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Phosphorus compounds 97 [1]. Synthesis of polycyclic phosphorus cage compounds containing diphosphirane and phosphirane units by tandem Diels-Alder and ene reactions: a contribution to the cycloaddition and enophile chemistry of phosphaalkynes†

Heinrich Heydt[1], Uwe Bergsträßer[1], Rainer Fäßler[1], Eberbard Fuchs[1], Nasr Kamel[1], Thomas Mackewitz[1], Gisbert Michels[1], Wolfgang Rösch[1], Manfred Regitz[1]*, Pierre Mazerolles[2], Christian Laurent[2], Alfreda Faucher[2]

[1] *Department of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Straße, 67663 Kaiserslautern, Germany*
[2] *URA 477, Hétérochimie fondamentale et appliquée, Université Paul-Sabatier, 31062 Toulouse Cedex, France*

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Summary – When the open-chain 1,3-dienes **14a-k** are allowed to react with the phosphaalkyne **13** in a molar ratio of 1:2 under thermal conditions, the 1,7-diphosphatricyclo[3.2.1.$0^{2,7}$]oct-3-enes **19** and/or **20** are formed. The formation of isomers is attributable to the initial Diels-Alder reaction since both the subsequent ene reaction (specific formation of **17**, **18**) and the concluding intramolecular Diels-Alder reaction (→ **19**, **20**) proceed specifically. The constitutions of the tricyclic systems incorporating a diphosphirane unit were confirmed by NMR spectroscopic data and a crystal structure analysis of **19a** (≡ **20a**). The *s-cis*-configurated 1,3-butadienes **14l-u** react similarly with **13** (Diels-Alder reaction → phospha-ene reaction → intramolecular Diels-Alder reaction) to furnish the tetracyclic products **19l-u** (≡ **20l-u**). The same reaction sequence is also responsible for the regiospecific formation of the diphosphatetracyclic systems **19v-y** from the reactions of **13** with the semicyclic 1-vinylcycloalk-1-enes **14v-y**. In principle, phosphaalkynes such as **13**, independent of the above-mentioned reaction sequence, are suitable for use as enophiles in ene reactions. This is illustrated by the conversions **21** + **13** → **22** and **21** + **22** → **23**. The cyclohexa-1,4-diene **24a** reacts with **13** to furnish the phosphatricyclooctene **29a**, a result in complete harmony with the reaction sequence **15/16** → **19/20**. Product **29a** now contains a phosphirane unit instead of the diphosphirane in the former substances. The regioselectivity of the ene reaction is lost when the substituted 1,4-dienes **24b-e** and the annelated derivatives **24f,g** are used as reaction partners for **13**. The cyclohexa-1,4-diene **24b** participates in a completely nonspecific reaction with **13** (→ **29b**, **30b**, **31b**, **32b**).

phosphaalkyne / phosphirane / diphosphirane / [4 + 2] cycloaddition / phospha-ene reaction / tandem reaction / intramolecular Diels-Alder reaction

Introduction

Cycloaddition reactions play a major role in the chemistry of phosphaalkynes [2-4]. This is nicely illustrated by the ease with which 1*H*-phosphirenes [5, 6] and heterophospholes [7-11] are accessible by way of [2 + 1] and [3 + 2] cycloaddition reactions, respectively. Thus, it seemed worthwhile to examine the synthetic potential of phosphaalkynes as dienophiles in Diels-Alder reactions.

As indicated by the examples shown in scheme 1, this methodology provides an access to a broad spectrum of novel organophosphorus compounds, most of which contain phosphorus in an unusual coordination. For example, compound **1** (for stability reasons the substituent R^1 is usually *t*Bu) reacts with anti-aromatic cyclobutadienes **2** to yield the Dewar phosphinines **3** which can undergo subsequent valency isomerizations [12, 13]. Reactions of **1** with the cyclopentadienes **4** provide an access to the phospha[2.2.1]alka-2,5-dienes **5**; the latter products participate in homo-Diels-Alder reactions with a further molecule of **1** to furnish the diphosphatetracyclic system **6** [14-16]. Six-membered ring compounds containing a 1,3-diene element also react readily with phosphaalkynes. For example, reactions of **1** with α-pyrones **7** lead to the substituted phosphinines after extrusion of carbon dioxide from the primarily formed Diels-Alder adducts; this synthesis is extremely flexible with regard to the substituent R^2 [16, 17]. When the parent cyclohexa-1,3-diene **9** is selected as the reaction

† Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 65th birthday.

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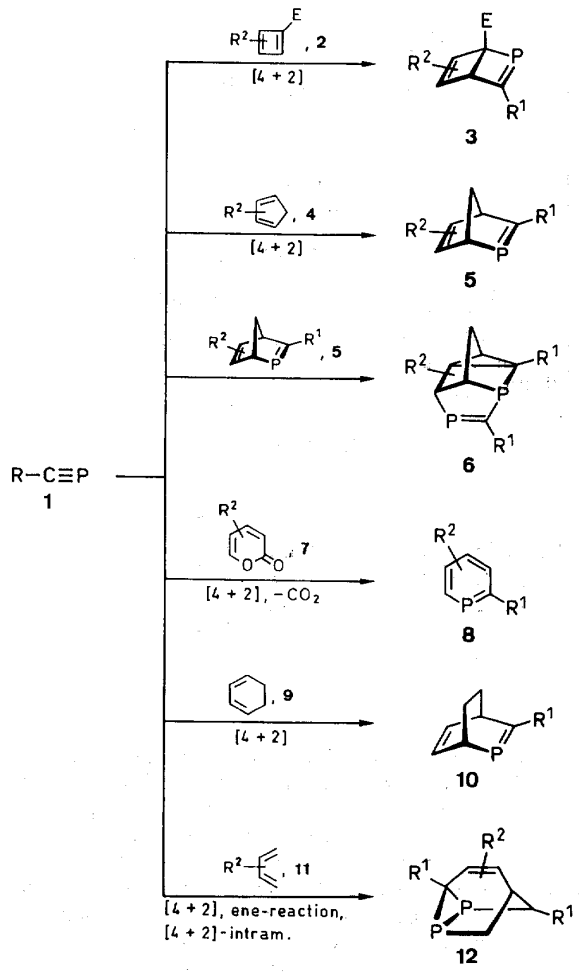


Scheme 1

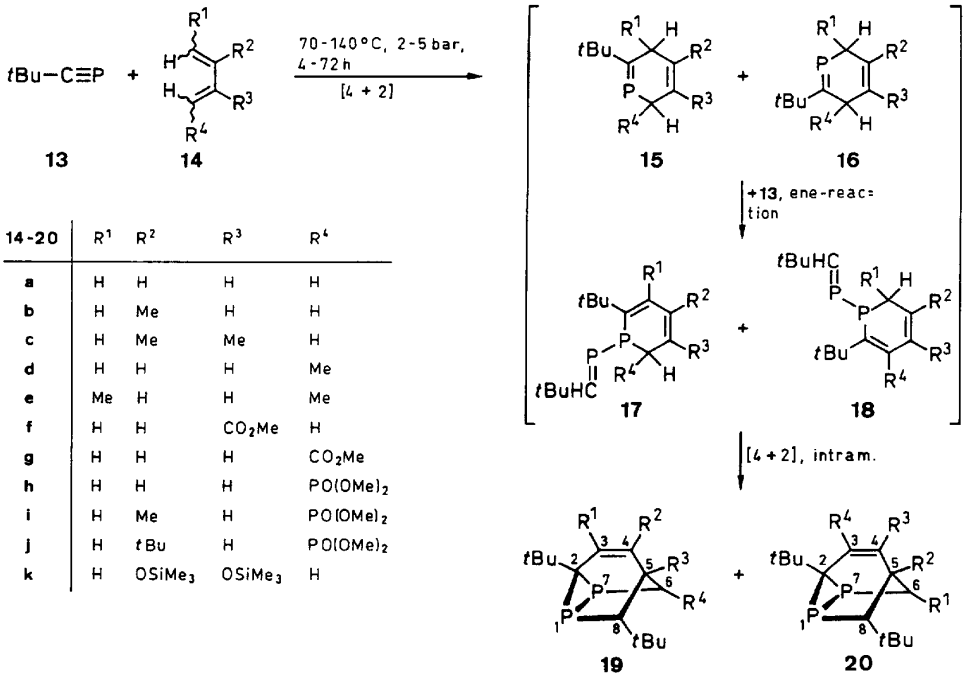
partner for **1**, the resultant [4 + 2] cycloadduct **10** is stable. However, under flash vacuum pyrolysis conditions, **10** can undergo elimination of ethylene to furnish 2-*tert*-butylphosphinine (R^1 = *t*Bu) [17]. The reactions of **1** with open-chain 1,3-dienes **11** follow a seemingly unexpected course. Irrespective of the employed stoichiometry, the diphosphatricyclic compounds **12** containing a diphosphirane unit are isolated, *ie* consumption of two molecules of phosphaalkyne per 1,3-diene unit [18]. An acceptable rationale for the result of these syntheses comprises an initial, intermolecular Diels-Alder cycloaddition reaction, followed by a phospha-ene reaction, and a final intramolecular [4 + 2] cycloaddition process. The first reaction apparently forces the second which, in turn, induces the third reaction to occur; thus use of the term *tandem Diels-Alder/phospha-ene/Diels-Alder reaction* is fully justified for this reaction sequence.

This reaction sequence is the topic of the present paper. In particular, emphasis is placed on the questions of the possible substituent variations in the 1,3-diene component, of whether experimental indications in support of the putative phospha-ene reaction can be obtained, and which parameters determine the regio- and stereochemistry of the products.

1,3-Dienes 14a-k

tert-Butylphosphaethyne **13** reacts with the 1,3-dienes **14a-k** in accord with the postulated tandem reaction sequence in a pressure Schlenk tube (2-5 bar, 80-140°C) to afford the 1,7-diphosphatricyclo[3.2.1.$0^{2,7}$]oct-3-enes **19** and/or **20**, respectively. The yields range from 90% in the case of the reaction with **14a** to < 10% for **14e-g**.

The compounds are formed either as colorless crystals or as colorless to yellow oils which can be purified by bulb-to-bulb distillation. Reactions of the unsymmetrically substituted 1,3-dienes **14b**, **14d**, and **14f,g** give rise to mixtures of the isomers **19** and **20** in which products of the type **19** predominate; reactions of **14h-j** yield products **19** exclusively (see table II). Taken together with the observation that analogous reactions of all the symmetrically substituted 1,3-dienes investigated to date furnish only one isomer, these results lead to the conclusion that the last two reaction steps **15** + **13** ⇒ **17** ⇒ **19** or, respectively, **16** + **13** ⇒ **18** ⇒ **20** proceed specifically. In particular, the phospha-ene reaction must occur specifically with formation of the phosphorus-phosphorus bond since otherwise isomers would be formed in the reactions of symmetrically substituted 1,3-dienes (attack of **13** also at the C=C bond of **15** or **16**, respectively). The formation of isomers must therefore be the result of the initial, intermolecular Diels-Alder reaction **13** + **14** ⇒ **15** or **16** which, of course, is influenced by the prevailing steric situation. Thus, reactions of **14b** and **14f**, in which one of the respective substituents is situated relatively far from the reacting center, yield **19** and **20** in the ratio 1.5:1.0 whereas those of **14d** and **14g** give a ratio of 5.6:1 since, in these cases, the substituents are at one of the carbon atoms of the diene unit where bond formation occurs. Thus, the formation of **15** in which the bulky *t*Bu substituent and the group R^4 are widely separated dominates for steric reasons. When the alka-1,3-dienylphosphonates **14h-j** are employed as the diene components, the voluminous dimethoxyphosphoryl group effects the exclusive formation of **19h-j**. As can be anticipated from these results, the presence of substituents at the carbon atoms 1 and 4 of the diene unit drastically reduces the yields, as is illustrated for the example of the reaction of (*E*,*E*)-**14e** (yield of **19e** (≡ **20e**) : << 10%). Like 1,4-diphenylbuta-1,3-diene, (*Z*,*E*)-**14e** does not react at all with **13** under the chosen reaction conditions. Geminal substitution at the terminal carbon atom also hampers the reaction severely. In the case of 1,1-dimethylbuta-1,3-diene, a product with the assumed structure **19** can be detected in minimal yield by ^{31}P NMR spectroscopy. However, not only steric constraints but also the electronic situation result in low yields. Thus, the yields from the reactions of buta-1,3-diene-1- or -2-carboxylates **14f** and **14g** with **13** are drastically reduced to < 10%. If it is assumed that the involved Diels-Alder and ene reactions follow the normal electronic relationships, the use of the mentioned electron-poor 1,3-dienes should have a detrimental influence on the reaction rate and yield. The electron-poor nature of the diene unit is apparently not so pronounced in the cases of the phosphonate derivatives since here, and in the case of 2,3-bis(trimethylsiloxy)buta-1,3-diene **14k** as a representa-



14-20	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	H	H
c	H	Me	Me	H
d	H	H	H	Me
e	Me	H	H	Me
f	H	H	CO_2Me	H
g	H	H	H	CO_2Me
h	H	H	H	$PO(OMe)_2$
i	H	Me	H	$PO(OMe)_2$
j	H	*t*Bu	H	$PO(OMe)_2$
k	H	$OSiMe_3$	$OSiMe_3$	H

Scheme 2

tive of the electron-rich 1,3-dienes, the yields are in the usual range.

The constitutions of the major products **19a-k** are unambiguously confirmed by the spectroscopic data. The signals in the ^{31}P NMR spectra appear at high field (between $\delta = -216$ and -164), usually as doublets with typical $^1J_{P,P}$ coupling constants of 130-158 Hz. The magnitudes of these coupling constants and the high field positions of the ^{31}P NMR signals provide irrevocable evidence for the presence of a diphosphirane unit in the tricyclic products **19** [19]. Of particular interest is the fact that the chemical shifts for the diphosphirane phosphorus atoms in **19i** and **19j** must by chance be practically identical since no $^1J_{P,P}$ couplings can be observed. However, similar to the case of **19h**, the $^2J_{P,P}$ (15-21 Hz) and $^3J_{P,P}$ (7-12 Hz) couplings with the λ^5 phosphorus atom of the dimethoxyphosphoryl group at C-6 are clearly recognizable; as expected, the integration ratios for λ^3-P:λ^5-P amount to 2:1. The ^{13}C NMR spectral data for the skeletal carbon atoms C-2 to C-6 and C-8 provide further proof of the tricyclic nature of compounds **19**. Accordingly, the C-2 signals are observed in a narrow range between δ = 43-44 as doublets of doublets or pseudo-triplets, respectively, with $^1J_{C,P}$ coupling constants of 41.4-49.0 Hz as a result of the direct neighborhood of this carbon atom with the two diphosphirane phosphorus atoms P-1 and P-7. Corresponding $^1J_{C,P}$ coupling constants between of 28.2 and 46.7 Hz are observed for the signals of C-6 (δ = 32.5-45.8) and C-8 (δ = 57.2-61.7) since these two carbon atoms are also each directly adjacent to one of the diphosphirane phosphorus atoms. In some cases, an additional splitting of between 6.5 and 15.7 Hz is seen and is attributed to $^2J_{C,P}$ coupling. The signal of the skeletal carbon atom C-5 for all compounds appears as a singlet between δ = 32.0 and 40.7, with the sole exception of **19k** (δ = 78.4). The trimethylsiloxy group at C-5 in this case apparently exerts the expected downfield shift of about 40 ppm on the signal of this carbon atom. The two olefinic skeletal carbon atoms C-3 and C-4 each give rise to singlet signals in the region typical for sp^2-hybridized carbons (δ = 101.1-146.5) with the extreme values being observed in the case of **19k** as would be expected for the polarization of the C=C bond in **19k** by the trimethylsiloxy group at C-4. ^1H-Coupled ^{13}C NMR spectroscopy provides a means for distinguishing between the isomers **19** and **20**, as will be illustrated for the isomer pair **19b/20b**. In **19b** the methyl substituent R^2 is located at the olefinic carbon atom C-4 with the result that only the signal for C-3 experiences a $^1J_{C,H}$ coupling of 160 Hz whereas the signal for C-4 remains as a singlet. In contrast, the methyl substituent R^2 in **20b** is at the sp^3-hybridized carbon atom C-5 and, accordingly, both C-3 and C-4 appear as doublets in the ^1H-coupled ^{13}C NMR spectrum with coupling constants of 159.0 and 161.0 Hz, respectively. Further confirmation for the proposed assignments can be derived from the ^1H NMR spectra of **19a-k/20a-k**. In those cases where the double bond is not substituted (**19a** (≡ **20a**), **20b**, **19d**, **19f-h**), the olefinic protons at C-3 and C-4 appear as an AB spin system between δ = 5.45 and δ = 6.48 with $^3J_{H,H}$ coupling constants of 9.0-10.5 Hz, *ie* in the region typical for olefins. In addition, the signal for H-4 may be split by the substituent R^3 (for **19**) or R^2 (for **20**), respectively, at C-5 (see *Experimental section*). In all other cases where a substituent is present at C-3 or C-4, the typical coupling pattern of the olefinic protons is not observed. Further spectroscopic data in support of the constitu-

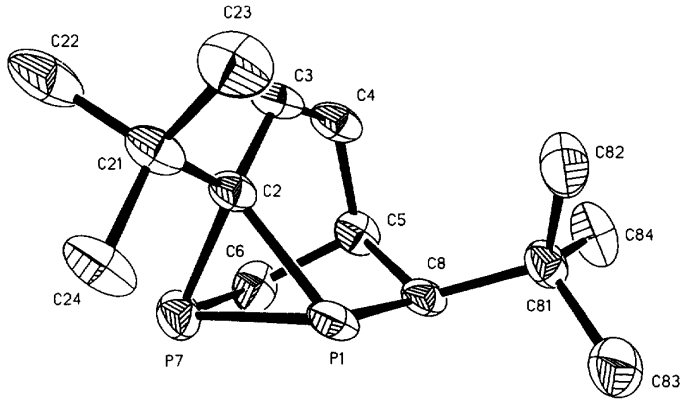


Fig 1. ORTEP – Plot of **19a** (≡ **20a**).

tions of **19a-k/20a-k**, with particular regard to the substituents R^1-R^4 and the presence of the *tert*-butyl groups at C-2 and C-8 are listed in the *Experimental section* and will not be discussed further here.

