Organophosphorus Compounds, 137[≠]

On the Unusual Dienophilicity of Trimethylsilylphosphaacetylene

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Dedicated to Professor Wolfgang Steglich on the occasion of his 65th birthday

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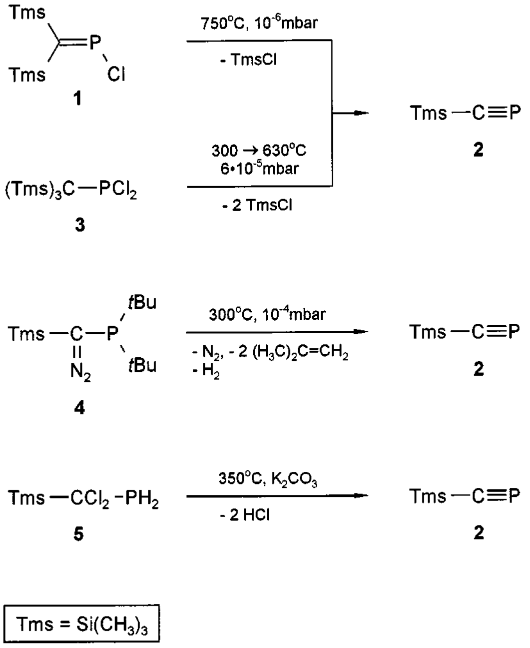
The diphosphatricyclooctenes **8a**, **b** are obtained from reactions of the phosphaacetylene **2** with the buta-1,3-dienes **6a**, **b** through a reaction sequence involving Diels–Alder, ene, and intramolecular [4 + 2] cycloaddition reactions with the intermediates **7** and **9**. An ab initio MO investigation at the MP2/6-31+G* level of theory has provided reasons why the postulated intermediates cannot be detected. The polycyclic products **8a**, **b** were characterized in the form of the corresponding metal carbonyl complexes **10a**, **b**, and **11**. Reaction of the silylated phosphaalkyne **2** with cyclohexa-1,4-diene (**12**) furnishes the monophosphatricyclooctene **14**; this reaction has also been studied by means of ab initio calculations. The result of the reaction of **2** with cyclopentadiene (**15**), however, is a complete surprise: the triphosphaspiropolycyclic system **17** is formed, apparently through Diels–Alder, homo-Diels–Alder, and homo [4 + 1] cycloaddition reactions with the intermediates **16** and **18**.

Introduction

Phosphaalkynes (**2**, R in place of Tms) have played a major role in the development of the chemistry of low-coordinated phosphorus.[2] Following the synthesis of the first stable member of this class of compounds, namely *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms),[3,4] most studies were focused on its reactivity in cycloaddition reactions and as a new ligand system.[2]

The kinetically stabilized trimethylsilylphosphaacetylene (**2**) is the center point of the current reactivity study. It is thermally less stable than the *t*Bu derivative and its reactivity has not been studied in detail previously, possibly because of its limited accessibility. Flash vacuum pyrolysis of the phosphaalkene **1**[5] or of the phosphane **3**[6] provide only low yields of **2** in impure form.

Flash vacuum pyrolysis of the diazo compound **4** − with cleavage of nitrogen, isobutene, and hydrogen − is also not suitable for the synthesis of **2** on a preparatively useful scale.[7] The current method of choice is the vacuum gas-solid reaction of dichloro(trimethylsilyl)methylphosphane (**5**) which furnishes the phosphaalkyne as a diethyl ether solution in high purity and up to 70% yield.[8] In contrast to earlier reports[5] this product has a considerably higher half-life time at room temperature ($\tau_{1/2}$ = 12 h as compared to 50 min), presumably because of its greater purity.



Scheme 1

Results and Discussion

We have reported elsewhere[9] on the reaction behavior of **2** towards 1,3-dipoles; the present investigations are addressed to the reactions of the silylated phosphaalkyne with 1,3-dienes and enes. When the ^{31}P- and ^{13}C-NMR signals of the P/C triple bond unit of **2** (δ = 98.2 and 200.9, respectively) are compared with those of *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms, δ = −69.2 and 184.8, respec-

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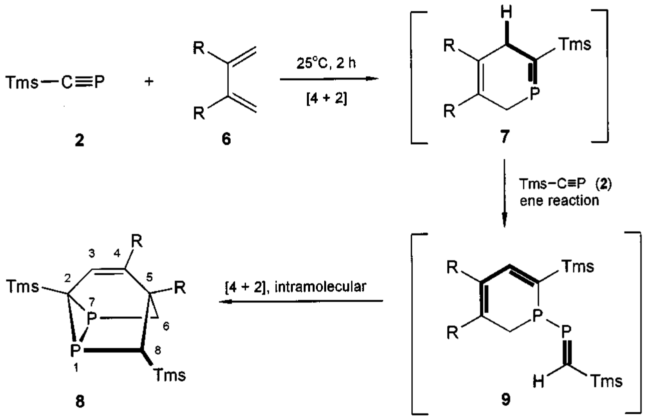
tively),[3] an at least gradual difference in reactivity may be expected on account of electronic effects.

