), 128.2 (s), 128.6 (s), 128.7 (s), 129.1 (s), 132.4 (s), aryl-*C*, 126.7 (s), 148.3 (s), C-2 and C-7, 139.0 (d, $^3J_{C,P}$=4.3 Hz, C-1′), 140.0 (d, $^2J_{C,P}$=10.4 Hz, C-1″), 189.7 (d, $^3J_{C,P}$=9.5 Hz, C-8), 213.9 (d, $^1J_{C,P}$=46.7 Hz, C-10); IR (CCl_4): $\tilde{\nu}$=3062 (w, CH), 2930 (vs, CH), 2856 (m, CH), 1702 (vs, CO), 1677 (m), 1596 (w), 1494 (w), 1447 (s), 1282 (m), 1261 (m), 1201 (m), 1029 (m), 697 (vs); MS (EI, 35 eV): *m/z* (%)=438 (47.2) $[M]^+$, 342 (40.0) $[M-C_7H_{12}]^+$, 105 (88.9) $[PhCO]^+$; $C_{29}H_{27}O_2P$ (438.50 g/mol).

10-(Adamant-1-yl)-1,9-diphenyl-12-oxa-11-phosphatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraen-8-one (4d). From 1000 mg oxirane (**1**, 3.35 mmol) and 3.35 mmol phosphaalkyne **3d**, yield: 846 mg (52%), mp 105°C, ^{31}P NMR (C_6D_6): δ=267.8 (s); ^1H NMR (C_6D_6): δ=1.30–2.06 (m, 15H, alkyl-*H*), 6.75–8.43 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=28.6 (d, $^4J_{C,P}$=1.6 Hz), 36.1 (s), 42.9 (d, $^2J_{C,P}$=10.4 Hz), 44.4 (s, $^3J_{C,P}$=13.3 Hz), alkyl-*C*, 94.6 (d, $^1J_{C,P}$=38.2 Hz, C-1), 97.6 (d, $^2J_{C,P}$=8.4 Hz, C-9), 122.8 (s), 127.6 (s), 127.9 (s), 128.0 (d, $J_{C,P}$=4.0 Hz), 128.0 (d, $J_{C,P}$=5.2 Hz), 128.3 (s), 128.6 (s), 128.6 (s), 129.0 (s), 132.4 (s), aryl-*C*, 126.7 (s), 148.4 (d, $J_{C,P}$=1.6 Hz), C-2 and C-7, 138.9 (d, $^3J_{C,P}$=4.4 Hz, C-1′), 140.0 (d, $^2J_{C,P}$=10.4 Hz, C-1″), 189.7 (d, $^3J_{C,P}$=10.0 Hz, C-8), 213.8 (d, $^1J_{C,P}$=45.8 Hz, C-10); IR (CCl_4): $\tilde{\nu}$=3066 (w, CH), 2909 (vs, CH), 2852 (m, CH), 1703 (m, CO), 1596 (w), 1493

(w), 1448 (m), 1281 (w), 1198 (w), 1030 (w), 698 (w); HRMS: calcd for $C_{32}H_{29}O_2P$: 476.1905; found: 476.1875; $C_{32}H_{29}O_2P$ (476.55 g/mol).

Synthesis of compounds 5a,b

General procedure. To a solution of 150 mg (0.38 mmol) of the compound **4a** in 5 ml of CH_2Cl_2 are added 70 μl (0.50 mmol) of triethylamine and an equimolar amount of the appropriate chalcogen. The reaction mixture is stirred for 2 days at 25°C. After evaporation of the solvent the crude products are purified by column chromatography with an *n*-pentane/ether mixture (10:1) as eluent.

Remark: Compound **5a** cannot be obtained analytically pure due to traces of sulfur in the product.