Crystal structure analysis of 19a (≡ 20a)

Last doubts about the structures of the tetracyclic systems **19** and **20** were resolved by an X-ray crystallographic analysis of **19a** (≡ **20a**); figure 1 shows a molecular plot and table I lists selected structural parameters for this previously unknown polycyclic ring system.

Table I. Selected bond lengths [Å] and angles [°] for **19a** (= **20a**).

Bond lengths [Å]		Bond angles [°]	
P-1–P-7	2.183(2)	P-1–C-2–P-7	70.7(2)
P-1–C-2	1.886(4)	C-2–P-1–P-7	54.7(1)
P-7–C-2	1.888(4)	C-2–P-7–P-1	54.6(1)
P-1–C-8	1.869(4)	C-2–P-1–C-8	100.9(2)
P-7–C-6	1.847(6)	C-2–P-7–C-6	98.6(2)
C-2–C-3	1.478(6)	P-1–C-2–C-3	116.3(3)
C-3–C-4	1.317(6)	P-7–C-2–C-3	114.7(3)
C-4–C-5	1.492(6)	P-1–P-7–C-6	93.8(2)
C-5–C-6	1.511(7)	P-7–P-1–C-8	94.8(1)
C-5–C-8	1.553(6)	P-1–C-8–C-5	108.2(3)
		P-7–C-6–C-5	111.5(3)
		C-2–C-3–C-4	123.3(4)
		C-3–C-4–C-5	118.3(4)
		C-4–C-5–C-6	108.5(4)
		C-4–C-5–C-8	111.2(3)
		C-6–C-5–C-8	107.1(4)

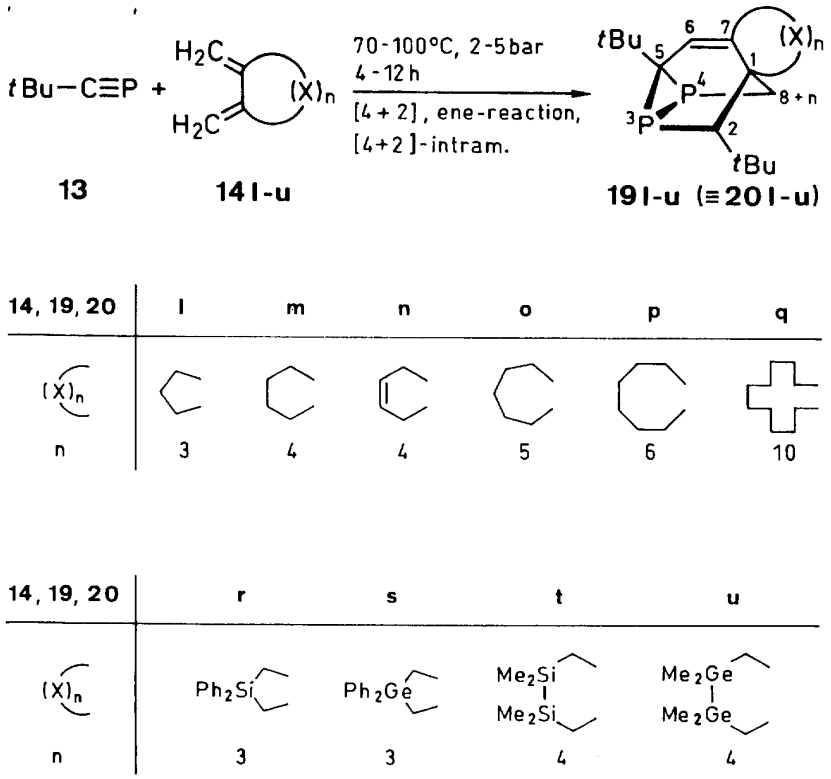
In comparison with those in other polycyclic systems containing a diphosphirane unit, the P-1/P-7 bond length of 2.183(2) Å can be considered as shortened; moreover, the P-1/C-2/P-7 bond angle of 70.7(2)° is smaller by 1-2° than those in comparable systems [20]. The two P/C bonds in the three-membered ring have almost identical lengths (P-1/C-2 : 1.886(4) Å, P-7/C-2 : 1.888(4) Å). The P-1/C-8 bond (1.869(4) Å) is markedly longer than the P-7/C-6 bond (1.847(6) Å); this is presumably a consequence of the bulky *tert*-butyl substituent at C-8, which, as can be seen from the Ortep plot (fig 1), occupies an equatorial position on the boat conformation defined by P-1/C-2/P-7/C-6/C-5/C-8.

1,3-Dienes 14l-u

The *s-cis*-fixed 1,3-dienes **14l-q** and the similarly *s-cis*-fixed 1,2-bis(methylene)sila- and 1,2-bis(methylene) germacycloalkanes **14r-u** [40-43] react with **13** to furnish the tetracyclic products **19l-u** (≡ **20l-u**) as colorless, crystalline solids in good to very good yields (70-100%). The higher reactivity (markedly reduced reaction temperatures and times) in comparison to the reactions of **13** with **14a-k** can be rationalized as follows : the geometrically favorable fixation of the 1,3-diene unit in the *s-cis* conformation gives rise to 1,4-separations ideally suited for Diels-Alder reactions; the fact that the 1,4-positions of the diene unit are unsubstituted; and the electron-rich nature of the bis(methylene)cycloalkanes with alkyl substituents in the 2- and 3-positions of the 1,3-diene unit. With the help of the proposed mechanism (scheme 2), it can be concluded directly that the formation of the tetracyclic system must be regiospecific, as is indeed the case. Similar to the above-mentioned examples, intermediates corresponding to **15-18** could not be isolated or even detected.

A conspicuous structural feature of the tetracyclic compounds **19l-u** (≡ **20l-u**) is the double bond between C-6 and C-7 which assigns them to the group of bridgehead olefins [21, 22]. Twisted π-bonds are not involved because of the sizes of the annelated rings at C-1 and C-7 (5- to 14-membered rings) and this provides an explanation for their high thermal stabilities.

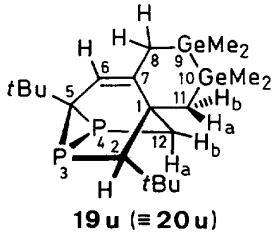
The elemental compositions and relative molecular masses of products **19l-u** (≡ **20l-u**) are substantiated by correct elemental analysis and the mass spectra recorded for most of the products. The presence of the heteroatom germanium in **19s** (≡ **20s**) and **19u** (≡ **20u**) is immediately apparent from the natural germanium isotope splitting pattern of the molecular ion peaks in the mass spectra; the agreement between calculated and measured distribution patterns of the molecular ion peaks is perfect, as is shown for the example of **19u** (≡ **20u**).



Scheme 3

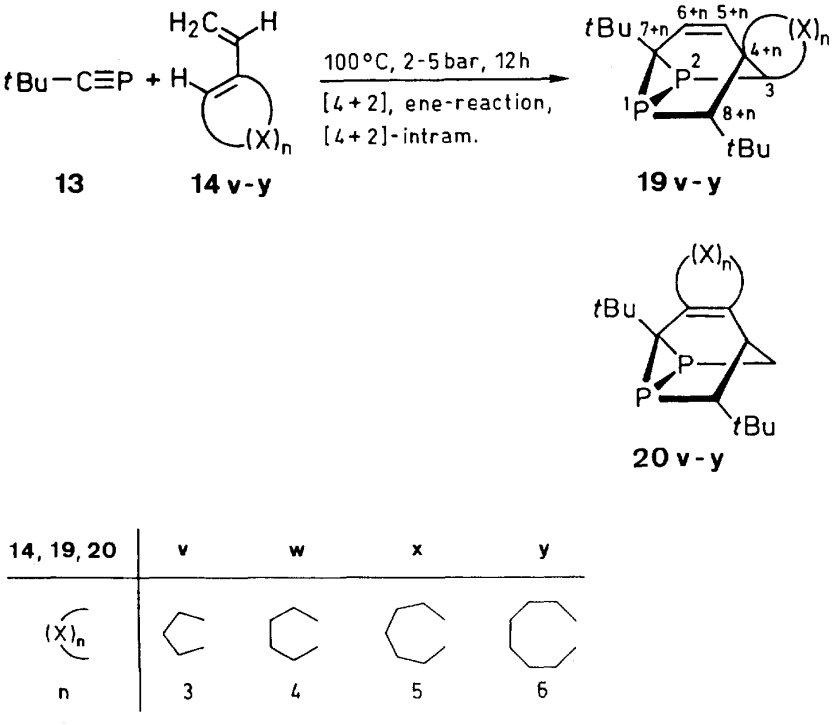
The structures of **19l-u** (≡ **20l-u**) can be deduced without difficulty from the spectroscopic data. In the ^{31}P NMR spectra, the AB spin system with $^{1}J_{P,P}$ coupling constants of 129.6-150.0 Hz typical for a diphosphirane unit is observed in the high field region. Since $^{2}J_{P,H}$ coupling (10-13 Hz) in the high field part of the AB pattern is observed in the proton-coupled ^{31}P NMR spectra and again for the methine proton at C-2 in the ^{1}H NMR spectra, these signals (δ = −208.0 to −219.6) can be reliably assigned to P-3. Accordingly, the low field part (δ = −160.4 to −185.0) represents the signals for P-4. The skeletal carbon atoms C-1, C-2, C-5, C-6, C-7, and C-(8 + n) can be located and readily assigned in the ^{13}C NMR spectra on the basis of their typical splitting patterns. Thus, the signals for C-5 appear as doublets of doublets with $^{1}J_{C,P}$ coupling constants of 41.6-50.4 and 41.5-44.0 Hz within a very narrow range (δ = 43.3-44.9) at relatively low field, as expected for a carbon atom in a three-membered ring. The low field positions are the result of paramagnetic shifts induced by the two neighboring phosphorus atoms and the *tert*-butyl group at C-5. The atoms C-2 (δ = 57.5-66.0, $^{1}J_{C,P}$ = 45.4-48.8 Hz) and C-(8 + n) (δ = 38.1-46.6, $^{1}J_{C,P}$ = 35.6-39.5 Hz) each have a phosphorus atom as direct neighbor and their signals are accordingly split into doublets. The relatively low field position of C-2 as compared to C-(8 + n) again reflects the influence of the *tert*-butyl group. It is also worthy of note that the $^{1}J_{C,P}$ coupling constants of C-2 are about 10 Hz larger than those of C-(8 + n). In the case of compounds **19m, n, p** and **q** (≡ **20 m, n, p** and **q**), $^{2}J_{C,P}$ coupling constants of 3.3-4.2 Hz can be determined for C-2 in contrast to C-(8 + n) where this is not possible in any case. The signals for C-1 (δ = 41.8-47.1), C-6 (δ = 116.7-125.6), and C-7 (δ = 130.8-139.6) each appear as a singlet in the expected region; the assignment of the signals for C-6 in the olefinic high field part of the spectra is facilitated by the observation of $^{1}J_{C,H}$ couplings solely for this signal. All other signals in the ^{13}C NMR spectra can be assigned without difficulty to the carbon atoms of the *tert*-butyl groups and those of the ring segment annelated at C-1 and C-7 (see *Experimental section*).

A detailed analysis of the ^{1}H NMR spectrum (400 MHz) of **19u** (≡ **20u**) was performed; this enabled conclusions to be drawn about the conformations of the tetracyclic compounds **19l-u** (≡ **20l-u**).



19u (≡20u)

Fig 2. 2,5-Di-*tert*-butyl-9,9,10,10-tetramethyl-3,4-diphospha-9,10-digermatetracyclo[5.4.$10^{1,7}$.$0^{3,5}$]dodec-6-ene **19u** (≡ **20u**).



14, 19, 20	v	w	x	y
(X)n				
n	3	4	5	6

Scheme 4

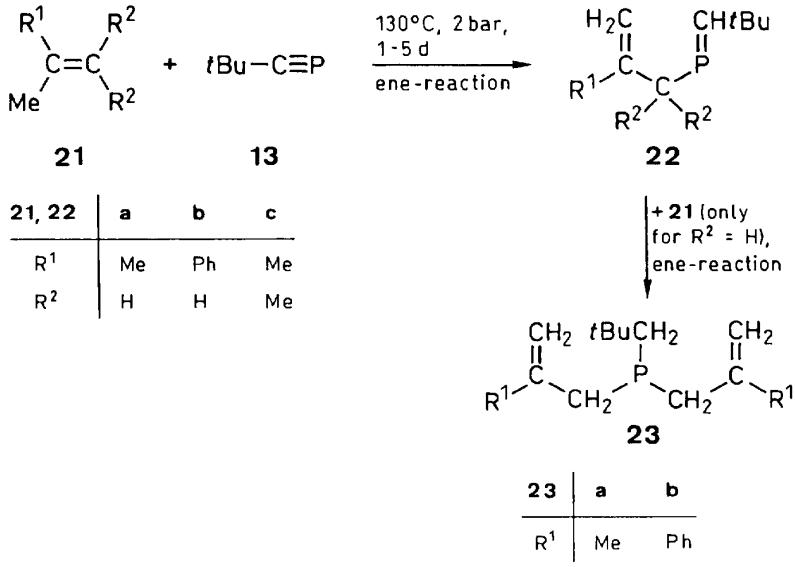
The methylene hydrogen atoms at C-12 appear as an ABXY spin system at $\delta = 0.73$ (H_a) and 1.30 (H_b) with a geminal $^2J_{H,H}$ coupling of 12.4 Hz, a $^2J_{H,P-4}$ coupling of 11.6 Hz, and with the form of a complex, but well structured, 8 line-multiplet in the high field part of the spectrum caused by a vicinal $^3J_{H,P}$ coupling in addition to the above-mentioned couplings. The magnitude of the $^3J_{H,P}$ coupling depends on the position of the coupling proton with respect to the free electron pair at phosphorus and on the dihedral angle [23].