Reaction of 2 with Buta-1,3-dienes 6

This trend is already apparent in the reactions of trimethylsilylphosphaacetylene (**2**) with an excess of the buta-1,3-dienes **6a**, **b**; the resulting reaction sequences proceed at room temperature in a 2:1 stoichiometry to furnish the diphosphatricyclooctenes **8a** (50%) and **8b** (55%), respectively. The Diels−Alder adduct **7** as well as the product **9** of a phospha-ene reaction are assumed to be formed as intermediates prior to the intramolecular [4 + 2] cycloaddition (**9** → **8**) leading to the polycyclic product. The corresponding reaction sequence with *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms) only occurs on heating to 90°C.[10]



6-9	a	b
R	H	Me

Scheme 2

The constitutions of products **8** are clearly demonstrated by their NMR and mass spectral data as discussed below for the example of **8a**. The presence of the diphosphirane unit can readily be deduced from the ^{31}P-NMR spectrum: the signals for P1 and P7 at $\delta = -186.5$ and $\delta = -201.8$ appear as an AB spin system with a $^{1}J_{P,P}$ coupling constant of 178.3 Hz, in complete harmony with the chemical shifts and coupling constants previously reported for similar systems.[10,11] Assignments of the skeletal atoms can be made on the basis of the ^{13}C-NMR data: C2 gives rise to a signal at $\delta = 15.8$ split into a double doublet structure by two almost equal $^{1}J_{C,P}$ coupling constants (57.8 and 55.8 Hz). The signals for the two carbon atoms C6 and C8 occur at $\delta = 34.3$ and $\delta = 32.1$ with $^{1}J_{C,P}$ coupling constants of 48.9 and 60.8 Hz, respectively. In comparison with the corresponding *tert*-butyl-substituted derivative (**8a**, *t*Bu in place of Tms)[10] it is seen that the signals of the two skeletal atoms C2 and C8 are shifted by about 27 ppm to higher field. This may be attributed to the deshielding effect of the trimethylsilyl groups. The signal for C5 does not exhibit any coupling with the phosphorus atoms and is observed as a singlet at $\delta = 33.5$. The remaining carbon atoms give rise to signals in the regions typical for their chemical environments and do not require explicit discussion. The ^{1}H-NMR spectrum contains signals at $\delta = -2.4$ and $\delta = 0.0$ for one trimethylsilyl group each, three multiplets between $\delta = 0.68$ and $\delta = 1.22$ that can be assigned to the skeletal hydrogen atoms 6-H and 8-H, and an extremely split multiplet at $\delta = 3.12$ for 5-H in the region typical for allylic hydrogen atoms. The olefinic hydrogen atoms give rise to a triple doublet at $\delta = 6.01$ and a pseudo-triplet at $\delta = 5.73$ with the adjacency of the two protons being confirmed by a $^{3}J_{H,H}$ coupling of 8.5 Hz. An exact analysis of the spin system was possible with the help of phosphorus decoupled ^{1}H-NMR spectra and spectral simulations but will not be discussed here.