10-*tert*-Butyl-1,9-diphenyl-13-oxa-11-thia-12-phosphatetracyclo[7.3.1.0^{2,7}.0^{10,12}]trideca-2,4,6-trien-8-one (5a). From 150 mg phosphaalkene (**4a**, 0.38 mmol) and 13 mg (0.41 mmol) of sulfur, yield: 93 mg (57%), mp 125°C (dec.); ^{31}P NMR (C_6D_6): δ=−65.0 (s); ^{1}H NMR ($CDCl_3$): δ=1.06 (d, 9H, $^4J_{H,P}$=0.9 Hz, –C(C*H*$_3$)$_3$), 6.94–8.27 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=32.1 (d, $^3J_{C,P}$=6.4 Hz, –C(*C*H$_3$)$_3$), 36.5 (d, $^2J_{C,P}$=7.2 Hz, –*C*(CH$_3$)$_3$), 73.2 (d, $^1J_{C,P}$=43.8 Hz, C-10), 86.9 (d, $^1J_{C,P}$=41.8 Hz, C-1), 88.5 (d, $^2J_{C,P}$=8.5 Hz, C-9), 124.8 (d, $J_{C,P}$=4.4 Hz), 126.8 (s), 128.1 (s), 128.3 (s), 128.4 (s), 128.5 (s), 128.6 (s), 128.9 (d, $J_{C,P}$=2.0 Hz), 129.4 (d, $J_{C,P}$=2.8 Hz), 129.7 (s), aryl-*C*, 133.7 (d, $J_{C,P}$=2.0 Hz), 137.0 (s), C-2 and C-7, 138.5 (d, $^3J_{C,P}$=6.8 Hz C-1′), 144.5 (d, $^2J_{C,P}$=17.7 Hz, C-1″), 193.8 (s, C-8); IR (CCl_4): $\bar{\nu}$=2978 (s, CH), 2869 (s, CH), 1709 (s, C=O), 1447 (m), 1264 (m), 1120 (vs), 700 (s); $C_{26}H_{23}O_2PS$ (430.50 g/mol).

10-*tert*-Butyl-1,9-diphenyl-13-oxa-11-selena-12-phosphatetracyclo[7.3.1.0^{2,7}.0^{10,12}]trideca-2,4,6-trien-8-one (5b). From 150 mg phosphaalkene (**4a**, 0.38 mmol) and 30 mg (0.38 mmol) of gray selenium, yield: 108 mg (59%), mp 162°C (dec.); ^{31}P NMR (C_6D_6): δ=−41.4 (s, $^1J_{P,Se}$=125.0 Hz); ^{1}H NMR ($CDCl_3$): δ=1.05 (s, 9H, –C(C*H*$_3$)$_3$), 6.87–8.14 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=31.5 (d, $^3J_{C,P}$=6.6 Hz, –C(*C*H$_3$)$_3$), 35.3 (d, $^2J_{C,P}$=8.0 Hz, –*C*(CH$_3$)$_3$), 80.0 (d, $^1J_{C,P}$=53.4 Hz, C-10), 85.5 (d, $^1J_{C,P}$=42.3 Hz, C-1), 88.3 (d, $^2J_{C,P}$=2.5 Hz, C-9), 123.4 (d, $J_{C,P}$=4.5 Hz), 125.2 (s), 126.6 (s), 126.9 (s), 126.9 (s), 127.0 (s), 127.1 (s), 127.5 (d, $J_{C,P}$=2.4 Hz), 127.9 (d, $J_{C,P}$=3.1 Hz), 128.4 (s), aryl-*C*, 132.3 (d, $J_{C,P}$=2.4 Hz), 136.3 (s), C-2 and C-7, 137.5 (d, $^3J_{C,P}$=6.9 Hz, C-1′), 143.2 (d, $^2J_{C,P}$=17.7 Hz, C-1″), 191.3 (s, C-8); IR (CCl_4): $\bar{\nu}$=3064 (w, CH), 2963 (w, CH), 1710 (vs, C=O), 1447 (m), 1280 (m), 1031 (vs), 699 (s); MS (EI, 70 eV): *m*/*z*(%)=478 (48.4) [M]$^+$, 463 (26.5)[M−CH$_3$]$^+$, 398 (44.5) [M−Se]$^+$, 383 (12.7) [M−Se−CH$_3$]$^+$, 342 (48.6) [M−Se−C$_4$H$_8$]$^+$, 105 (100.0) [PhCO]$^+$, 77 (73.3), [Ph]$^+$, 57 (23.2) [C$_4$H$_9$]$^+$; $C_{26}H_{23}O_2PSe$ (477.40 g/mol).