The signals of the methylene protons at C-11 appear as an AB spin system at $\delta = 0.90$ and 1.89 with a geminal $^2J_{H,H}$ coupling of 14.6 Hz. The low field signal is assigned to the hydrogen atom H_a which, on account of its spatial orientation, lies in the anisotropic region of the *tert*-butyl group at C-2. The signals for the protons at C-8 are not well structured, but rather appear as a broad singlet at $\delta = 1.84$. The methine proton at C-2 experiences a $^2J_{H,P}$ coupling of 5.0 Hz with the phosphorus atom P-3 adjacent to C-2. The last remaining proton of tetracyclic skeleton to be localized, the olefinic proton at C-6, appears as a broad singlet at $\delta = 5.84$. The *tert*-butyl groups at C-2 and C-5 as well as the methyl groups at the germanium atoms Ge-9 and Ge-10 are all observed as sharp singlets; the resonances for the methyl protons appear at relatively high field between $\delta = 0.16$ and 0.33.

1,3-Dienes 14v-y

In order to further probe the reaction behavior of phosphaalkynes in the presented tandem reaction, the semicyclic 1,3-dienes **14v-y** were allowed to react with **13**. When benzene solutions of **14v-y** were treated with a two-fold molar amount of **13**, the tetracyclic products **19v-y** were obtained as colorless crystals in 42-52% yield after 12 h heating at 100°C with subsequent bulb-to-bulb distillation and recrystallization. These yields are markedly lower than those from the reactions of **13** with **14l-u** although longer reaction times and higher reaction temperatures are employed. Within the context of the mechanistic interpretation of the reaction sequence, it would appear that the initial [4 + 2] cycloaddition reaction is sterically impaired by the substitution at the carbon atoms C-3 and C-4. At the same time, this substitution pattern enforces the regioselectivity of the reaction for both electronic and steric reasons (scheme 2). Regioisomers with the structure **19** (but not **20**), in which the annelation occurs over the C/C double bond, are isolated. The initial Diels-Alder reaction (**13** + **14** ⇒ **15** or **16**) is so controlled that the most electron-rich center of the 1,3-diene unit reacts with the phosphorus of the phosphaalkyne; this corresponds to the polarity of the P/C triple bond (positive partial charge at phosphorus and negative partial charge at carbon). Concomitantly, the putative intermediate **15** experiences a lower steric hindrance in comparison to **16** since the *tert*-butyl substituent and the cycloalkyl group are further separated in **15**.

The structures of the tetracyclic products **19v-y** are very similar to those of **19l-u** so that all structural parameters need not be discussed again at this point (see *Experimental section*). Worthy of mention, however, are the signals in the ^{31}P NMR spectra for the diphosphirane unit ($\delta = -187.9$ to -195.6 and -161.8 to -179.6), which appear as doublets with $^1J_{P,P}$ coupling constants



21, 22	a	b	c
R^1	Me	Ph	Me
R^2	H	H	Me

23	a	b
R^1	Me	Ph

Scheme 5

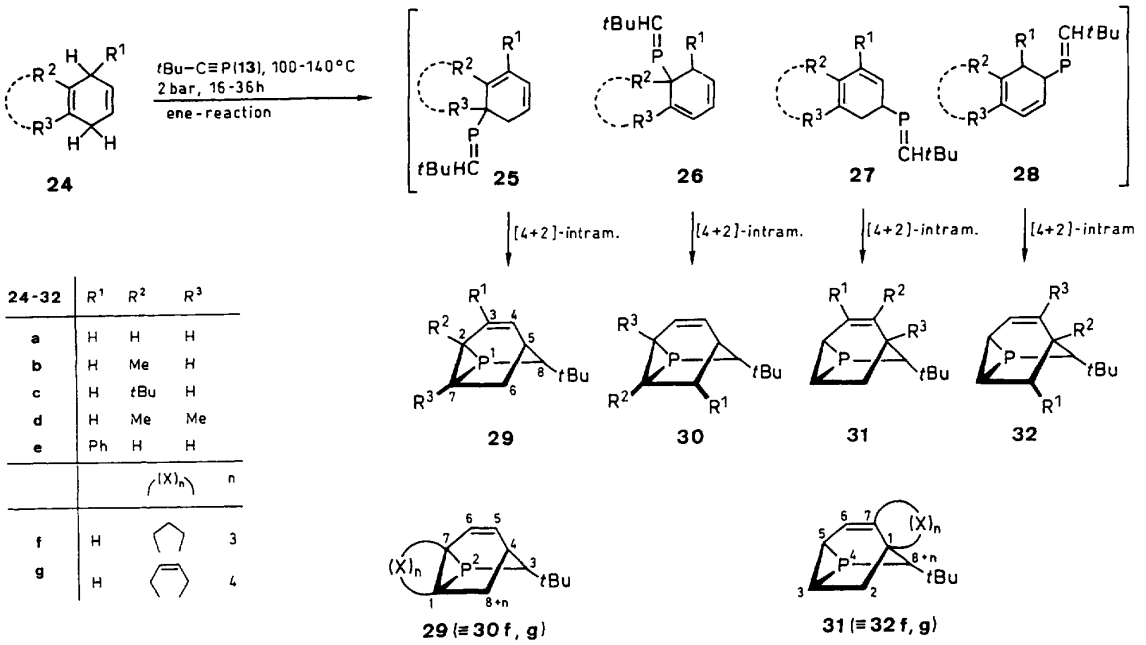
of 151.2-156.8 Hz. A specific assignment of the chemical shifts to P-1 and P-2 has not been made. In the ^{1}H NMR spectra, the olefinic protons at C-(5 + n) and C-(6 + n) give rise to an AB spin system at δ = 5.13-5.83 and 6.26-6.40, respectively, with a vicinal $^3J_{H,H}$ coupling of 9.7 Hz. In harmony with this, the signals of the olefinic carbon atoms C-(5 + n) and C-(6 + n) in the proton-coupled ^{13}C NMR spectra are split into doublets. These two spectroscopic observations can only be reconciled with structure **19** and thus constitute a convincing criterion for discounting structure **20**.

Ene reactions of 13 with 21a-c

The mechanistic concept proposed above to explain the formation of the polycyclic systems **19/20** incorporating a diphosphirane unit poses the principle question of the extent to which phosphaaalkynes are able to undergo ene reactions, especially since it was not possible to detect any intermediates in the syntheses of **19/20**.

Other reactions have been reported in the literature in which phosphaalkynes are assumed to act as enophiles, for example, the reactions of **13** with 2-methyl-6-*tert*-butylphosphinine [16], a germaalkene [25], or a silaalkene [26]. A phospha-ene reaction with P/P bond formation analogous to **15** ⇒ **17** is observed when **13** is allowed to react with η^1-complexed phosphaalkenes [27]. In these cases the phospha-ene reaction leads to stable phosphaalkenes, as does the reaction of **13** with pentamethylcyclopentadiene [14].

The ene reaction of acetylene with isobutene **21a** is known to furnish 2-methylpenta-1,4-diene [28]. When the analogous reaction is performed with the phosphaacetylene **13** and the alkenes **21a** or **b**, the [diallyl-(2,2-dimethylpropyl)]phosphines **23a** and **b** are formed in 24-27% yield. However, in contrast to the ene reaction with alkynes, the reactions of the phosphaalkyne **13** do not come to a standstill at the phosphaalkene stage. Since the primarily formed phosphaalkenes **22a** and **b** are themselves good enophiles, they each react spontaneously with a further molecule of **21** to yield the phosphines **23a** and **b**. The low yields obtained are a result of high losses during the distillative workup; product **23a** is formed as a colorless oil and **23b** as colorless crystals which deliquesce at room temperature. The constitutions of the phosphines **23** can be elucidated readily from their spectroscopic data. In the ^{31}P NMR spectra, the phosphorus atoms each give rise to singlet signals at δ = −43.6 and −38.5, respectively, in the high field region typical for tertiary phosphines [29]. The mass spectrum of **23b** exhibits a clear molecular ion peak (79%) and thus provides further support for the 1:2 adduct structure. In the ^{1}H NMR spectra, the expected signals for *tert*-butyl, methyl, and phenyl groups are seen in addition to the characteristic signal sets for methylene and vinyl protons. The methylene protons of the allyl groups are diastereotopic on account of the prochiral phosphorus atoms and appear as AB spin systems between δ = 2.16 and 2.66 with $^2J_{H,H}$ couplings of 12.8-13.5 Hz. Noteworthy is the fact that no coupling with the neighboring phosphorus atom can be observed; this is confirmed by the ^{31}P-decoupled ^{1}H NMR spectrum. The vinyl protons appears as a broad singlet between δ = 4.84 and 5.29, the region typical of olefinic protons. The enantiotopic methylene protons of the 2,2-dimethylpropyl group appear between δ = 1.39 and 1.40 and exhibit $^2J_{H,P}$ couplings of 3.8-4.2 Hz. The ^{13}C NMR spectra of **23a** and **b** are also in accord with the proposed structures. The carbon atoms of the allyl groups give doublet signals between δ = 36.8 and 41.6 with a $^1J_{C,P}$ coupling of 17.7 Hz. The olefinic carbons also appear as doublets between δ = 112.6 and 144.9 with $^2J_{C,P}$ couplings of 4.8-6.4 Hz and a $^3J_{C,P}$ coupling of 8.0 Hz. The methylene carbon atom of the 2,2-dimethylpropyl groups similarly gives rise to doublet signals between δ = 43.6 and 45.0 with $^1J_{C,P}$ couplings of 19.3-20.9 Hz. Further spectroscopic data are listed in the *Experimental section*.



24-32	R^1	R^2	R^3	
a	H	H	H	
b	H	Me	H	
c	H	*t*Bu	H	
d	H	Me	Me	
e	Ph	H	H	
		$(X)_n$		n
f	H			3
g	H			4

Scheme 6

When the steric demands of the ene component are increased by use of the tetramethyl-substituted alkene **21c**, only the primary ene product **22c** can be detected by ^{31}P NMR spectroscopy. The signal at $\delta = 268.0$ can only be realistically assigned to the $\lambda^3\sigma^2$-phosphorus of a phosphaalkene [30, 31]. Attempted purification by distillation led to complete decomposition of the compound.

1,4-Dienes 24a-g

We have shown that phosphaalkynes are also able to take part in phospha-ene reactions with acyclic enes. This prompts the question as to whether such reactions are also possible with cyclic dienes and, in particular, 1,4-dienes. Compounds of this type are direct analogues of the intermediate 1-phospha-1,4-dienes **15** and/or **16** postulated in scheme 2. A comparable reaction of cyclohexa-1,4-diene **24a** with dimethyl but-2-ynedioate has been reported in the literature to give rise to a product analogous to **29** (MeOCOC in place of P, MeOCO in place of *tert*-butyl, R^1-R^3 = H) [32, 33].

Indeed, the reaction of cyclohexa-1,4-diene **24a** with the phosphaalkyne **13** at 120°C for 16 h did give rise to the tricyclic phosphorus cage compound **29a** (≡ **30a** ≡ **31a** ≡ **32a**) as a colorless oil in 89% yield.

The structure of **29a** can be derived convincingly from the spectroscopic data. The presence of the phosphirane ring is demonstrated first by the ^{31}P NMR spectrum which exhibits a high field signal at $\delta = -234.0$ typical for a phosphirane [19]. The two phosphirane carbon atoms C-2 and C-7 are easily recognized in the ^{13}C NMR spectrum : the former appears at $\delta = 22.2$ and the latter at $\delta = 19.1$; both signals are split into doublets by $^1J_{C,P}$ couplings of 36.6 and 41.0 Hz, respectively. The sp^3-hybridized skeletal carbon atoms C-5, C-6, and C-8 give signals in the expected regions; the signals for C-5 and C-6 exhibit $^2J_{C,P}$ couplings of 2.7 and 4.4 Hz, respectively, while the signal for C-8 reveals the expected larger $^1J_{C,P}$ coupling of 39.7 Hz. Because of the close proximity of the *tert*-butyl group, the signal is characteristically shifted to low field in comparison to those of C-5 and C-6 ($\delta = 56.2$ as compared to 33.8 and 33.5, respectively). The olefinic skeletal carbon atoms C-3 and C-4 as well as the carbon atoms of the *tert*-butyl group produce signals in the expected positions and require no further explanation. The ^1H NMR spectrum of **29a** has the expected appearance since all the skeletal hydrogen atoms can be localized. The signals for the protons of the three-membered ring, H-2 and H-7, between $\delta = 1.8$ and 2.0 as well as those of the protons at C-5, C-6, and C-7 are complex multiplets and have not been analyzed further. The olefinic protons H-3 and H-4 give rise to an AB spin system at $\delta = 5.46$ and 6.03 with a $^3J_{H,H}$ coupling constant of 7.5 Hz. Both the A and the B parts are further split by vicinal couplings with H-2 or H-5, respectively.

The reaction is regiospecific in so far as, similar to the examples discussed further below, exclusively the hydrogen atom of the ene is transferred to the carbon atom of the phosphaalkyne. Transfer to the phosphorus atom of **13** would inevitably give rise to products with a P–H bond, and this would, of course, be instantly recognizable by NMR spectroscopy. In addition, the characteristic phosphirane increment in the product would then be absent. This situation has not been observed in any case.

When the substituted 1,4-dienes **24b-e** or the annelated representatives **24f** and **g** are employed as reaction partners for **13**, the regiospecificity of the ene

reaction is lost, *ie* in contrast to the reactions with the 1-phospha-1,4-dienes **15** or **16**, attack of the enophilic phosphorus in **13** can occur at C-1, C-2, C-4, and C-5 with formation of the ene products **25-28**. Similar to the reactions discussed above, these intermediates cannot be isolated or even detected spectroscopically since they all also undergo rapid intramolecular Diels-Alder reactions to furnish the phosphapolycyclic systems **29-32**. Thus, product mixtures exhibiting correct elemental compositions but which cannot be further separated are usually isolated from these reactions (see table III). The reaction of 1-methylcyclohexa-1,4-diene **24b** with **13** is completely unselective and gives the four isomers **29b-32b**, characterized by four signals between $\delta = -203.3$ and -231.9 in the typical ^{31}P NMR region for phosphiranes. As estimated from the ^{31}P NMR spectrum, the isomer distribution amounts to approximately 1:2:2:11 although assignments to individual isomers cannot be made. When the steric demands in the 1,4-diene part are increased by introduction of, for example, a *tert*-butyl group at C-1 (**24c**), two methyl groups at C-1 and C-2 (**24d**), or annelated rings at C-1 and C-2 (**24f** and **g**), the regioselectivity is increased for both electronic and thermodynamic reasons.

Since thermodynamic control of the reactions can be assumed on the basis of the reaction conditions (high temperatures and long reaction times) and the known reversibility of ene and Diels-Alder reactions, it seems reasonable to attribute the preferred formation of **29c, d, f, g/30c, d, f, g** in comparison to **31c, d, f, g/32c, d, f, g** to the fact that the *tert*-butyl group at C-8 and the substituents at C-2 and/or C-7 have the maximum separation in the structures **29** and **30**. In structures **31** and **32**, in contrast, one of these substituents would be directly adjacent to the *tert*-butyl group at C-8. On the other hand, the substituted, more electron-rich double bond of the 1,4-diene may preferentially react as an ene, which would be in accord with the normal electronic features of an ene reaction, and thus could also be responsible for the preferred formation of **29/30** over **31/32**.

In the cases of **24c** and the symmetrical 1,4-dienes **24d, f, g**, a pronounced regioselectivity in favor of the isomers **29** (≡ **30**) over **31** (≡ **32**) is observed accordingly; for the reaction of **24g**, this results in the exclusive formation of **29g** (≡ **30g**). The following ratios were determined by ^{31}P NMR spectroscopy : **29c/30c** to **31c/32c** = 99:1, **29d** (≡ **30d**) to **31d** (≡ **32d**) = 63:37, **29f** (≡ **30f**) to **31f** (≡ **32f**) = 91:9; the system **29c/30c** itself consists of two isomers in a ratio of 57:43 which could not be separated further.