Since the reaction of **2** with the buta-1,3-dienes **6** led to the tricyclic compounds **8** analogous to those obtained with *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms), a principally identical series of steps must be assumed for both reactions. The sequence begins with a Diels−Alder reaction between the phosphaalkyne **2** and the butadiene **6**. The initially formed [4 + 2] cycloadduct **7** then reacts with a further molecule of **2** in a phospha-ene reaction in the course of which formation of the phosphorus−phosphorus bond occurs. Ene reactions with the phosphaacetylene playing the role of the enophile have been studied in detail in recent years.[12] The phosphorus−carbon bond in **9**, in turn, undergoes an intramolecular [4 + 2] cycloaddition to the diene unit with formation of the diphosphatricyclic product **8**. When the necessary conditions for the reactions of the phosphaalkynes with the butadienes are considered [**2** + **6a**: 25°C, 2 h; **2** (*t*Bu in place of Tms) + **6a**: 90°C, 7 h[10]] it becomes clear that the silylated phosphaalkyne **2** must have a considerably higher dienophile character in comparison to the *tert*-butyl derivative **2** (*t*Bu in place of Tms). Frontier orbital considerations which have proved to be highly suitable for the prediction of reactions of organic compounds[13,14] are also of great value in cases such as that described here. A decisive factor for the rate of a pericyclic reaction is the energy difference between the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two starting compounds. We have thus calculated the HOMO and LUMO energies of the participating molecules, trimethylsilylphosphaacetylene, *tert*-butylphosphaacetylene, and *s-trans*-butadiene at the MP2/6-31+G* level of theory with the help of the GAUSSIAN94 program.[15] The frontier orbital energies [eV] are summarized graphically in Figure 1.

Both cycloadditions (**A**, **B**) are $\mathrm{HOMO_{diene}}$−$\mathrm{LUMO_{dienophile}}$-controlled reactions, the electronic situation thus corresponds to that of a *normal* Diels−Alder reaction between an electron-rich diene and an electron-poor dienophile.[14] It can be seen immediately from Figure 1 that the decisive HOMO−LUMO interaction in case **A**, i.e., in the reaction of the trimethylsilyl-substituted phosphaacetylene, is more favorable by 0.37 eV than that for the reaction of the *tert*-butyl compound (**B**). This difference of 0.37 eV or, respectively, of 8.53 kcal/mol should result in a markedly

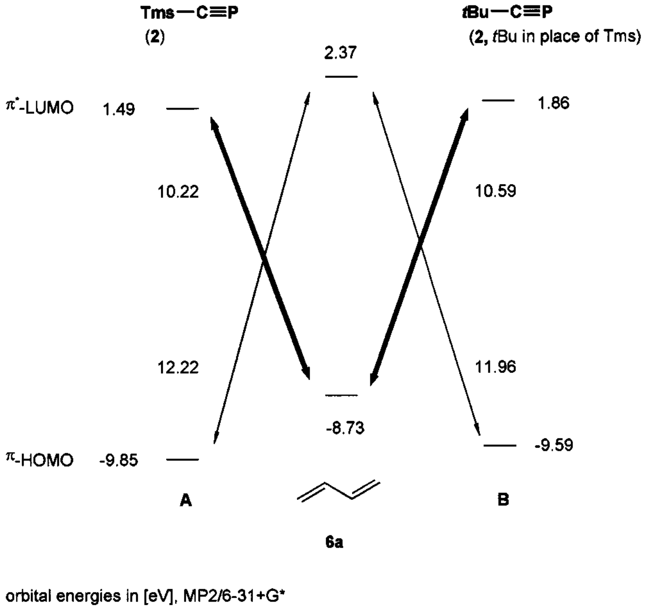


Figure 1. Frontier orbital interactions in the reaction of *s-trans*-butadiene **6a** with trimethylsilylphosphaalkyne (**2**) and *tert*-butylphosphaalkyne (**2**, *t*Bu in place of Tms); MP2/6−31+G* level of theory, energies in [eV]

lower activation barrier for the reaction of the trimethylsilylphosphaalkyne and thus explains the observed difference in reactivity. Accordingly, the lower energy position of the π*-LUMO of trimethylsilylphosphaacetylene is the reason for its increased reactivity in comparison with the *tert*-butylphosphaalkyne.

Previously the phosphacyclohexa-1,4-diene corresponding to **7** (R = H, Mes in place of Tms) was only isolated in the case of the reaction of mesitylphosphaacetylene (**2**; 2,4,6-$Me_3C_6H_2$ in place of Tms) with excess **6a**; it was subsequently allowed to react with a further equivalent of the phosphaalkyne to furnish the corresponding diphosphatricyclooctene.[16] In all other cases the reaction of butadienes with phosphaalkynes led directly to the tricyclooctenes and intermediates could not even be detected by ^{31}P-NMR spectroscopy.

In order to obtain more information in possible support of the proposed mechanism we have employed quantum chemical means to study the reaction of *s-trans*-butadiene with methylidynephosphane (**2**, H in place of Tms), serving as a model substance for the phosphaalkynes. All ab initio calculations were performed using the GAUSSIAN94 program packet.[15] The energy profile of the reaction as well as structures of the determined intermediates and transition states optimized at the MP2/6-31+G* level are shown in Figure 2. All MP2 energies contain an HF/6-31+G* zero point energy scaled with the factor 0.89. Characterization of the stationary points as minimum structures and transition structures was achieved by calculation of the analytical vibration frequencies (NIMAG = 0 for minimum, NIMAG = 1 for transition structure).