10-*tert*-Butyl-1,9-diphenyl-12-thioxo-13-oxa-11-thia-12λ^5-phosphatetracyclo-[7.3.1.0^{2,7}.0^{10,12}]trideca-2,4,6-trien-8-one (6). *Method A:* To a solution of 350 mg phosphaalkene (**4a**, 0.89 mmol) in 5 ml of CH_2Cl_2 are added 160 μl (1.14 mmol) of triethylamine and 86 mg (2.69 mmol) of sulfur. After stirring for 2 days at 25°C the solvent is removed and the residue purified by column chromatography with a *n*-pentane/ether mixture (10:1) as eluent. yield: 282 mg (69%), mp 90°C (dec.); *Method B:* To a solution of 350 mg of compound **5a** (0.21 mmol) in 5 ml of CH_2Cl_2 are added 42 μl (0.30 mmol) of triethylamine and 13 mg (0.41 mmol) of sulfur. After stirring for 2 days at 25°C the solvent is removed and the residue is worked up as described above. ^{31}P NMR ($CDCl_3$): δ=21.5 (s); ^{1}H NMR (C_6D_6): δ=1.27 (s, 9H, –C(C*H*$_3$)$_3$), 6.89–8.26 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=31.1 (d, $^3J_{C,P}$=4.0 Hz, –C(*C*H$_3$)$_3$), 36.7 (s, –*C*(CH$_3$)$_3$), 58.8 (d, $^1J_{C,P}$=28.1 Hz, C-1), 85.0 (d, $^1J_{C,P}$=51.8 Hz, C-10), 86.6 (d, $^2J_{C,P}$=7.2 Hz, C-9), 127.3 (s), 128.1 (s), 128.2 (s), 128.2 (d, $J_{C,P}$=2.8 Hz), 128.7 (s), 128.8 (s), 128.9 (s), 129.3 (s), 129.8 (d, $J_{C,P}$=3.6 Hz), 129.9 (s), aryl-*C*, 133.8 (d, $J_{C,P}$=3.2 Hz), 135.2 (d, $J_{C,P}$=7.6 Hz), 135.5 (d, $J_{C,P}$=1.6 Hz) C-2, C-7, C-1′, 141.5 (d, $^2J_{C,P}$=9.2 Hz, C-1″), 192.4 (s, C-8); IR (CCl_4): $\bar{\nu}$=3066 (w, CH), 2966 (m, CH), 1709 (vs, C=O), 1596 (m), 1447 (s), 1369 (m), 1282 (m), 1263 (m), 1030 (m), 845 (m), 711 (s), 699 (s); MS (EI, 70 eV): *m*/*z* (%)=463 (10.8) [M]$^+$, 105 (28.9) [PhCO]$^+$, 77 (50.0) [Ph]$^+$, 57 (33.4) [C$_4$H$_9$]$^+$; $C_{26}H_{23}O_2PS_2$ (462.57 g/mol).