The spectroscopic data of these compounds are very similar to those of **29a** (≡ **30a** ≡ **31a** ≡ **32a**) and need not be discussed in detail at this point (see *Experimental section*). As expected, high field singlets typical for phosphiranes appear between -192.0 and -216.8 in the ^{31}P NMR spectra of **29c/30c**, and **29d, f, g** (≡ **30d, f, g**). In the ^{13}C NMR spectra the phosphirane carbon atoms C-2 and C-7 (**29d** (≡ **30d**)) or, respectively, C-1 and C-7 (**29f, g** (≡ **30f, g**)) are shifted to low field by about 13 ppm in comparison to **29a** (≡ **30a** ≡ **31a** ≡ **32a**) and appear as doublets between $\delta = 32.9$ and 45.8 with $^1J_{C,P}$ coupling constants of 32.9-40.9 Hz. Furthermore, the olefinic carbon atoms C-3 and C-4 (**29c, 30c, 29d** (≡ **30d**)) or, respectively, C-5 and C-6 (**29f, g** (≡ **30f, g**)) give characteristic signals between $\delta = 123.9$ and 142.6 which appear as doublets with the usual $^1J_{C,H}$ couplings of approximately 160 Hz in the proton coupled ^{13}C NMR spectra. This observation rules out structures such as **31** or **32** where at least one of the olefinic carbon atoms would not show any splitting. Of the spectroscopic data of the minor products **31d, f** (≡ **32d, f**), the signals at $\delta = -207.9$ and -208.1 in the ^{31}P NMR spectra and at $\delta = 113.6$ and 124.6 in the ^{13}C NMR spectra deserve mention. The phosphorus signals confirm the polycyclic structures with incorporated phosphirane unit and the carbon signals the presence of a C/C double bond; furthermore, only one of the latter signals, namely that at higher field, is split into a doublet in the proton-coupled spectra as to be expected for the structure **31d, f** (≡ **32d, f**).

The reaction of **13** with 3-phenylcyclohexa-1,4-diene **24e** gives rise to the two tricyclic products **29e** (≡ **31e**) and **30e** (≡ **32e**) in a ratio of 85:15. The preferential formation of the isomer **29/31** over **30/32** reveals that transfer of the hydrogen atom activated by the phenyl group to C-1 is favored. The spectroscopic data of the isomers are in full accord with the proposed structures and in full harmony with the data mentioned above for the isomers **29-32** (see *Experimental section*).

Experimental section

All reactions were carried out under argon (purity > 99.998%) in previously baked-out and evacuated apparatus (glass tubes (3 × 5 cm, wall thickness 2 mm) with screw thread, teflon stopper and teflon stop-cock). Melting points (uncorrected, sealed capillary tubes) : Mettler FP 61 (heating rate 3°/min). Microanalyses : Perkin-Elmer Analyser 240. Bulb-to-bulb distillations : Büchi GKR 50 apparatus (temperatures given refer to the heating mantle). MS : Finnigan MAT 90. IR : Perkin-Elmer 710 B, Perkin-Elmer IR 394. ^1H NMR : Varian EM 360, Varian EM 390, Bruker WP 200, and Bruker AM 400 spectrometers at 60 MHz, 90 MHz, 200 MHz, and 400 MHz, respectively. ^{13}C NMR and ^{31}P NMR : Bruker WP 200 and Bruker AM 400 spectrometers at 50.32 MHz and 100.64 MHz (^{13}C) and 80.8 MHz and 161.6 MHz (^{31}P). Chemical shifts for ^1H and ^{13}C are reported in parts per million (ppm) relative to tetramethylsilane as internal standard; the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid.

t-Butylphosphaethyne **13** [8, 34], 1,3-dienes **14h** [35], **14i, j** [36], **14k** [37], **14l, m** [38], **14n** [39], **14o-q** [38], **14r-u** [43], **14v-y** [44], and 1,4-cyclohexadienes **24c** [45-47], **24d** [45,46], **24e** [45, 48], **24g** [49] were prepared according to reported procedures. All other starting materials were purchased from commercial suppliers.

Synthesis of 19/20

The solution of the phosphaalkyne **13** and the appropriate 1,3-diene **14** without or in a suitable solvent (see table II) was heated in a pressure tube under argon up to 140°C and 2 bar. The final products were isolated after evaporation of the solvent by bulb-to-bulb distillation or by recrystallization. Further details concerning the reaction conditions are summarized in table II.

Table II. Reaction conditions for the synthesis of **19/20**.

13 [g (mmol)]	**14** [g (mmol)]	solvent	time/temperature [h/°C]	distillation temperature[a] [°C (Pa)] or mp [°C] consistence	yield [g (%)][b] ratio **19:20**[c]
0.5 (5.0)	**a** : 2.00 (37.0)	–	7/90	$100/5 \cdot 10^{-1}$ colorless crystals	0.57 (90) –
0.5 (5.0)	**b** : 2.00 (29.4)	–	14/90	$100/5 \cdot 10^{-1}$ colorless oil	0.57 (85) 60:40
0.5 (5.0)	**c** : 0.42 (5.1)	benzene	24/120	$125/5 \cdot 10^{-1}$ colorless oil	0.61 (86) –
0.9 (9.0)	**d** : 0.88 (13.9)	petroleum ether (30-75°C)	50/140	$140/5 \cdot 10^{-2}$ colorless oil	0.80 (66) 85:15
0.7 (7.0)	**e** : 1.30 (15.8)	petroleum ether (30-75°C)	72/120	$120/5 \cdot 10^{-3}$ yellow oil	(<< 10) –
0.6 (6.0)	**f** : 0.64 (5.7)[d]	benzene	48/80	$150/5 \cdot 10^{-3}$ colorless crystals	(<< 10) 62:38
0.7 (7.0)	**g** : 1.60 (14.3)	benzene	48/120	$140/5 \cdot 10^{-3}$ colorless crystals	0.17 (16) 85:15
1.0 (10.0)	**h** : 0.80 (4.9)	benzene	72/130	141 colorless crystals	0.45 (25) 100:0
0.9 (9.0)	**i** : 0.70 (4.0)	benzene	60/130	$250/5 \cdot 10^{-3}$ orange oil	1.10 (73) 100:0
0.6 (6.0)	**j** : 1.00 (4.6)	benzene	60/130	$250/5 \cdot 10^{-3}$ orange crystals	1.10 (88) 100:0
0.9 (9.0)	**k** : 1.04 (4.5)	benzene	30/120	170/1.0 colorless oil	1.30 (67) –
1.2 (12.0)	**l** : 0.58 (6.1)	benzene	4/70	66 colorless crystals	1.43 (81)
1.3 (13.0)	**m** : 0.70 (6.5)	benzene	8/90	69 colorless crystals	1.57 (80)
1.4 (14.0)	**n** : 0.74 (7.0)	benzene	8/90	46 colorless crystals	1.39 (65)
1.3 (13.0)	**o** : 0.79 (6.5)	benzene	12/90	91 colorless crystals	1.70 (81)
0.9 (9.0)	**p** : 0.61 (4.5)	benzene	12/90	91 colorless crystals	1.20 (79)
0.7 (7.0)	**q** : 0.67 (3.5)	benzene	12/100	154 colorless crystals	1.09 (82)
0.4 (4.0)	**r** : 0.51 (1.9)	benzene	8/90	141 colorless crystals	0.68 (77)
0.4 (4.0)	**s** : 0.45 (1.5)	benzene	8/90	137 colorless crystals	0.61 (80)
0.6 (6.0)	**t** : 0.45 (2.3)	benzene	10/100	84 colorless crystals	0.74 (81)
0.4 (4.0)	**u** : 0.52 (1.8)	benzene	10/100	106 colorless crystals	0.68 (78)
1.2 (12.0)	**v** : 0.53 (5.6)[e]	benzene	12/100	180/1.0 yellow resin	0.69 (44) 100:0
1.0 (10.0)	**w** : 0.50 (4.6)[e]	benzene	12/100	190/1.0 yellow resin	0.69 (49) 100:0
1.0 (10.0)	**x** : 0.58 (4.7)[e]	benzene	12/100	200/1.0; 92 (mp) colorless crystals[f]	0.71 (47) 100:0
1.0 (10.0)	**y** : 0.62 (4.6)[e]	benzene	12/100	210/1.0; 122 (mp) colorless crystals[f]	0.78 (50) 100:0

[a] Temperatures refer to the heating mantle; [b] yields refer to **13** except for the reactions with **14h, i**, and **14r-y**; [c] determined by ^{31}P NMR spectroscopy; [d] generated *in situ* from methyl 2,5-dihydrothiophene-S,S-dioxide-3-carboxylate by extrusion of SO_2; [e] benzene solution (12-22%, determined by ^{1}H NMR spectroscopy); [f] after recrystallization from *n*-pentane (−78°C).

• *2,8-Di*-tert-*butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **19a** *(≡ 20a)*

^{31}P NMR (C_6D_6) : $\delta = -194.0$ (d, $^1J_{P,P} = 158.7$ Hz), -190.0 (d, $^1J_{P,P} = 158.7$ Hz).

^{1}H NMR ($CDCl_3$) : $\delta = 0.78, 1.31, 1.41, 3.06$ (each m, each 1H, H-5, H-6$_{exo}$, H-6$_{endo}$, H-8), 1.00, 1.04 (each s, each 9H, *t*Bu), 5.66 (d, $^3J_{H,H} = 9.0$ Hz, 1H, H-4), 6.29 (d, $^3J_{H,H} = 9.0$ Hz, 1H, H-3).

^{13}C NMR (C_6D_6) : $\delta = 29.3$ [dd, $^3J_{C,P} = 6.6$ Hz, $^3J_{C,P} = 6.6$ Hz, C(CH_3)$_3$], 31.5 [d, $^3J_{C,P} = 6.6$ Hz, C(CH_3)$_3$], 32.5 (dd, $^1J_{C,P} = 45.0$ Hz, $^2J_{C,P} = 6.5$ Hz, C-6), 32.0 (s, C-5), 34.7 [dd, $^2J_{C,P} = 10.5$ Hz, $^2J_{C,P} = 10.0$ Hz, C(CH_3)$_3$], 43.2 (dd, $^1J_{C,P} = 49.0$ Hz, $^1J_{C,P} = 44.9$ Hz, C-2), 59.4 (dd, $^1J_{C,P} = 45.5$ Hz, $^2J_{C,P} = 7.5$ Hz, C-8), 124.2, 128.4 (each s, C-3, C-4).

Anal : Calc for $C_{14}H_{24}P_2$, 254.29 : C, 66.13; H, 9.51. Found : C, 66.2; H, 9.35.

• *2,8-Di*-tert-*butyl-4-methyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **19b**

^{31}P NMR (C_6D_6) : $\delta = -194.5$ (d, $^1J_{P,P} = 152.7$ Hz), -192.5 (d, $^1J_{P,P} = 152.7$ Hz).

^{1}H NMR (C_6D_6) : $\delta = 0.95, 1.15$ (each s, each 9H, *t*Bu), 1.2-1.7 (m, 3H, H-6, H-8), 1.80 (s, 3H, Me), 2.7 (m, 1H, H-5), 6.00 (s, 1H, H-3).

^{13}C NMR (C_6D_6) : $\delta = 28.7$ (s, CH$_3$), 29.4 [d, $^3J_{C,P} = 6.5$ Hz, C(CH_3)$_3$], 30.9 [d, $^3J_{C,P} = 6.5$ Hz, C(CH_3)$_3$], 32.3 [d, $^2J_{C,P} = 10.0$ Hz, C(CH_3)$_3$], 34.5 [d, $^2J_{C,P} = 6.5$ Hz, C(CH_3)$_3$], 37.9 (s, C-5), 43.8 (pseudo-t, $^1J_{C,P} = 47.5$ Hz, C-2), 44.0 (d, $^1J_{C,P} = 46.5$ Hz, C-6), 57.2 (dd, $^1J_{C,P} = 38.2$ Hz, $^2J_{C,P} = 12.1$ Hz, C-8), 121.9 (s, C-3), 130.4 (s, C-4).

• *2,8-Di*-tert-*butyl-5-methyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **20b**

^{31}P NMR (C_6D_6) : $\delta = -202.2$ (d, $^1J_{P,P} = 152.6$), -165.5 (d, $^1J_{P,P} = 152.6$ Hz).

^{1}H NMR (C_6D_6) : $\delta = 1.15, 1.05$ (each s, each 9H, *t*Bu), 1.2-1.7 (m, 2H, H-6), 1.25 (s, 3H, Me), 2.05 (m, 1H, H-8), 5.35 (d, $^3J_{H,H} = 10.5$ Hz, 1H, H-4), 6.30 (d, $^3J_{H,H} = 10.5$ Hz, 1H, H-3).

^{13}C NMR (C_6D_6) : $\delta = 22.9$ (s, CH$_3$), 29.6 [dd, $^3J_{C,P} = 9.0$ Hz, $^3J_{C,P} = 9.0$ Hz, C(CH_3)$_3$], 32.8 [d, $^3J_{C,P} = 11.0$ Hz, C(CH_3)$_3$], 33.3 [d, $^2J_{C,P} = 10.0$ Hz, C(CH_3)$_3$], 43.7 [d, $^2J_{C,P} = 10.0$ Hz, C(CH_3)$_3$], 37.9 (d, $^2J_{C,P} = 2.5$ Hz, C-5), 43.8 (pseudo-t, $^1J_{C,P} = 47.5$ Hz, C-2), 44.0 (d, $^1J_{C,P} = 46.5$ Hz, C-6), 61.7 (dd, $^1J_{C,P} = 48.8$ Hz, $^2J_{C,P} = 4.3$ Hz, C-8), 124.7, 128.6 (each s, C-3, C-4).

Anal : Calc for $C_{15}H_{26}P_2$, 268.32 (isomeric mixture of **19b** and **20b**) : C, 67.10; H, 9.76. Found : C, 67.0; H, 9.63.

• *2,8-Di*-tert-*butyl-4,5-dimethyl-1,7-diphosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **19c** *(≡ 20c)*

^{31}P NMR ($CDCl_3$) : $\delta = -210.6$ (d, $^1J_{P,P} = 150.0$ Hz), -165.6 (d, $^1J_{P,P} = 150.0$ Hz).

^{1}H NMR ($CDCl_3$) : $\delta = 0.75$ (m, 2H, H-6), 1.00, 1.05 (each s, each 9H, *t*Bu), 1.31 (d, $^2J_{H,P} = 4.8$ Hz, 1H, H-8), 1.42, 1.83 (each s, each 3H, Me), 6.00 (s, 1H, H-3).

^{13}C NMR ($CDCl_3$) : $\delta = 20.6$ (s, CH$_3$-4), 26.2 (dd, $^3J_{C,P} = 2.7$ Hz, $^3J_{C,P} = 2.7$ Hz, CH$_3$-5), 29.15 [dd, $^3J_{C,P} = 7.4$ Hz, $^3J_{C,P} = 6.4$ Hz, C(CH_3)$_3$], 31.9 [d, $^3J_{C,P} = 9.7$ Hz, C(CH_3)$_3$], 34.55 [dd, $^2J_{C,P} = 10.7$ Hz, $^2J_{C,P} = 10.7$ Hz, C(CH_3)$_3$], 34.8 [d, $^2J_{C,P} = 10.6$ Hz, C(CH_3)$_3$], 40.7 (s, C-5), 43.4 (pseudo-t, $^1J_{C,P} = 47.3$ Hz, C-2), 45.1 (d, $^1J_{C,P} = 37.5$ Hz, C-6), 61.7 (dd, $^1J_{C,P} = 46.4$ Hz, C-8), 123.6 (s, C-3), 131.6 (s, C-4).

Anal : Calc for $C_{16}H_{28}P_2$, 283.35 : C, 68.06; H, 10.00. Found : C, 68.1; H, 9.90.

• *2,8-Di*-tert-*butyl-6-methyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **19d**

^{31}P NMR ($CDCl_3$) : $\delta = -176.3$ (d, $^1J_{P,P} = 158.4$ Hz), -174.2 (d, $^1J_{P,P} = 158.4$ Hz).

^{1}H NMR ($CDCl_3$) : $\delta = 0.96, 0.98$ (each s, each 9H, *t*Bu), 1.10 (m, 3H, Me), 1.48 (m, 2H, H-6, H-8), 2.83 (m, 1H, H-5), 5.45 (dd, $^3J_{H,H} = 9.6$ Hz, $^3J_{H,H} = 9.6$ Hz, 1H, H-4), 6.38 (d, $^3J_{H,H} = 9.6$ Hz, 1H, H-3).