When the activation barriers of the three involved partial steps are considered it is found that the primary intermolecular Diels−Alder reaction has by far the highest activation energy of 11.28 kcal/mol. The activation barrier for the phospha-ene reaction (9.06 kcal/mol) is about 2 kcal/mol lower, and that for the final intramolecular [4 + 2] cycloaddition (8.27 kcal/mol) is about 3 kcal/mol lower. Thus, on application of a sufficient amount of thermal energy to overcome the first activation barrier, the subsequent reactions should occur automatically. The deduced energy profile and the localized intermediates and transition states impressively confirm the reaction mechanism postulated earlier and provide a simple explanation for the direct formation of the final products without any intermediates being detectable by spectroscopy.

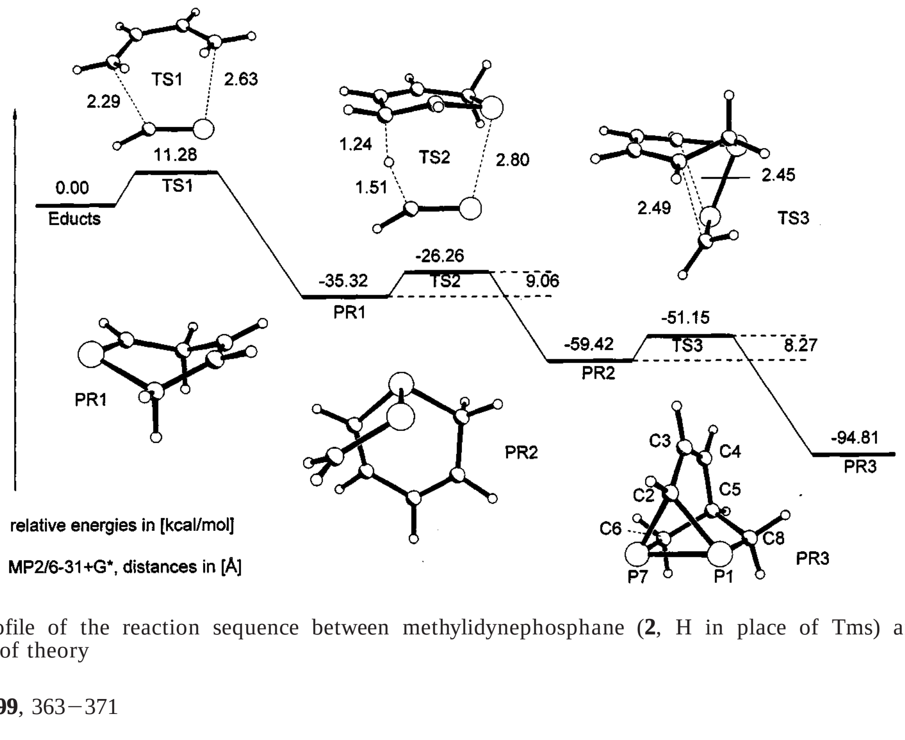
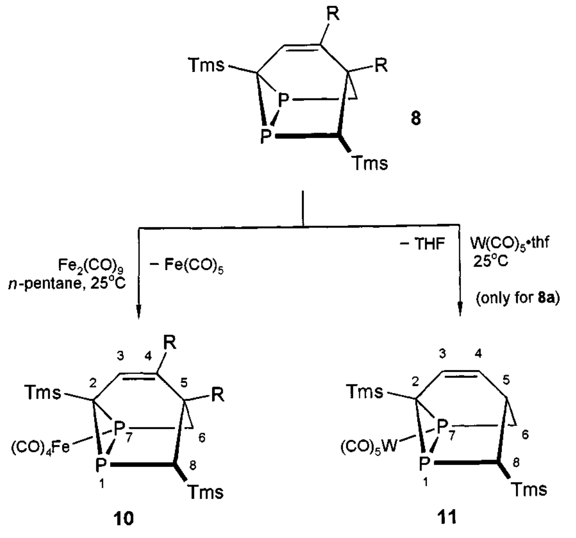


Figure 2. Energy profile of the reaction sequence between methylidynephosphane (**2**, H in place of Tms) and *s-trans*-butadiene; MP2/6−31+G* level of theory

Ligand Behavior of the Tricyclooctenes 8

The η^1-complexes **10** and **11** were obtained by treatment of the tricyclooctenes **8a**, **b** with a solution of nonacarbonyldiiron in *n*-pentane or of $W(CO)_5 \cdot$ thf in THF as red-brown or pale yellow crystals, respectively, after work-up by column chromatography and recrystallization.