(4-Hydroxy-1-phenyl-isophosphinoline-3-yl)-phenylmethanone (7). A solution of the phosphaalkene **4a–c** in 15 ml toluene is heated for 3 days to 150°C. The solvent is removed and the residue subjected to flash column chromatography on silica gel 60 with a *n*-pentane/ether mixture (50:1) as eluent. From 1000 mg phosphaalkene (**4a**, 2.51 mmol), yield: 700 mg (82%), mp 115°C; ^{31}P NMR ($CDCl_3$): δ=197.4 (s); ^{1}H NMR ($CDCl_3$): δ=7.29–7.56 (m, 10H), 7.68–7.71 (m, 2H), 8.71–8.73 (m, 2H), aryl-H, 15.6 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ=122.7 (s), 123.3 (s), C-4a and C-8a, 125.3 (d, $J_{C,P}$=9.7 Hz), 126.8 (d, $J_{C,P}$=4.1 Hz), 127.0 (d, $J_{C,P}$=5.6 Hz), 127.6 (s), 127.9 (s), 128.2 (s), 129.9 (d, $J_{C,P}$=8.1 Hz), 130.6 (d, $J_{C,P}$=10.3 Hz), 131.4 (d, $J_{C,P}$=3.8 Hz), 131.6 (s) aryl-*C*, 138.1 (d, $^2J_{C,P}$=10.3 Hz, C-1″), 138.6 (s, C-1′), 140.9 (d, $^1J_{C,P}$=27.3 Hz, C-3), 164.9 (d, $^2J_{C,P}$=38.5 Hz, C-4), 170.5 (d, $^2J_{C,P}$=10.5 Hz, C-9), 203.8 (d, $^1J_{C,P}$=32.9 Hz, C-1); IR (CCl_4): $\bar{\nu}$=3200–2300 (bw, OH), 2946 (w, CH), 1601 (bm, C=O), 1513 (m), 1378 (s), 1301 (m), 1272 (m), 1181 (w), 1053 (w); MS (EI, 70 eV): *m*/*z* (%)=342 (100) [M]$^+$, 265 (52.3) [M−Ph]$^+$, 236 (7.4) [M−Ph−CHO]$^+$, 207.1 (22.7) [M−Ph−2CHO]$^+$, 105 (29.7) [PhCO]$^+$, 77 (29.8) [Ph]$^+$; $C_{22}H_{15}O_2P$ (342.33 g/mol): calcd C 77.19, H 4.39; found C 76.54, H 4.72.

(3-Benzoyl-1-phenyl-isophosphinoline-4-yl) 2,2-dimethylpropanoate (9). To a cooled (−78°C) mixture of 150 mg **7** (0.43 mmol) in THF is added an equimolar amount of an *n*-BuLi solution (1.6 M) in *n*-hexane (183 μl). After stirring this mixture at −78°C for 20 min 54 μl (0.43 mmol) of 2,2-dimethylpropanoyl chloride (**8**) is added. The reaction mixture is allowed to warm to room temperature overnight and the reaction process is monitored by TLC. After evaporation of the solvent the crude products are subjected to flash column chromatography with a *n*-pentane/ether mixture (20:1) as eluent. yield: 75 mg (40%), mp 145°C; ^{31}P NMR ($CDCl_3$): δ=185.8 (s); ^{1}H NMR ($CDCl_3$): δ=1.17 (s, 9H, –C(C*H*$_3$)$_3$), 7.45–8.01 (m, 14H, aryl-*H*); ^{13}C NMR ($CDCl_3$): δ=26.8 (s, –C(*C*H$_3$)$_3$), 39.5

(s, $-C(CH_3)_3$), 124.1 (d, $^3J_{C,P}$=4.6 Hz), 126.0 (d, $^2J_{C,P}$=9.9 Hz), 127.9 (d, $J_{C,P}$=1.9 Hz), 128.1 (s), 128.2 (s), 128.3 (s), 128.4 (s), 128.6 (d, $J_{C,P}$=4.2 Hz), 128.7 (s), 130.3 (s), 130.5 (d, $J_{C,P}$=2.0 Hz), 133.6 (s), aryl-*C*, 137.1 (s), 137.6 (d, $J_{C,P}$=11.8 Hz), *ipso*-*C*, 140.5 (d, $^1J_{C,P}$=26.7 Hz, C-3), 167.7 (s), 175.9 (s), C-9 and C-10, 174.2 (d, $^2J_{C,P}$=46.5 Hz, C-4), 195.3 (d, $^1J_{C,P}$=22.1 Hz, C-1); IR (CCl_4): $\overline{\nu}$=2963 (m, –CH), 1753 and 1711 (vs, C=O), 1665 (s), 1597 (m), 1551 (w), 1449 (s), 1261 (s), 1080 (m), 810 (w); MS (EI, 70 eV): *m*/*z* (%)=426 (1.9) $[M]^+$, 342 (9.5) $[M-t\text{Bu}-CO+H]^+$, 105 (24.4) $[PhCO]^+$, 77 (15.6) $[Ph]^+$, 57 (100) $[t\text{Bu}]^+$; $C_{27}H_{23}O_3P$ (426.45 g/mol).