^{13}C NMR ($CDCl_3$) : $\delta = 13.9$ (dd, $^2J_{C,P} = 10.5$ Hz, $^3J_{C,P} = 4.8$ Hz, CH$_3$), 28.9 [dd, $^3J_{C,P} = 5.8$ Hz, $^3J_{C,P} = 5.8$ Hz, C(CH_3)$_3$], 33.1 [d, $^3J_{C,P} = 2.5$ Hz, C(CH_3)$_3$], 34.3 [dd, $^2J_{C,P} = 10.0$ Hz, $^3J_{C,P} = 10.0$ Hz, C(CH_3)$_3$], 37.7 (s, C-5), 39.5 (dd, $^1J_{C,P} = 28.2$ Hz, $^2J_{C,P} = 13.0$ Hz, C-6), 42.9 (pseudo-t, $^1J_{C,P} = 47.5$ Hz, C-2), 58.9 (dd, $^1J_{C,P} = 33.4$ Hz, $^2J_{C,P} = 15.7$ Hz, C-8), 120.1, 128.3 (each s, C-3, C-4).

• *2,8-Di*-tert-*butyl-3-methyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **20d**

^{31}P NMR ($CDCl_3$) : $\delta = -195.2$ (d, $^1J_{P,P} = 160.1$ Hz), -169.2 (d, $^1J_{P,P} = 160.1$ Hz).

Further spectroscopic data could not be obtained.

Anal : Calc for $C_{15}H_{26}P_2$, 268.32 (isomeric mixture of **19d** and **20d**) : C, 67.10; H, 9.76. Found : C, 67.3; H, 9.69.

• *2,8-Di*-tert-*butyl-3,6-dimethyl-1,7-diphosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **19e** *(≡ 20e)*

^{31}P NMR ($CDCl_3$) : $\delta = -166.9$ (d, $^1J_{P,P} = 150.5$ Hz), -164.1 (d, $^1J_{P,P} = 150.5$ Hz).

Further spectroscopic and analytical data could not be obtained.

• *Methyl 2,8-di*-tert-*butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene-5-carboxylate* **19f**

^{31}P NMR ($CDCl_3$) : $\delta = -199.6$ (d, $^1J_{P,P} = 153.4$ Hz), -176.8 (d, $^1J_{P,P} = 153.4$ Hz).

^{1}H NMR ($CDCl_3$) : $\delta = 0.94, 1.04$ (each s, each 9H, *t*Bu), 3.72 (s, 3H, COOMe), 6.28, 6.40 (each d, $^3J_{H,H} = 9.8$ Hz, each 1H, H-3 and H-4).

• *Methyl 2,8-di*-tert-*butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene-4-carboxylate* **20f**

IR (KBr) : $\nu = 1\,730$ (strong, C=O).

^{31}P NMR ($CDCl_3$) : $\delta = -178.8$ (s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.94$ and 1.07 (each s, each 9H, *t*Bu), 3.77 (s 3H, COOMe), 7.70 (s, 1H, H-3).

In addition, the following data were obtained for the mixture of **19f/20f** :

^{1}H NMR ($CDCl_3$) : $\delta = 0.8$-1.4 (m), 1.50 (m), 1.52 (m), 1.86 (d, $J = 10.8$ Hz), 1.93 (d, $J = 10.8$ Hz), 2.17 (d, $J = 5.2$ Hz); the signals could not be assigned.

MS (EI, 70 eV) : m/z (%) = 313 (M^+, 60), 256 (20), 211 (86), 196 (97), 164 (36), 156 (31), 57 (100), 41 (65).

Anal : Calc for $C_{16}H_{26}O_2P_2$, 312.33 : C, 61.53; H, 8.39. Found : C, 60.7; H, 8.08.

• *Methyl 2,8-di*-tert-*butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene-6-carboxylate* **19g**

^{31}P NMR ($CDCl_3$) : $\delta = -181.6$ (d, $^1J_{P,P} = 151.8$ Hz), -177.6 (d, $^1J_{P,P} = 151.8$ Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.99 (s, 9H, *t*Bu), 1.03 (d, $^4J_{H,H}$ = 0.6 Hz, *t*Bu), 1.55 (m, 1H, H-8), 2.55 (dd, $^3J_{H,H}$ = 4.5 Hz, $^3J_{H,H}$ = 4.5 Hz, 1H, H-5), 3.49 (m, 1H, H-6), 3.63 (s, 3H, COOMe), 5.61, 6.42 (each d, $^3J_{H,H}$ = 9.4 Hz, each 1H, H-3 and H-4).

• *Methyl 2,8-di-*tert*-butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene-3-carboxylate* **20g**

IR (KBr) : ν = 1 715 (strong, broad C=O).

^{31}P NMR ($CDCl_3$) : δ = −191.5 (d, $^1J_{P,P}$ = 159.3 Hz), −172.1 (d, $^1J_{P,P}$ = 159.3 Hz).

^{1}H NMR ($CDCl_3$) : δ = 1.01, 1.02 (each s, each 9H, *t*Bu), 3.72 (dd, $^6J_{H,P}$ = << 0.5 Hz, COOMe), 6.34 (d, $^3J_{H,H}$ = 9.0 Hz, H-4).

In addition, the following data were obtained for the mixture of **19g/20g** :

Anal : Calc for $C_{16}H_{26}O_2P_2$, 312.33 : C, 61.53; H, 8.39. Found : C, 61.7; H, 8.27.

• *Dimethyl (2,8-di-*tert*-butyl-1,7-diphosphatricyclo [3.2.1.0 ^{2,7}]oct-3-en-6-yl)phosphonate* **19h**

IR (KBr) : ν = 1 250 (strong, P=O), 1 070, 1 040 (P-O-C).

^{31}P NMR ($CDCl_3$) : δ = −182.1 (d, $^1J_{P,P}$ = 153.2 Hz, P-1), −177.6 (dd, $^1J_{P,P}$ = 153.2 Hz, $^2J_{P,P}$ = 21.3 Hz, P-7), 31.5 [d, $^2J_{P,P}$ = 21.3 Hz, $PO(OMe)_2$].

^{1}H NMR ($CDCl_3$) : δ = 0.96, 1.03 (each s, each 9H, *t*Bu), 1.13-2.33 (m, 3H, H-5, H-6, H-8), 3.68, 3.73 [each d, $^3J_{H,P}$ = 9.0 Hz, each 3H, $PO(OMe)_2$], 5.73 (t, $^3J_{H,H}$ = 9.0 Hz, 1H, H-4), 6.48 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H-3).

^{13}C NMR ($CDCl_3$) : δ = 28.9 [s, $C(CH_3)_3$], 31.4 [s, $C(CH_3)_3$], 33.4 [m, $C(CH_3)_3$], 34.6 [m, $C(CH_3)_3$], 52.7 [dd, $^2J_{C,P}$ = 49.5 Hz, $^4J_{C,P}$ = 7.4 Hz, $PO(OCH_3)_2$], 59.2 (dd, $^1J_{C,P}$ = 46.7 Hz, $^2J_{C,P}$ = 26.2 Hz, C-8), 120.1, 129.4 (each s, C-3, C-4).

In addition, signals between 40.7 and 44.5 for C-2, C-5 and C-6 are obtained which could not be assigned to individual carbon atoms.

Anal : Calc for $C_{16}H_{29}O_3P_3$, 362.33 : C, 53.04; H, 8.07. Found : C, 52.3; H, 7.79

• *Dimethyl (2,8-di-*tert*-butyl-4-methyl-1,7-diphosphatricyclo[3.2.1.0 ^{2,7}]oct-3-en-6-yl) phosphonate* **19i**

IR (film) : ν = 1 245 (strong, P=O), 1 055, 1 035 (strong, P-O-C).

^{31}P NMR (C_6D_6) : δ = −183.2 (d, $^3J_{P,P}$ = 7.0 Hz, P-1), −183.1 (d, $^2J_{P,P}$ = 15.7 Hz, P-7), 30.3 [dd, $^2J_{P,P}$ = 15.7 Hz, $^3J_{P,P}$ = 7.0 Hz, $PO(OMe)_2$].

^{1}H NMR (C_6D_6) : δ = 0.90 and 1.05 (each s, each 9H, *t*Bu), 1.0-2.0 (m, 3H, H-5, H-6, H-8), 2.10 (s, 3H, Me), 3.40 [d, $^3J_{H,P}$ = 10.5 Hz, 6H, $PO(OMe)_2$], 6.50 (s, 1H, H-3).

^{13}C NMR (C_6D_6) : δ = 23.3 (s, CH_3), 28.8 [dd, $^3J_{C,P}$ = 6.5 Hz, $^3J_{C,P}$ = 6.5 Hz, $C(CH_3)_3$], 30.3 [s, $C(CH_3)_3$], 33.1 [d, $^2J_{C,P}$ = 5.0 Hz, $C(CH_3)_3$], 34.4 [dd, $^2J_{C,P}$ = 11.3 Hz, $^2J_{C,P}$ = 11.3 Hz, $C(CH_3)_3$], 38.0 (s, C-5), 43.3 (pseudo-t, $^1J_{C,P}$ = 46.9 Hz, C-2), 44.3 (m, C-6), 51.8 [dd, $^2J_{C,P}$ = 41.8 Hz, $^4J_{C,P}$ = 6.3 Hz, $PO(OCH_3)_2$], 58.8 (m, C-8), 123.6 (s, C-3), 128.0 (s, C-4).

Anal : Calc for $C_{17}H_{31}O_3P_3$, 376.35 : C, 54.25; H, 8.30. Found : C, 54.8; H, 8.20.

• *Dimethyl (2,4,8-tri-*tert*-butyl-1,7-diphospha-tricyclo[3.2.1.0 ^{2,7}]oct-3-en-6-yl)phosphonate* **19j**

^{31}P NMR (C_6D_6) : δ = −191.3 (d, $^2J_{C,P}$ = 16.7 Hz, P-7), −191.3 (d, $^2J_{C,P}$ = 11.6 Hz, P-1), 29.6 [dd, $^2J_{C,P}$ = 11.6 Hz, $^2J_{C,P}$ = 16.7 Hz, $PO(OMe)_2$].

^{1}H NMR (C_6D_6) : δ = 0.95, 1.10, 1.40 (each s, each 9H, *t*Bu), 1.0-1.9 (m, 3H, H-5, H-6, H-8), 3.35 [d, $^3J_{H,P}$ = 11.1 Hz, $^5J_{H,P}$ = 1.2 Hz, 6H, $PO(OMe)_2$], 6.40 (s, 1H, H-3).

^{13}C NMR (C_6D_6) : δ = 28.9 [pseudo-t, $J_{C,P}$ = 7.3 Hz, $C(CH_3)_3$], 30.5 [pseudo-t, $J_{C,P}$ = 3.9 Hz, $C(CH_3)_3$], 32.5 [s, $C(CH_3)_3$], 45.8 (dd, $^1J_{C,P}$ = 30.7 Hz, $^1J_{C,P}$ = 26.0 Hz, C-6), 51.7 [dd, $^2J_{C,P}$ = 26.1 Hz, $^4J_{C,P}$ = 6.4 Hz, $PO(OCH_3)_2$], 60.0 (m, C-8), 124.8 (s, C-3), 137.2 (s, C-4).

In addition, signals for C-2, C-5, $C(CH_3)_3$ and $C(CH_3)_3$ are obtained between 30.0 and 35.0 which could not be assigned to individual carbon atoms.

MS (EI, 70 eV) : *m/z* (%) = 419 (M^+, 49), 318 (56), 309 (16), 109 (33), 57 (100).

Anal : Calc for $C_{20}H_{37}O_3P_3$, 418.43 : C, 57.41; H, 8.91. Found : C, 57.2; H, 8.57.

• *2,8-Di-*tert*-butyl-4,5-bis-trimethylsiloxy-1,7-diphosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **19k** *(≡* **20k***)*

^{31}P NMR (C_6D_6) : δ = −216.3 (d, $^1J_{P,P}$ = 129.6 Hz), −185.0 (d, $^1J_{P,P}$ = 129.6 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.20, 0.37 (each s, each 9H, $SiMe_3$), 1.10 (s, 18H, 2-*t*Bu, 8-*t*Bu), 1.00-1.93 (m, 3H, H-6, H-8), 5.23 (s, 1H, H-3).

^{13}C NMR ($CDCl_3$) : δ = 0.5, 2.7 [each s, $Si(CH_3)_3$], 29.2 [t, $^3J_{C,P}$ = 7.0 Hz, $C(CH_3)_3$], 31.2 [d, $^3J_{C,P}$ = 9.0 Hz, $C(CH_3)_3$], 34.2 [d, $^2J_{C,P}$ = 8.0 Hz, $C(CH_3)_3$], 35.0 [t, $^2J_{C,P}$ = 11.1 Hz, $C(CH_3)_3$], 40.3 (d, $^1J_{C,P}$ = 39.2 Hz, C-6), 44.0 (dd, $^1J_{C,P}$ = 46.6 Hz, $^1J_{C,P}$ = 41.4 Hz, C-2), 59.9 (dd, $^1J_{C,P}$ = 46.3 Hz, $^2J_{C,P}$ = 3.0 Hz, C-8), 78.4 (s, C-5), 101.1 (s, C-3), 146.5 (s, C-4).

MS (EI, 70 eV) : *m/z* (%) = 430 (M^+, 1), 147 (100), 73 (19), 57 (3), 41 (2).

Anal : Calc for $C_{20}H_{40}O_2P_2Si_2$, 430.65 : C, 55.78, H, 9.36. Found : C, 55.6; H, 9.20.

• *2,5-Di-*tert*-butyl-3,4-diphosphatetracyclo [5.3.1.0 ^{1,7}.0 ^{3,5}]undec-6-ene* **19l** *(≡* **20l***)*

^{31}P NMR (C_6D_6) : δ = −213.9 (d, $^1J_{P,P}$ = 134.3 Hz), −168.3 (d $^1J_{P,P}$ = 143.3 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.80-2.45 (m, 9H, H-2, H-8, H-9, H-10, H-11), 1.05, 1.09 (each s, each 9H, *t*Bu), 6.08 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = 25.3 (s, C-9), 29.2 [t, $^3J_{C,P}$ = 6.2 Hz, $C(CH_3)_3$], 32.0 [d, $^3J_{C,P}$ = 11.3 Hz, $C(CH_3)_3$], 32.6 (s, C-10), 34.3 (t, $^2J_{C,P}$ = 11.1 Hz, $C(CH_3)_3$], 34.6 (d, $^2J_{C,P}$ = 9.8 Hz, $C(CH_3)_3$], 36.6 (s, C-8), 42.5 (d, $^1J_{C,P}$ = 39.5 Hz, C-11), 43.8 (dd, $^1J_{C,P}$ = 50.4 Hz, $^1J_{C,P}$ = 44.0 Hz, C-5), 46.1 (s, C-1), 57.5 (d, $^1J_{C,P}$ = 45.4 Hz, C-2), 116.7 (s, C-6), 139.6 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 294 (M^+, 94), 279 (5), 237 (81), 193 (26), 137 (100), 57 (70), 41 (19).

Anal : Calc for $C_{17}H_{28}P_2$, 294.35 : C, 69.37; H, 9.59. Found : C, 69.5; H, 9.50.

• *2,5-Di-*tert*-butyl-3,4-diphosphatetracyclo [5.4.1.0 ^{1,7}.0 ^{3,5}]dodec-6-ene* **19m** *(≡* **20m***)*

^{31}P NMR (C_6D_6) : δ = −211.7 (d, $^1J_{P,P}$ = 147.4 Hz), −173.3 (d, $^1J_{P,P}$ = 147.4 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.95-2.66 (m, 11H, H-2, H-8, H-9, H-10, H-11, H-12), 1.06 and 1.15 (each s, each 9H, *t*Bu), 6.02 (s,1H, H-6).

^{13}C NMR (C_6D_6) : δ = 21.7, 20.3 (each s, C-9, C-10), 29.5 [t, $^3J_{C,P}$ = 6.5 Hz, C(CH_3)$_3$], 30.0 (s, C-11), 32.6 [d, $^3J_{C,P}$ = 11.5 Hz, C(CH_3)$_3$], 32.7 (s, C-8), 34.8 [t, $^2J_{C,P}$ = 10.5 Hz, C(CH_3)$_3$], 35.1 [d, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 41.1 (d, $^1J_{C,P}$ = 38.7 Hz, C-12), 41.8 (s, C-1), 43.9 (dd, $^1J_{C,P}$ = 49.0 Hz, $^1J_{C,P}$ = 42.8 Hz, C-5), 60.0 (dd, $^1J_{C,P}$ = 48.5 Hz, $^2J_{C,P}$ = 3.7 Hz, C-2), 120.9 (s, C-6), 135.6 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 308 (M^+, 97), 293 (10), 251 (86), 207 (80), 151 (100), 57 (87), 41 (82).