10	a	b
R	H	Me

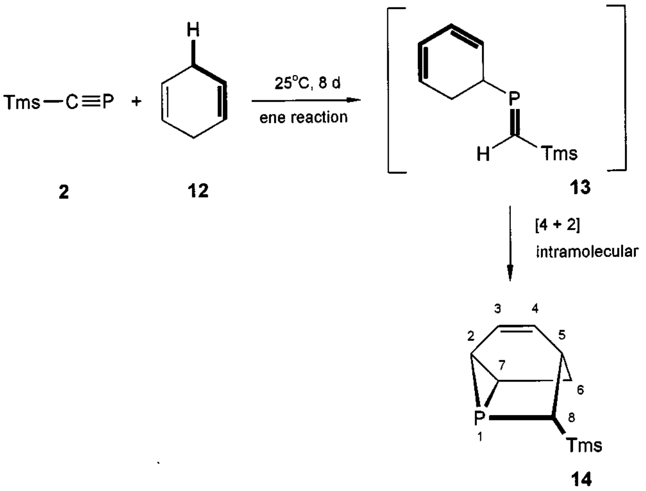
Scheme 3

A slight excess of nonacarbonyldiiron is necessary in these reactions in order to achieve complete conversion. The ^{31}P-NMR spectrum of the crude reaction mixture reveals the presence of a second species, presumably the doubly complexed diphosphatricyclic compound;[17] however, its isolation was not possible. When a large excess of nonacarbonyldiiron is used the formation of the doubly complexed tricyclooctene should be favored but, even so, isolation of the product by column chromatography was not possible either at normal or at low temperatures. On the other hand, a double complexation was not observed by ^{31}P-NMR spectroscopy in the reaction of **8a** with $W(CO)_5$·thf even in the presence of a large excess of the carbonyl compound.

The *end-on*-coordination of the diphosphatricyclic species **8** to the respective metal fragments in compounds **10** and **11** can be deduced from the analytical and spectroscopic data. The ^{31}P-NMR spectra of compounds **10** and **11** reveal shifts to lower field of between $\Delta\delta = 124.9$ ppm and $\Delta\delta = 46.2$ ppm for the signals of P7 in comparison to those of the uncomplexed starting materials. On the other hand, the positions of the signal for the other phosphorus atom (P1) remain more or less unchanged. The $^1J_{P,P}$ coupling constants of about 200 Hz confirm that the diphosphirane rings are retained in **10** and **11**. The $^1J_{P,W}$ coupling of 196.1 Hz in **11** and the IR spectrum provide further evidence for the η^1-coordination. The complexation occurs each time at P7 for steric reasons: P1 is sterically highly shielded by the two neighboring, voluminous trimethylsilyl groups. Since the bonding situation is almost unaffected by the *end-on* coordination, the ^{13}C-NMR data for complexes **10** and **11** differ only slightly from those of the uncomplexed starting materials. It merely needs to be mentioned that the couplings of carbon with the complexed phosphorus atom P7 become very small or break down completely: thus the couplings of C6 to P7 of 15.3 Hz (**10a**) and 11.9 Hz (**11**) are markedly smaller than that in the substrate (**8a**, 48.9 Hz).

Reaction of 2 with Cyclohexa-1,4-diene 12

Since the phosphaacetylene **2** reacted under very mild conditions (room temperature) and relatively rapidly (ca. 2 h) with the open-chain buta-1,3-dienes **8a**, **b**, it was of interest to examine whether this phosphaalkyne would also exhibit a higher reactivity than the *tert*-butyl derivative (**2**, *t*Bu in place of Tms) towards olefins with allylic hydrogen atoms in ene reactions. Accordingly, **2** was allowed to react with an excess of cyclohexa-1,4-diene **12** at room temperature: after a few hours the selective formation of one product was evident from the ^{31}P-NMR spectrum of the crude reaction mixture. This signal with a chemical shift of $\delta = -226.2$, in the region typical for phosphiranes, provides strong indications for the formation of the phosphatricyclic product **14**. In contrast to the reactions of **2** with the buta-1,3-dienes **8a**, **b**, however, this reaction was appreciably slower; the ^{31}P-NMR signal for the phosphaalkyne **2** disappears only after about one week. Removal of all volatile materials under high vacuum and work-up of the residue by distillation furnished the phosphatricyclooctene **14** in 10% yield. A similar increase in reaction time was also observed in the reaction of *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms) with cyclohexa-1,4-diene in comparison to that with buta-1,3-diene.[10] On account of this relatively long reaction time a large proportion of the short-lived phosphaalkyne is lost for formation of the desired product through oligo- and polymerization processes, as is reflected in the low yield of the isolated product.