(10-Hydroxy-6,7-dimethyl-4b-phenyl-5,8-dihydro-4b*H*-8a-phosphaphenanthren-9-yl)-phenylmethanone (11). A solution of the isophosphinoline **7** and a small excess of 2,3-dimethylbutadiene **(10)** in 15 ml of toluene is heated for 3 days to 150°C. After removal of the solvent the crude product is purified by flash column chromatography with a *n*-pentane/ether mixture (50:1) as eluent. From 150 mg isophosphinoline (**7**, 0.43 mmol) and 43 mg diene (**10**, 0.50 mmol), yield: 109 mg (60%), mp 151°C; ^{31}P NMR ($CDCl_3$): δ=−49.5 (s); ^{1}H NMR ($CDCl_3$): δ=1.48 (s, 3H), 1.61 (s, 3H, –*H* at C-12, C-13), 1.90 (m, 1H), 2.10 (m, 1H), 2.87 (m, 2H, –*H* at C-5,C-8), 6.87–8.10 (m, 14H, aryl-*H*), 17.8 (s, –*OH*); ^{13}C NMR ($CDCl_3$): δ=20.2 (s, C-12), 21.8 (d, $^3J_{C,P}$=5.3 Hz, C-13), 30.3 (d, $^2J_{C,P}$=16.8 Hz, C-5), 42.2 (d, $^1J_{C,P}$=3.9 Hz, C-4b), 45.0 (d, $^1J_{C,P}$=16.0 Hz, C-8), 99.6 (d, $^1J_{C,P}$=20.6 Hz, C-9), 125.0 (d, $J_{C,P}$=1.5 Hz), 126.8 (s), C-6, C-7, 126.2 (s), 126.7 (s), 127.0 (s), 127.5 (s), 127.6 (s), 127.9 (s), 128.2 (s), 128.9 (s), 131.0 (s), 132.6 (s), 132.7 (s), 137.0 (s), aryl-*C*, 142.9 (d, $J_{C,P}$=4.5 Hz), 145.9 (d, $J_{C,P}$=8.4 Hz), *ipso*-*C*, 185.2 (d, $^2J_{C,P}$=3.1 Hz, C-11), 195.0 (d, $^2J_{C,P}$=34.3 Hz, C-10); IR (*n*-pentane): $\overline{\nu}$=3100–2300 (bw, OH), 2926 (w, CH), 1600 (bm), 1441 (m), 1288 (m), 1223 (m), 1074 (w); MS (EI, 70 eV): *m*/*z* (%)=424 (29.9) $[M]^+$, 342 (53.8) $[M-C_6H_{10}]^+$, 298 (100) $[M-C_6H_{10}-HCP]^+$, 265 (21.9) $[M-C_6H_{10}-Ph]^+$, 105 (63.9) $[PhCO]^+$, 77 (32.5) $[Ph]^+$; $C_{28}H_{25}O_2P$ (424.47 g/mol).