Anal : Calc for $C_{18}H_{30}P_2$, 308.38 : C, 70.11; H, 9.81. Found : C, 70.3; H, 9.60.

• *2,5-Di*-tert-*butyl-3,4-diphosphatetracyclo [5.4.1.0 ^{1,7}.0 ^{3,5}]dodeca-6,9-diene* **19n** *(≡* **20n***)*

^{31}P NMR (C_6D_6) : δ = −211.6 (d, $^1J_{P,P}$ = 149.4 Hz), −167.6 (d, $^1J_{P,P}$ = 149.4 Hz).

^{1}H NMR ($CDCl_3$) : δ = 1.03 (s, 9H, *t*Bu), 1.06 (s, 10H, *t*Bu, H_a-12), 1.38 (dd, $^2J_{H,H}$ = 13.8 Hz, $^2J_{H,P}$ = 10.6 Hz, 1H, H_b-12), 1.45 (d, $^2J_{H,P}$ = 3.6 Hz, 1H, H-2), 2.13 (d, $^2J_{H,H}$ = 14.9 Hz, 1H, H_a-11), 2.79 (d, $^2J_{H,H}$ = 14.9 Hz, 1H, H_b-11), 2.91 (s, 2H, H-8), 5.89 (s, 2H, H-9, H-10), 6.07 (s, 1H, H-6).

^{13}C NMR (C_6D_6) : δ = 29.2 [t, $^3J_{C,P}$ = 6.1 Hz, C(CH_3)$_3$], 31.5 (s, C-11), 32.0 [d, $^3J_{C,P}$ = 11.3 Hz, C(CH_3)$_3$], 34.5 [t, $^2J_{C,P}$ = 11.2 Hz, C(CH_3)$_3$], 34.7 [d, $^2J_{C,P}$ = 10.4 Hz, C(CH_3)$_3$], 35.9 (s, C-8), 40.6 (s, C-1), 44.0 (dd, $^1J_{C,P}$ = 48.1 Hz, $^1J_{C,P}$ = 42.6 Hz, C-5), 44.7 (d, $^1J_{C,P}$ = 38.9 Hz, C-12), 60.3 (dd, $^1J_{C,P}$ = 48.8 Hz, $^2J_{C,P}$ = 3.3 Hz, C-2), 121.6, 126.2, 128.5 (each s, C-6, C-9, C-10), 130.8 (s, C-7).

Anal : Calc for $C_{18}H_{28}P_2$, 306.37 : C, 70.57; H, 9.21. Found : C, 70.6; H, 9.10.

• *2,5-Di*-tert-*butyl-3,4-diphosphatetracyclo [5.5.1.0 ^{1,7}.0 ^{3,5}]tridec-6-ene* **19o** *(≡* **20o***)*

^{31}P NMR (C_6D_6) : δ = −208.6 (d, $^1J_{P,P}$ = 149.5 Hz), −163.8 (d, $^1J_{P,P}$ = 149.5 Hz).

^{1}H NMR ($CDCl_3$) : δ = 1.03 and 1.06 (each s, each 9H, *t*Bu), 1.0-2.6 (m, 13H, H-2, H-8, H-9, H-10, H-11, H-12, H-13), 6.06 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = 28.5, 31.9, 32.3, 38.5, 41.2 (each s, C-8, C-9, C10, C-11, C-12), 29.5 [t, $^3J_{C,P}$ = 6.2 Hz, C(CH_3)$_3$], 32.8 [d, $^3J_{C,P}$ = 11.0 Hz, C(CH_3)$_3$], 34.8 [t, $^2J_{C,P}$ = 10.8 Hz, C(CH_3)$_3$], 35.3 [d, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 41.8 (d, $^1J_{C,P}$ = 37.3 Hz, C-13), 44.1 (dd, $^1J_{C,P}$ = 47.9 Hz, $^1J_{C,P}$ = 42.0 Hz, C-5), 45.4 (s, C-1), 63.3 (d, $^1J_{C,P}$ = 48.0 Hz, C-2), 123.7 (s, C-6), 138.5 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 322 (100, M^+), 307 (18), 265 (94), 221 (94), 165 (97), 57 (96), 41 (91).

Anal : Calc for $C_{19}H_{32}P_2$, 322.41 : C, 70.78; H, 10.00. Found : C, 70.8; H, 10.00.

• *2,5-Di*-tert-*butyl-3,4-diphosphatetracyclo [6.5.1.0 ^{1,7}.0 ^{3,5}]tetradec-6-ene* **19p** *(≡* **20p***)*

^{31}P NMR (C_6D_6) : δ = −208.0 (d, $^1J_{P,P}$ = 149.3 Hz), −171.2 (d, $^1J_{P,P}$ = 149.3 Hz).

^{1}H NMR ($CDCl_3$) : δ = 1.03 and 1.04 (each s, each 9H, *t*Bu), 1.2-2.7 (m, 15H, H-2, H-8, H-9, H-10, H-11, H-12, H-13, H-14), 6.13 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = 25.9, 26.7, 28.6, 32.7, 33.0, 38.3 (each s, C-8, C-9, C-10, C-11, C-12, C-13), 29.0 [t, $^3J_{C,P}$ = 6.3 Hz, C(CH_3)$_3$], 32.1 [d, $^3J_{C,P}$ = 10.7 Hz, C(CH_3)$_3$], 34.4 [t, $^2J_{C,P}$ = 10.7 Hz, C(CH_3)$_3$], 34.7 [d, $^2J_{C,P}$ = 10.7 Hz, C(CH_3)$_3$], 38.1 (d, $^1J_{C,P}$ = 36.0 Hz, C-14), 43.2 (s, C-1), 43.6 (dd, $^1J_{C,P}$ = 46.7 Hz, $^1J_{C,P}$ = 42.0 Hz, C-5), 66.0 (dd, $^1J_{C,P}$ = 48.2 Hz, $^2J_{C,P}$ = 4.2 Hz, C-2), 125.0 (s, C-6), 135.4 (s, C-7).

Anal : Calc for $C_{20}H_{34}P_2$, 336.44 : C, 71.40; H, 10.19. Found : C, 71.4; H, 10.00.

• *2,5-Di*-tert-*butyl-3,4-diphosphatetracyclo [10.5.1.0 ^{1,7}.0 ^{3,5}]octadec-6-ene* **19q** *(≡* **20q***)*

^{31}P NMR (C_6D_6) : δ = −208.5 (d, $^1J_{P,P}$ = 147.8 Hz), −170.0 (d, $^1J_{P,P}$ = 147.8 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.9-2.6 (m, 23H, H-2, H-8, H-9), H10, H-11, H-12, H-13, H-14, H-15, H-16, H-17 H-18), 6.13 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = 23.4, 24.2, 26.8, 27.0, 27.9, 28.1, 29.2, 30.0, 30.7, 39.2 (each s, C-8, C-9, C-10, C-11, C-12, C-13, C-14, C-15, C-16, C-17), 29.0 [t, $^3J_{C,P}$ = 6.4 Hz, C(CH_3)$_3$], 32.2 [d, $^3J_{C,P}$ = 10.4 Hz, C(CH_3)$_3$], 34.6 [t, $^2J_{C,P}$ = 10.2 Hz, C(CH_3)$_3$], 34.7 [d, $^2J_{C,P}$ = 9.7 Hz, C(CH_3)$_3$], 39.6 (d, $^1J_{C,P}$ = 35.6 Hz, C-18), 43.3 (pseudo-t, $^1J_{C,P}$ = 41.6 Hz, C-5), 44.6 (s, C-1), 63.8 (dd, $^1J_{C,P}$ = 47.2 Hz, $^2J_{C,P}$ = 4.2 Hz, C-2), 125.6 (s, C-6), 134.9 (s, C-7).

Anal : Calc for $C_{24}H_{42}P_2$, 392.55 : C, 73.43; H, 10.78. Found : C, 73.6; H, 10.60.

• *2,5-Di*-tert-*butyl-9,9-diphenyl-3,4-diphospha-9-silatetracyclo[5.3.1.0 ^{1,7}.0 ^{3,5}]undec-6-ene* **19r** *(≡* **20r***)*

^{31}P NMR (C_6D_6) : δ = −213.2 (d, $^1J_{P,P}$ = 148.5 Hz), −162.5 (d, $^1J_{P,P}$ = 148.5 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.78 (m, 1H, H_a-11), 1.02, 1.14 (each s, each 9H, *t*Bu), 1.28 (d, $^2J_{H,H}$ = 16.3 Hz, 1H, H_a-10), 1.41 (dd, $^2J_{H,H}$ = 13.7 Hz, $^2J_{H,P}$ = 10.6 Hz, 1H, H_b-11), 1.60 (d, $^2J_{H,P}$ = 5.0 Hz, 1H, H-2), 2.31 (s, broad, 2H, H-8), 2.39 (d, $^2J_{H,H}$ = 16.3 Hz, 1H, H_b-10), 6.19 (s, 1H, H-6), 7.3-7.6 (m, 10H, H-phenyl).

^{13}C NMR ($CDCl_3$) : δ = 22.1, 22.3 (each s, C-8, C-10), 29.8 [t, $^3J_{C,P}$ = 6.0 Hz, C(CH_3)$_3$], 32.9 [d, $^3J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 35.1 [t, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 35.5 [d, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 44.9 (dd, $^1J_{C,P}$ = 48.9 Hz, $^1J_{C,P}$ = 42.0 Hz, C-5), 46.6 (d, $^1J_{C,P}$ = 38.2 Hz, C-11), 47.1 (s, C-1), 60.6 (d, $^1J_{C,P}$ = 48.3 Hz, C-2), 122.5 (s, C-6), 128.4, 130.0, 135.2, 135.7, 135.9 (each s, C-phenyl), 136.7 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 462 (100, M^+), 447 (3), 405 (23), 361 (16), 305 (44), 57 (25), 41 (8).

Anal : Calc for $C_{28}H_{36}P_2Si$, 462.63 : C, 72.69; H, 7.84. Found : C, 72.6; H, 7.80.

• *2,5-Di*-tert-*butyl-9,9-diphenyl-3,4-diphospha-9-germatetracyclo[5.3.1.0 ^{1,7}.0 ^{3,5}]undec-6-ene* **19s** *(≡* **20s***)*

^{31}P NMR (C_6D_6) : δ = −213.6 (d, $^1J_{P,P}$ = 150.0), −160.4 (d, $^1J_{P,P}$ = 150.0 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.86 (m, 1H, H_a-11), 1.03, 1.11 (each s, each 9H, *t*Bu), 1.47 (d, $^2J_{H,H}$ = 15.4 Hz, 1H, H_a-10), 1.52 (dd, $^2J_{H,H}$ = 13.5 Hz, $^2J_{H,P}$ = 10.0 Hz, 1H, H_b-11), 1.64 (d, $^2J_{H,P}$ = 5.0 Hz, 1H, H-2), 2.43 (s, broad, 2H, H-8), 2.43 (d, $^2J_{H,H}$ = 15.4 Hz, 1H, H_b-10), 6.20 (s, 1H, H-6), 7.3-7.5 (m, 10H, H-phenyl).

^{13}C NMR ($CDCl_3$) : δ = 22.0, 25.5 (each s, C-8, C-10), 29.3 [t, $^3J_{C,P}$ = 6.0 Hz, C(CH_3)$_3$], 32.4 [d, $^3J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 34.6 [t, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 35.0 [d, $^2J_{C,P}$ = 10.1 Hz, C(CH_3)$_3$], 44.3 (dd, $^1J_{C,P}$ = 47.9 Hz, $^1J_{C,P}$ = 41.9 Hz, C-5), 46.5 (d, $^1J_{C,P}$ = 38.2 Hz, C-11),

47.5 (s, C-1), 60.2 (d, $^1J_{C,P}$ = 48.3 Hz, C-2), 122.3 (s, C-6), 128.3, 129.0, 134.1, 143.2, 137.2 137.6 (each s, C-phenyl), 136.7 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 508 (100, M^+), 493 (3), 451 (14), 407 (9), 351 (27), 227 (14), 151 (21), 57 (60), 41 (25).

Anal : Calc for $C_{28}H_{36}GeP_2$, 507.15 : C, 66.31; H, 7.15. Found : C, 66.5; H, 7.20.

• *2,5-Di*-tert-*butyl-9,9,10,10-tetramethyl-3,4-diphospha-9,10-disilatetracyclo [5.4.1.0 ^{1,7}.0 ^{3,5}]dodec-6-ene* **19t** *(≡* **20t***)*

^{31}P NMR (C_6D_6) : δ = −219.6 (d, $^1J_{P,P}$ = 145.8 Hz), −175.3 (d, $^1J_{P,P}$ = 145.8 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.01, 0.09, 0.14, 0.15 (each s, each 3H, $SiMe_2$), 0.68 (d, $^2J_{H,H}$ = 13.6 Hz, 1H, H_a-11), 0.77 (m, 1H, H_a-12), 1.02, 1.09 (each s, each 9H, *t*Bu), 1.30, (dd, $^2J_{H,H}$ = 12.6 Hz, $^2J_{H,P}$ = 12.6 Hz, 1H, H_b-12), 1.37 (d, $^2J_{H,P}$ = 5.0 Hz, 1H, H-2), 1.73 (s, broad, 2H, H-8), 1.75 (d, $^2J_{H,H}$ = 13.6 Hz, 1H, H_b-11), 5.85 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = −4.8, −3.3, −1.8, −0.8 [each s, $Si(CH_3)_2$], 26.4, 29.1 (each s, C-8, C-11), 29.4 [d, $^3J_{C,P}$ = 6.0 Hz, $C(CH_3)_3$], 32.7 [d, $^3J_{C,P}$ = 11.1 Hz, $C(CH_3)_3$], 34.8 [t, $^2J_{C,P}$ = 10.5 Hz, $C(CH_3)_3$], 35.4 [d, $^2J_{C,P}$ = 9.9 Hz, $C(CH_3)_3$], 44.2 (s, C-1), 44.6 (dd, $^1J_{C,P}$ = 47.1 Hz, $^1J_{C,P}$ = 41.8 Hz, C-5), 45.0 (d, $^1J_{C,P}$ = 37.2 Hz, C-12), 64.2 (d, $^1J_{C,P}$ = 47.3 Hz, C-2), 121.1 (s, C-6), 133.2 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 396 (50, M^+), 381 (3), 339 (5), 295 (24), 239 (100), 57 (19), 41 (8).

Anal : Calc for $C_{20}H_{38}Si_2P_2$, 396.64 : C, 60.56; H, 9.66. Found : C, 60.4; H, 9.60.

• *2,5-Di*-tert-*butyl-9,9,10,10-tetramethyl-3,4-diphospha-9,10-digermatetracyclo [5.4.1.0 ^{1,7}.0 ^{3,5}]dodec-6-ene* **19u** *(≡* **20u***)*

^{31}P NMR (C_6D_6) : δ = −214.4 (d, $^1J_{P,P}$ = 147.4 Hz), −168.5 (d, $^1J_{P,P}$ = 147.4 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.16, 0.24, 0.32, 0.33 (each s, each 3H, $GeMe_2$), 0.73 (m, 1H, H_a-12), 0.90 (d, $^2J_{H,H}$ = 14.6 Hz, H_a-11), 1.00, 1.07 (each s, each 9H, *t*Bu), 1.30 (dd, $^2J_{H,H}$ = 14.2 Hz, $^2J_{H,P}$ = 11.6 Hz, 1H, H_b-12), 1.37 (d, $^2J_{H,P}$ = 5.0 Hz, 1H, H-2), 1.84 (s, broad, 2H, H-8), 1.89 (d, $^2J_{H,H}$ = 14.6 Hz, 1H, H_b-11), 5.84 (s, 1H, H-6).

^{13}C NMR ($CDCl_3$) : δ = −5.5, −3.5, −2.5, −0.4 [each s, $Ge(CH_3)_2$], 25.0, 29.2 (each s, C-8, C-11), 29.1 [t, $^3J_{C,P}$ = 6.2 Hz, $C(CH_3)_3$], 32.3 [d, $^3J_{C,P}$ = 10.6 Hz, $C(CH_3)_3$], 34.4 [t, $^2J_{C,P}$ = 10.5 Hz, $C(CH_3)_3$], 35.0 [d, $^2J_{C,P}$ = 9.4 Hz, $C(CH_3)_3$], 44.3 (dd, $^1J_{C,P}$ = 47.1 Hz, $^1J_{C,P}$ = 41.5 Hz, C-5), 44.5 (s, C-1), 44.9 (d, $^1J_{C,P}$ = 37.3 Hz, C-12), 63.8 (d, $^1J_{C,P}$ = 47.3 Hz, $^2J_{C,P}$ = 3.7 Hz, C-2), 120.1 (s, C-6), 133.5 (s, C-7).

MS (EI, 70 eV) : *m/z* (%) = 485 (100, M^+), 471 (18), 429 (6), 385 (55), 329 (90), 57 (68), 41 (20).

Anal : Calc for $C_{20}H_{38}Ge_2P_2$, 485.68 : C, 49.46; H, 7.89. Found : C, 49.7; H, 7.80.

• *10,11-Di*-tert-*butyl-1,2-diphosphatetracyclo [5.3.1.0 ^{2,10}.0 ^{3,7}]undec-8-ene* **19v**

^{31}P NMR (C_6D_6) : δ = −195.6 (d, $^1J_{P,P}$ = 156.8 Hz), −161.8 (d, $^1J_{P,P}$ = 156.8 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.6-2.6 (m, 8H, H-3, H-4, H-5, H-6, H-11), 1.07, 1.08 (each s, each 9H, *t*Bu), 5.83, 6.26 (each d, each $^3J_{H,H}$ = 9.7 Hz, each 1H, H-8, H-9).

^{13}C NMR ($CDCl_3$) : δ = 24.3, 27.4 (each d, $^3J_{C,P}$ = 7.0 Hz, $^3J_{C,P}$ = 13.1 Hz, C-4, C-6), 29.7 [t, $^3J_{C,P}$ = 7.0 Hz, $C(CH_3)_3$], 33.2 [d, $^3J_{C,P}$ = 9.1 Hz, $C(CH_3)_3$], 34.9 [d, $^2J_{C,P}$ = 9.1 Hz, $C(CH_3)_3$], 34.9 (s, C-5), 35.1 [t, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 46.7 (dd, $^1J_{C,P}$ = 49.8 Hz, $^1J_{C,P}$ = 47.2 Hz, C-10), 52.1 (s, C-7), 54.3 (d, $^1J_{C,P}$ = 46.3 Hz, C-11), 57.2 (d, $^1J_{C,P}$ = 38.2 Hz, C-3), 128.2, 129.7 (each s, C-8, C-9).

MS (EI, 70 eV) : *m/z* (%) = 294 (M^+), 237 (13), 193 (10), 137 (100), 57 (47), 41 (41).

Anal : Calc for $C_{17}H_{28}P_2$, 294.35 : C, 69.37; H, 9.59. Found : C, 69.5; H, 9.30.

• *11,12-Di*-tert-*butyl-1,2-diphosphatetracyclo [6.3.1.0 ^{2,11}.0 ^{3,8}]dodec-9-ene* **19w**

^{31}P NMR (C_6D_6) : δ = −193.1 (d, $^1J_{P,P}$ = 154.4 Hz), −179.6 (d, $^1J_{P,P}$ = 154.4 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.6-2.6 (m, 10H, H-3, H-4, H-5, H-6, H-7, H-12), 1.03, 1.04 (each s, each 9H, *t*Bu), 5.32, 6.32 (each d, $^3J_{H,H}$ = 9.7 Hz, each 1H, H-9, H-10).

^{13}C NMR ($CDCl_3$) : δ = 24.3, 39.8 (each s, C-5, C-6), 27.3, 28.1 (each d, $^3J_{C,P}$ = 12.1 Hz, $^3J_{C,P}$ = 14.1 Hz, C-4, C-7), 29.4 [t, $^3J_{C,P}$ = 6.0 Hz, $C(CH_3)_3$], 33.2 [d, $^3J_{C,P}$ = 11.1 Hz, $C(CH_3)_3$], 34.6 [t, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 35.5 [d, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 41.3 (s, C-8), 43.2 (t, $^1J_{C,P}$ = 46.2 Hz, C-11), 50.3 (d, $^1J_{C,P}$ = 36.2 Hz, C-3), 65.0 (d, $^1J_{C,P}$ = 49.3 Hz, C-12), 124.6, 127.9 (each s, C-9, C-10).

MS (EI, 70 eV) : *m/z* (%) = 308 (57, M^+), 251 (14), 207 (10), 151 (100), 57 (42), 41 (15).

Anal : Calc for $C_{18}H_{30}P_2$, 308.38 : C, 70.11; H, 9.81. Found : C, 70.2; H, 9.80.

• *12,13-Di*-tert-*butyl-1,2-diphosphatetracyclo [7.3.1.0 ^{2,12}.0 ^{3,9}]tridec-10-ene* **19x**

^{31}P NMR (C_6D_6) : δ = −181.0 (d, $^1J_{P,P}$ = 152.0 Hz), −166.5 (d, $^1J_{P,P}$ = 152.0 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.5-2.7 (m, 12H, H-3, H-4, H-5, H-6, H-7, H-8, H-13), 1.06, 1.09 (each s, each 9H, *t*Bu), 5.34, 6.40 (each d, $^3J_{H,H}$ = 9.7 Hz, each 1H, H-10, H-11).

^{13}C NMR ($CDCl_3$) : δ = 23.3, 27.1, 44.4 (each s, C-5, C-6, C-7), 26.4, 26.7 (each d, $^3J_{C,P}$ = 12.1 Hz, $^3J_{C,P}$ = 20.1 Hz, C-4, C-8), 29.5 [t, $^3J_{C,P}$ = 6.0 Hz, $C(CH_3)_3$], 33.6 [d, $^3J_{C,P}$ = 13.1 Hz, $C(CH_3)_3$], 34.6 [t, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 35.8 [d, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 42.9 (dd, $^1J_{C,P}$ = 49.3 Hz, $^1J_{C,P}$ = 46.3 Hz, C-12), 43.1 (s, C-9), 49.6 (d, $^1J_{C,P}$ = 35.2 Hz, C-3), 65.4 (dd, $^1J_{C,P}$ = 49.3 Hz, $^2J_{C,P}$ = 3.5 Hz, C-13), 125.5, 128.7 (each s, C-10, C-11).

MS (EI, 70 eV) : *m/z* (%) = 323 (49, M^+), 265 (18), 221 (13), 165 (100), 57 (39), 41 (14).

Anal : Calc for $C_{19}H_{32}P_2$, 322.41 : C, 70.78; H, 10.00. Found : C, 70.6; H, 10.20.

• *13,14-Di*-tert-*butyl-1,2-diphosphatetracyclo [8.3.1.0 ^{2,13}.0 ^{3,10}]tetradec-11-ene* **19y**

^{31}P NMR (C_6D_6) : δ = −178.9 (d, $^1J_{P,P}$ = 151.2 Hz), −169.5 (d, $^1J_{P,P}$ = 151.2 Hz).

^{1}H NMR ($CDCl_3$) : δ = 0.6-2.6 (m, 14H, H-3, H-4, H-5, H-6, H-7, H-8, H-9, H-14), 1.00, 1.03 (each s, each 9H, *t*Bu), 5.13, 6.30 (each d, each $^3J_{H,H}$ = 9.7 Hz, H-11, H-12).

^{13}C NMR ($CDCl_3$) : δ = 22.5, 25.6 30.7, 33.6 (each s, C-5, C-6, C-7, C-8), 28.2, 28.4 (each d, $^3J_{C,P}$ = 5.3 Hz, $^3J_{C,P}$ = 3.0 Hz, C-4, C-9), 29.5 [t, $^3J_{C,P}$ = 6.0 Hz, $C(CH_3)_3$], 33.1 [d, $^3J_{C,P}$ = 13.1 Hz, $C(CH_3)_3$], 34.6 [t, $^2J_{C,P}$ = 10.1 Hz, $C(CH_3)_3$], 35.2 [d, $^2J_{C,P}$ = 10.1, $C(CH_3)_3$], 42.8 (s, C-10), 43.8 (t, $^1J_{C,P}$ = 49.6 Hz, C-13), 44.0 (d, $^1J_{C,P}$ = 32.0 Hz, C-3), 59.4 (d, $^1J_{C,P}$ = 47.3 Hz, C-14), 126.9, 128.0 (each d, C-11, C-12).

Table III. Reaction conditions for the synthesis of **29-32**.

13 [g (mmol)]	**24** [g (mmol)]	solvent	time/temperature [h/°C]	distillation temperature[a] [°C (Pa)] or mp [°C] consistence	yield [g (%)][b] ratio **29/30:31/32**[c]
0.5 (5.0)	**a** : 2.10 (26.2)	–	16/120	$100/5 \cdot 10^{-1}$ colorless oil	0.80 (89) –
0.5 (5.0)	**b** : 1.10 (11.7)	petroleum ether (30-75°C)	36/100	$120/5 \cdot 10^{-3}$ colorless oil	0.55 (57)[d]
0.6 (6.0)	**c** : 0.80 (5.9)	petroleum ether (30-75°C)	30/130	$120/5. \cdot 10^{-3}$ colorless oil	0.45 (32) 99:1
0.8 (8.0)	**d** : 1.15 (10.6)	petroleum ether (30-75°C)/*o*-xylene	36/125	$110/5 \cdot 10^{-3}$ colorless oil	1.00 (60) 63:37
0.8 (8.0)	**e** : 1.05 (6.7)	petroleum ether (30-75°C)	36/125	$140/5 \cdot 10^{-3}$ yellow oil	0.70 (41) 85:15[e]
0.8 (8.0)	**f** : 1.22 (10.2)	petroleum ether (30-75°C)	36/125	$110/5 \cdot 10^{-3}$ pale yellow oil	0.80 (45) 91:9
0.6 (6.0)	**g** : 0.80 (6.1)	petroleum ether (30-75°C)	18/140	$250/5 \cdot 10^{-3}$ pale yellow oil	0.45 (32) 100:0

[a] Temperatures refer to the heating mantle; [b] yields refers to **13** except for the reactions with **24c, d**; [c] determined by ^{31}P NMR spectroscopy; [d] assignment not possible by ^{31}P NMR spectroscopy; [e] ratio **29/31:30/32**.

MS (EI, 70 eV) : m/z (%) = 337 (45, M^+), 322 (9), 279 (23), 235 (10), 179 (63), 57 (68), 41 (24).

Anal : Calc for $C_{20}H_{34}P_2$, 336.44 : C, 71.40; H, 10.19. Found : C, 71.1; H, 10.40.

Ene reaction of **13** *with 2-methylpropene* **21a**, *2-phenylpropene* **21b**, *and 2,3-dimethylbut-2-ene* **21c**

The phosphaalkyne **13** and the appropriate alkene **21** without a solvent were heated in a pressure tube under argon at 130°C up to 2 bar for 1-5 days. The color of the solution changed to deep red. The final products were isolated after evaporation by bulb-to-bulb distillation.

• *2,2-Dimethylpropylbis(2-methylprop-2-enyl) phosphine* **23a**

From 0.56 g (5.59 mmol) **13** and 4.00 g (71.29 mmol) **21a**; yield : 0.28 g (24%) colorless oil (bp : 100°C/$2 \cdot 10^{-1}$ Pa).

^{31}P NMR (C_6D_6) : δ = −43.6 (s).

^{1}H NMR (C_6D_6) : δ = 1.08 (s, 9H, *t*Bu), 1.40 (d, $^2J_{H,P}$ = 4.2 Hz, 2H, PCH_2*t*Bu), 1.90 (s, 6H, Me), 2.16, 2.24 (each d, each $^2J_{H,H}$ = 12.8 Hz, 4H, PCH_2C=CH_2), 4.84 (s, 4H, PCH_2C=CH_2).

^{13}C NMR (C_6D_6) : δ = 24.1 (d, $^3J_{C,P}$ = 8.0 Hz, CH_3C=CH_2), 31.5 [d, $^2J_{C,P}$ = 14.5 Hz, $C(CH_3)_3$], 31.8 [d, $^3J_{C,P}$ = 8.0 Hz, $C(CH_3)_3$], 41.6 (d, $^1J_{C,P}$ = 17.7 Hz, PCH_2C=CH_2), 45.0 (d, $^1J_{C,P}$ = 19.3 Hz, PCH_2*t*Bu), 112.6 (d, $^3J_{C,P}$ = 8.0 Hz, PCH_2C=CH_2), 143.6 (d, $^2J_{C,P}$ = 6.4 Hz, PCH_2C=CH_2).

Anal : Calc for $C_{13}H_{25}P$, 212.31 : C, 73.54; H, 11.87. Found : C, 72.6; H, 11.50.

• *2,2-Dimethylpropylbis(2-phenylprop-2-enyl) phosphine* **23b**

From 0.56 g (5.6 mmol) **13** and 2.73 g (23.1 mmol) **21b**; yield : 0.71 g (38%) pale yellow oil (bp : 175°C/10^{-1} Pa), colorless crystals from pentane (−78°C), which melt at room temperature.

^{31}P NMR ($CDCl_3$) : δ = −38.5 (s).

^{1}H NMR ($CDCl_3$) : δ = 0.88 (s, broad, 9H, *t*Bu), 1.39 (d, $^2J_{H,P}$ = 3.8 Hz, PCH_2*t*Bu), 2.66, 2.56 (each d, each $^2J_{H,H}$ = 13.5 Hz, 4H, PCH_2C=CH_2), 5.04, 5.29 (each s, each broad, 4H, PCH_2C=CH_2), 7.14-7.37 (m, 10H, H-phenyl).

^{13}C NMR ($CDCl_3$) : δ = 30.7 [d, $^2J_{C,P}$ = 14.5 Hz, $C(CH_3)_3$], 30.9 [d, $^3J_{C,P}$ = 8.0 Hz, $C(CH_3)_3$], 36.8 (d, $^1J_{C,P}$ = 17.7 Hz, PCH_2C=CH_2), 43.6 (d, $^1J_{C,P}$ = 20.9 Hz, PCH_2*t*Bu), 113.7 (d, $^3J_{C,P}$ = 8.0 Hz, PCH_2C=CH_2), 126.3, 127.4, 128.1, 141.3 (each s, C-phenyl), 144.9 (d, $^2J_{C,P}$ = 4.8 Hz, PCH_2C=CH_2).

MS (EI, 70 eV) : m/z (%) = 337 (15, M^+ + H), 336 (79, M^+), 321 (9), 279 (11), 219 (100), 162 (31), 149 (23), 147 (53), 117 (10), 103 (13), 91 (28), 77 (10), 57 (119).

Anal : Calc for $C_{23}H_{29}P$, 336.46 : C, 82.11; H, 8.69. Found : C, 81.5; H, 8.60.

Synthesis of **29-32**

The solution of the phosphaalkyne **13** and the appropriate cyclohexa-1,4-diene **24** without or in a suitable solvent (see table III) was heated in a pressure tube under argon up to 140°C and 2 bar. The final products were isolated after evaporation of the solvent by bulb-to-bulb distillation or by recrystallization. Further details concerning the reaction conditions are summarized in table III.

• *8-*tert*-Butyl-1-phosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **29a** *(≡* **30a** *≡* **31a** *≡* **32a***)*

^{31}P NMR (C_6D_6) : δ = −234.0 (s).

^{1}H NMR (C_6D_6) : δ = 0.95 (s, *t*Bu), 0.9-1.4 (m, 3H, H-6, H-8), 1.8-2.0 (m, 2H, H-2, H-7), 2.60 (m, 1H, H-5), 5.46 (dd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 7.8 Hz, H-4), 6.03 (dd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 7.5 Hz, H-3).

^{13}C NMR (C_6D_6) : δ = 19.1 (d, $^1J_{C,P}$ = 41.0 Hz, C-7), 22.2 (d, $^1J_{C,P}$ = 36.6 Hz, C-2), 31.7 [d, $^3J_{C,P}$ = 5.0 Hz, $C(CH_3)_3$], 31.9 [d, $^2J_{C,P}$ = 7.4 Hz, $C(CH_3)_3$], 33.5 (d, $^2J_{C,P}$ = 4.4 Hz, C-6), 33.8 (d, $^2J_{C,P}$ = 2.7 Hz, C-5), 56.2 (d, $^1J_{C,P}$ = 39.7 Hz, C-8), 124.6, 124.7 (each s, C-3, C-4).