Phenyl-(8,9,10,11-tetrachloro-5-hydroxy-12a-phenyl-12a*H*-7,12-dioxa-6a-phosphabenzo-[*a*]anthracen-6-yl)methanone (13). A solution of 300 mg isophosphinoline (**7**, 0.88 mmol) in 15 ml of toluene is cooled to −78°C and 215 mg of tetrachloroorthobenzoquinone (**12**, 0.88 mmol) are added. The reaction mixture is allowed to warm to room temperature overnight. After removal of the solvent the crude product is recrystallized from a CH_2Cl_2/*n*-pentane mixture (1:2). Yield: 233 mg (45%), mp 178°C; ^{31}P NMR ($CDCl_3$): δ=79.6 (s); ^{1}H NMR ($CDCl_3$): δ=6.75–7.98 (m, 14H, aryl-*H*), 18.6 (s, 1H, O*H*); ^{13}C NMR (C_7D_8): δ=81.2 (d, $^1J_{C,P}$=12.1 Hz, C-12a), 100.2 (d, $^1J_{C,P}$=27.3 Hz, C-6); 122.6 (s), 123.4 (s), 127.0 (s), 125.5 (s), 125.9 (s), 127.2 (s), 127.6 (s), 128.1 (s), 128.7 (s), 128.9 (s), 129.0 (s), 129.2 (s), 129.3 (s), 132.2 (s), 132.3 (s), 134.6 (s), 136.9 (s), 139.0 (s), 139.7 (s), 140,7 (s), aryl-*C*, 187.7 (s, C-13), 196.4 (d, $^2J_{C,P}$=40.2 Hz, C-5); IR (*n*-pentane): $\overline{\nu}$=3000–2400 (bw, OH), 2966 (w, CH), 1612 (bm), 1411 (m), 1298 (m), 1249 (m), 1001 (w); MS (EI, 70 eV): *m*/*z* (%)=588 (100) $[M]^+$, 105 (2.6) $[PhCO]^+$, 77 (2.2) $[Ph]^+$; $C_{28}H_{15}O_4PCl_4$ (588.52 g/mol): calcd C 57.14, H 2.55; found C 56.30, H 2.61.

(6-Hydroxy-3-mesityl-10b-phenyl-10b*H*-isophosphinolino[2,1-*d*][1,2,4]oxazaphosphol-5-yl)phenylmethanone (15). A solution of 125 mg isophosphinoline (**7**, 0.37 mmol) in 5 ml of toluene is cooled to −78°C and 60 mg of mesityl nitrile oxide (**14**, 0.37 mmol) are added. The reaction mixture is allowed to warm to room temperature overnight. After removal of the solvent the crude product is purified by column chromatography with a *n*-pentane/ether mixture (5:1) as eluent. Yield: 151 mg (81%), mp 106°C (dec.); ^{31}P NMR ($CDCl_3$): δ=4.4 (s); ^{1}H NMR ($CDCl_3$): δ=1.50 (bs, 3H, *o*-CH_3), 1.95 (bs, 3H, *o*-CH_3), 2.08 (s, 3H, *p*-CH_3), 6.35 (bs, 1H, mesityl-*H*), 6.63 (bs, 1H, mesityl-*H*), 6.93–8.27 (m, 14H, aryl-*H*), 18.3 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ=20.0 (bs, *o*-CH_3), 20.9 (s, *p*-CH_3), 93.1 (d, $^1J_{C,P}$=18.1 Hz), 94.3 (d, $^1J_{C,P}$=31.7 Hz), C-5 and C-10b, 127.4 (s), 127.5 (s), 127.5 (s), 127.6 (s), 127.7 (s), 127.8 (s), 127.9 (s), 128.1 (s), 129.2 (s), 129.9 (d, $J_{C,P}$=1.6 Hz), 131.0 (s), 133.0 (s), 128.6 (bs), 136.9 (bs), 126.0 (d, $J_{C,P}$=13.3 Hz), 131.4 (s), 136.4 (s), 138.0 (d, $J_{C,P}$=1.6 Hz), 138.5 (s), 139.7 (d, $J_{C,P}$=24.1 Hz), aryl-*C*, 160.2 (d, $^1J_{C,P}$=49.4 Hz, C-3), 178.5 (s, C-11), 197.1 (d, $^2J_{C,P}$=21.7 Hz, C-6); IR (CCl_4): $\overline{\nu}$=2963 (w, CH), 1601 (vs, CO), 1495 (s), 1365 (s), 1286 (m), 1262 (m), 1093 (m), 1030 (m), 850 (w), 696 (s); HRMS: calcd for $C_{32}H_{26}O_3NP$: 503.1650; found: 503.1650; $C_{32}H_{26}O_3NP$ (503.53 g/mol).

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