Anal : Calc for $C_{11}H_{17}P$, 180.23 : C, 73.31; H, 9.51. Found : C, 73.1; H, 9.96.

• *8-tert-Butyl-2-methyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **29b**, *8-tert-Butyl-7-methyl-1-phosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **30b**, *8-tert-Butyl-4-methyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **31b**, *8-tert-Butyl-5-methyl-1-phosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **32b**

^{31}P NMR ($CDCl_3$) : $\delta = -231.9$ (6%), -209.1 (68%), -203.3 (13%), -204 (13%) (each s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.90$ (d, $^{4}J_{H,P} = 0.6$ Hz, *t*Bu), 0.93 (s, *t*Bu), 0.93 (s, *t*Bu), 0.98 (d, $^{4}J_{H,P} = 0.7$ Hz, *t*Bu).

Anal : Calc for $C_{12}H_{19}P$, 194.26 : C, 74.19; H, 9.86. Found : C, 74.0; H, 9.80.

The isomeric mixture could not be separated. Further spectroscopic and analytical data could not be obtained.

• *2,8-Di-tert-butyl-1-phosphatricyclo[3.2.1.0 ^{2,7}]oct-3-ene* **29c**, *7,8-Di-tert-butyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **30c**

^{31}P NMR ($CDCl_3$) : $\delta = -216.3$ (43%), -211.8 (57%) (each s).

^{13}C NMR ($CDCl_3$) : $\delta = 124.1$, 125.0, 125.6, 127.3 (each s, C-3, C-4).

The mixture of isomers could not be separated. Further spectroscopic and analytical data could not be obtained.

• *8-tert-Butyl-2,7-dimethyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **29d** *(≡* **30d***)*

^{31}P NMR ($CDCl_3$) : $\delta = -192.0$ (s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.9$ (s, *t*Bu), 1.36 (s, 3H, Me), 1.50 (d, $^{3}J_{H,P} = 2.7$ Hz, 3H, Me), 1.0-2.0 (m, 3H, H-6, H-8), 2.8 (m, 1H, H-5), 5.95 (m, 1H, H-4), 6.0 (m, 1H, H-3).

^{13}C NMR ($CDCl_3$) : $\delta = 16.8$ (d, $^{2}J_{C,P} = 12.8$ Hz, CH_3), 19.8 (d, $^{2}J_{C,P} = 19.8$ Hz, CH_3), 31.1 [d, $^{3}J_{C,P} = 5.7$ Hz, $C(CH_3)_3$], 32.3 [d, $^{2}J_{C,P} = 10.5$ Hz, $C(CH_3)_3$], 32.9 (d, $^{1}J_{C,P} = 37.7$ Hz, C-7), 35.9 (s, C-5), 37.3 (d, $^{1}J_{C,P} = 34.3$ Hz, C-2), 43.3 (d, $^{2}J_{C,P} = 3.2$ Hz, C-6), 59.5 (d, $^{1}J_{C,P} = 39.4$ Hz, C-8), 142.6, 131.5 (each s, C-3, C-4).

• *8-tert-Butyl-4,5-dimethyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **31d** *(≡* **32d***)*

^{31}P NMR ($CDCl_3$) : $\delta = -208.1$ (s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.93$ (s, *t*Bu), 2.26 (s, Me).

^{13}C NMR ($CDCl_3$) : $\delta = 113.6$, 120.2 (each s, C-3, C-4).

Further spectroscopic data could not be obtained.

Anal : Calc for $C_{13}H_{21}P$, 208.29 [mixture of isomers : **29d** (≡ **30d**)/**31d** (≡ **32d**)] : C, 74.96; H, 10.16. Found : C, 75.2; H, 10.1.

• *8-tert-Butyl-3-phenyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **29e** *(≡* **31e***)*

^{31}P NMR ($CDCl_3$) : $\delta = -231.8$ (s).

^{1}H NMR ($CDCl_3$) : $\delta =$ (s, *t*Bu), 1.0-3.2 (m, 6H, H-2, H-5, H-6, H-7, H-8), 5.8 (m, 1H, H-4), 7.1-7.5 (m, 5H, H-phenyl).

^{13}C NMR ($CDCl_3$) : $\delta = 21.4$ (d, $^{1}J_{C,P} = 35.8$ Hz, C-2), 21.5 (d, $^{1}J_{C,P} = 41.3$ Hz, C-7), 31.2 [d, $^{3}J_{C,P} = 5.6$ Hz, $C(CH_3)_3$], 32.1 [d, $^{2}J_{C,P} = 7.2$ Hz, $C(CH_3)_3$], 33.1 (d, $^{3}J_{C,P} = 4.4$ Hz, C-6), 33.5 (d, $^{3}J_{C,P} = 2.9$ Hz, C-5), 56.8 (d, $^{1}J_{C,P} = 39.2$ Hz, C-8), 120.2 (s, C-4), 123.0-135.5 (each s, C-phenyl), 141.4 (s, C-3).

• *8-tert-Butyl-6-phenyl-1-phosphatricyclo [3.2.1.0 ^{2,7}]oct-3-ene* **30e** *(≡* **32e***)*

^{31}P NMR ($CDCl_3$) : $\delta = -220.9$ (s).

Further spectroscopic data could not be obtained.

Anal : Calc for $C_{17}H_{21}P$, 256.33 [mixture of isomers : **29e** (≡ **31e**)/**30e** (≡ **32e**)] : C, 79.66; H, 8.26. Found : C, 80.0; H, 8.19.

• *3-tert-Butyl-2-phosphatetracyclo [6.2.1.0 ^{1,7}.0 ^{2,7}]undec-5-ene* **29f** *(≡* **30f***)*

^{31}P NMR ($CDCl_3$) : $\delta = -204.6$ (s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.93$ (s, *t*Bu), 1.1-3.1 (m, 10H, H-3, H-4, H-8, H-9, H-10, H-11), 5.60, 6.18 (each d, each $^{3}J_{H,H} = 8.4$ Hz, each 1H, H-5, H-6).

^{13}C NMR ($CDCl_3$) : $\delta = 23.9$ (d, $^{2}J_{C,P} = 9.5$ Hz, C-8 or C-10), 31.0 (d, $^{3}J_{C,P} = 6.2$ Hz, C-9), 31.0 [d, $^{3}J_{C,P} = 6.6$ Hz, $C(CH_3)_3$], 31.5 [d, $^{2}J_{C,P} = 10.5$ Hz, $C(CH_3)_3$], 32.6 (d, $^{2}J_{C,P} = 13.0$ Hz, C-8 or C-10), 35.6 (d, $^{2}J_{C,P} = 2.4$ Hz, C-4), 37.5 (d, $^{2}J_{C,P} = 3.0$ Hz, C-11), 41.0 (d, $^{1}J_{C,P} = 40.9$ Hz, C-1), 45.8 (d, $^{1}J_{C,P} = 34.6$ Hz, C-7), 58.2 (d, $^{1}J_{C,P} = 34.6$ Hz, C-3), 123.9, 129.5 (each s, C-5, C-6).

• *2-tert-Butyl-3-phosphatetracyclo [6.2.1.0 ^{1,7}.0 ^{3,5}]undec-6-ene* **31f** *(≡* **32f***)*

^{31}P NMR ($CDCl_3$) : $\delta = -207.9$ (s).

^{13}C NMR ($CDCl_3$) : $\delta = 113.6$ (d, $^{1}J_{C,P} = 161.0$ Hz, C-6), 124.8 (s, C-7).

Further spectroscopic data could not be obtained.

Anal : Calc for $C_{14}H_{21}P$, 220.29 [isomeric mixture : **29f** (≡ **30f**)/**31f** (≡ **32f**)] : C, 76.33; H, 9.61. Found : C, 76.6; H, 9.52.

• *3-tert-Butyl-2-phosphatetracyclo [7.2.1:0 ^{1,7}.0 ^{2,7}]dodeca-5,9-diene* **29g** *(≡* **30g***)*

^{31}P NMR ($CDCl_3$) : $\delta = -196.9$ (s).

^{1}H NMR ($CDCl_3$) : $\delta = 0.95$ (s, *t*Bu), 1.0-1.9 (m, 4H, H-3, H-4, H-12), 2.4-3.1 (m, 4H, H-8, H-11), 5.6-6.2 (m, H-5, H-6, H-9, H-10).

^{13}C NMR ($CDCl_3$) : $\delta = 29.3$ (d, $^{2}J_{C,P} = 12.0$ Hz, C-8 or C-11), 30.4 (d, $^{2}J_{C,P} = 16.5$ Hz, C-8 or C-11), 31.1 [d, $^{3}J_{C,P} = 5.0$ Hz, $C(CH_3)_3$], 32.1 [d, $^{2}J_{C,P} = 6.2$ Hz, $C(CH_3)_3$], 33.6 (d, $^{1}J_{C,P} = 38.1$ Hz, C-1), 36.1 (d, $^{2}J_{C,P} = 4.0$ Hz, C-4), 39.8 (d, $^{1}J_{C,P} = 32.9$ Hz, C-7), 41.1 (s, C-12), 57.5 (d, $^{1}J_{C,P} = 39.5$ Hz, C-3), 124.7, 125.0, 127.0, 130.3 (each s, C-5, C-6, C11, C-10).

Anal : Calc for $C_{15}H_{21}P$, 232.31 : C, 77.55; H, 9.11. Found : C, 73.5; H, 8.96.

X-Ray crystal structure analysis of **19a** *(≡* **20a***)*

Data were collected at 20°C on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the MULTAN 82 program package. The compound **19a** (= **20a**), $C_{14}H_{24}P_2$ crystallizes in space group $P\bar{1}$; $a = 6.422(1)$, $b = 9.681(4)$, $c = 12.761(3)$ Å; $\alpha = 109.01(2)$, $\beta = 96.00(2)$, $\gamma = 96.31(2)°$; $V = 737.2$ Å^3; $Z = 2$; $D_{calc} = 1.15$ g cm^{-3}; Cu-K_α-radiation ($\lambda = 1.54184$ Å) graphite monochromator; $\mu = 24.805$ cm^{-1}; $F_{(000)} = 138$. A total of 2 447 unique reflexions were recorded in the range $4° \leqslant 2\Theta \leqslant 128°$ of which 326 were considered as unobserved ($I \leqslant 2\sigma(I)$), leaving 2 121 for solution and refinement. The number of parameters are 217. The final agreement factors were $R = 0.053$ and $R_W = 0.053$ (shift/error ratio $\leqslant 0.33$; residual electron density $\leqslant 0.35$) [50].

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References

1 Part 96 of this series started by M Regitz : Geissler B, Wettling T, Barth S, Binger P, Regitz M, *Synthesis* (1994) 1337-1343

2 Regitz M, *In Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Eds : Regitz M, Scherer OJ, Thieme, Stuttgart, 1990, chap C-2

3 Regitz M, *Chem Rev* (1990) 90, 191-213

4 Regitz M, Binger P, *Angew Chem* (1988) 100, 1541-1565; *Angew Chem Int Ed Engl* (1988) 27, 1484-1508

5 Memmesheimer H, Regitz M, *Rev Heteroatom Chem* (1994) 10, 61-90

6 Wagner O, Ehle M, Birkel M, Hoffmann J, Regitz M, *Chem Ber* (1991) 124, 1207-1213

7 Rösch W, Regitz M, *Angew Chem* (1984) 96, 898-899; *Angew Chem Int Ed Engl* (1984) 900-901

8 Rösch W, Hees U, Regitz M, *Chem Ber* (1987) 120, 1645-1652

9 Rösch W, Richter H, Regitz M, *Chem Ber* (1987) 120, 1809-1813

10 Rösch W, Facklam T, Regitz M, *Tetrahedron* (1987) 43, 3247-3256

11 Rösch W, Regitz M, *Synthesis* (1987) 689-693

12 Fink J, Rösch W, Vogelbacher UJ, Regitz M, *Angew Chem* (1986) 98, 265-266; *Angew Chem Int Ed Engl* (1986) 25, 280-282

13 Blatter K, Rösch W, Vogelbacher UJ, Fink J, Regitz M, *Angew Chem* (1987) 99, 67-68; *Angew Chem Int Ed Engl* (1987) 26, 85-86

14 Annen U, Regitz M, *Tetrahedron Lett* (1988) 29, 1681-1684

15 Annen U, Regitz M, Kluge H, *Chem Ber* (1990) 123, 935-937

16 Annen U, in *Phosphaalkine Dienophile Bausteine in Diels-Alder-Reaktionen*, Dissertation, University of Kaiserslautern, 1989

17 Rösch W, Regitz M, *Z Naturforsch* (1986) 41b, 931-933

18 Fuchs EPO, Rösch W, Regitz M, *Angew Chem* (1987) 99, 1058-1059; *Angew Chem Int Ed Engl* (1987) 26, 1011-1012

19 Berger S, Braun S, Kalinowski H-O, in *NMR-Spektroskopie von Nichtmetallen, ^{31}P NMR-Spektroskopie*, Thieme, Stuttgart, 1993, Vol 3, p 11

20 Mathey F, *Chem Rev* (1990) 90, 997-1025.

21 Bredt J, *Liebigs Ann Chem* (1924) 437, 1-13

22 Köbrich G, *Angew Chem* (1973) 85, 494-503; *Angew Chem Int Ed Engl* (1973) 12, 464

23 See ref 19, p 129; vergl auch [24]

24 Appel R, Knoll F, Ruppert I, *Angew Chem* (1981)93, 771-784; *Angew Chem Int Ed Engl* (1981) 20, 731

25 Lazraq M, Escudié J, Couret C, Bergsträßer U, Regitz M, *J Chem Soc, Chem Commun* (1993), 569-570

26 Breit B, Boese R, Regitz M, *J Organomet Chem* (1994) 464, 41-45

27 Marinetti A, Ricard L, Mathey F, Slany M, Regitz M, *Tetrahedron* (1993) 49, 10279-10290

28 Cywinski NF, *J Org Chem* (1965) 30, 361-364

29 See ref 19, p 6

30 See ref 19, p 23

31 Karaghiosoff K, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Eds : Regitz M, Scherer OJ, Thieme, Stuttgart, 1990, p 464

32 Alder K, Brochhagen F, Kaiser C, Roth W, *Liebigs Ann Chem* (1955) 593, 1-22

33 Hübner CF, Donoghue E, Dorfman L, Stuber FA, Danieli N, Wenkert E, *Tetrahedron Lett* (1966) 11, 1185-1191

34 Becker G, Gresser G, Uhl W, *Z Naturforsch* (1981) 36b, 16-19

35 Pudovik AN, Konovalova IV, *Z Obshch Khim* (1961) 31, 1580

36 Welter W, Hartmann A, Regitz M, *Chem Ber* (1978) 111, 3068-3085

37 Reetz MT, Neumeier G, *Chem Ber* (1979) 112, 2209-2219

38 van Straten JW, van Norden JJ, van Schaik TAM, Franke GT, de Wolf H, Bickelhaupt F, *Recl Trav Chim Pays-Bas* (1978) 97, 105-106

39 Middlemas ED, Quin LD, *J Org Chem* (1979) 44, 2587-2589

40 Mazerolles P, Laurent C, *J Organomet Chem* (1991) 402, 35-41

41 Mazerolles P, Laurent C, *J Organomet Chem* (1991) 406, 119-122

42 Mazerolles P, Laurent C, Faucher A, *J Organomet Chem* (1989) 366, 57-60

43 Laurent C, Mazerolles P, *Synth React Inorg Met-Org Chem* (1992) 22, 1183-1193

44 Markgraf JH, Greeno EW, Miller MD, Zaks WJ, Lee GA, *Tetrahedron Lett* (1983) 24, 241-244

45 Rabideau PW, Marcinow Z, *Organic Reactions* (1992) 42, 1-334

46 Krapcho AP, Bothner-By AA, *J Am Chem Soc* (1959) 81, 3658-3666

47 Benkeser RA, Burrous ML, Hazdra JJ, Kaiser EM, *J Org Chem* (1963) 28, 1094-1097

48 Lindow DF, Cortez CN, Harvey RG, *J Am Chem Soc* (1972) 94, 5406-5412

49 Vogel E, Klug W, Breuer A, *Org Synth Coll Vol* (1988) VI, 731-736

50 Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90387 and are available on request from the Document Supply Center