Scheme 4

As already mentioned, the ^{31}P-NMR signal at $\delta = -226.2$ provides a clear indication for the constitution of **14**. Concrete evidence for the structure is given by the ^{13}C-NMR spectrum: the two phosphirane carbon atoms C2 and C7 give signals at $\delta = 19.9$ and $\delta = 20.6$ in the region typical for three-membered rings and are split into doublets by $^{1}J_{C,P}$ couplings of 39.2 Hz and 39.3 Hz, respectively. The signals for the remaining three sp^3-hybridized skeletal atoms C5 ($\delta = 34.4$), C6 ($\delta = 33.5$), and C8 ($\delta = 27.9$) appear in the expected region. The olefinic carbon atoms C3 and C4 also exhibit typical signals at $\delta = 123.7$ and $\delta = 125.0$. The ^{1}H-NMR spectrum of **14** furnishes further useful information: the olefinic protons 3-H and 4-H give signals at $\delta = 5.60$ and $\delta = 6.00$ as an AB spin system with a $^{3}J_{H,H}$ coupling of 8.3 Hz. Both the A and the B parts are split by further vicinal couplings with the protons 2-H ($^{3}J_{H,H} = 7.4$ Hz) and 5-H ($^{3}J_{H,H} = 7.6$ Hz) so that both signals appear as *pseudo*-triplets. Proton 5-H gives rise to an extremely split multiplet at a chemical shift typical for allylic protons, namely $\delta = 2.80$. The remaining hydrogen atoms produce signals between $\delta = 0.74$ and $\delta = 2.08$ as more or less complicated multiplets; a more exact analysis of the spin systems is only in part possible.

It is clear that the same mechanism must be assumed for the reaction of **2** with **12** as for the corresponding reaction of the *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms).[10] The initial ene reaction (generation of **13**) is followed by an intramolecular [4 + 2] cycloaddition with formation of the phosphatricyclooctene **14**. Again, no intermediates were detected on ^{31}P-NMR spectroscopic monitoring of the reaction. Thus it was also of interest to examine this reaction sequence with the help of ab initio MO calculations in order to obtain a better insight. The energetic positions and geometries of the involved transition structures and intermediates would be of particular interest in this case. In order to keep the mathematical effort within reasonable limits, methylidyne-phosphane (**2**, H in place of Tms) was again chosen as a model compound for the phosphaacetylenes. Geometries optimized at the MP2/6-31+G* level of theory and the energy profile of the reaction sequence are shown in Figure 3. The HF/6-31+G* zero point energies scaled by a factor of 0.89 have been taken into account in all energy values. Distinction between stationary points in minima and transition structures was possible by means of calculations of the analytical vibration frequencies.

It was found that the first partial step of the sequence, i.e., the phospha-ene reaction between the phosphaalkyne and the cyclohexadiene, has an appreciably higher activation energy than the following intramolecular [4 + 2] cycloaddition (15.35 kcal/mol as compared with 10.37 kcal/mol). Thus, when sufficient energy to overcome the first activation barrier is applied to the system, the subsequent reaction will follow directly with formation of the product PR5. It is, therefore, not surprising that intermediate PR4 cannot be detected in the ^{31}P-NMR spectrum. The activation barrier of 15.35 kcal/mol for the phospha-ene reaction as first step also explains the need for a higher temperature in comparison to that for the reaction of methylidynephosphane with the *s*-*trans*-butadiene. In the latter case, the activation barrier for the first step, an intermolecular Diels−Alder reaction, amounts to only 11.28 kcal/mol.

Reaction of 2 with Cyclopentadiene 15

Since the trimethylsilylphosphaacetylene **2** already demonstrated an exceptionally high reactivity towards normal butadienes there should be no reason why it cannot also react with cyclopentadiene **15**. When the two components

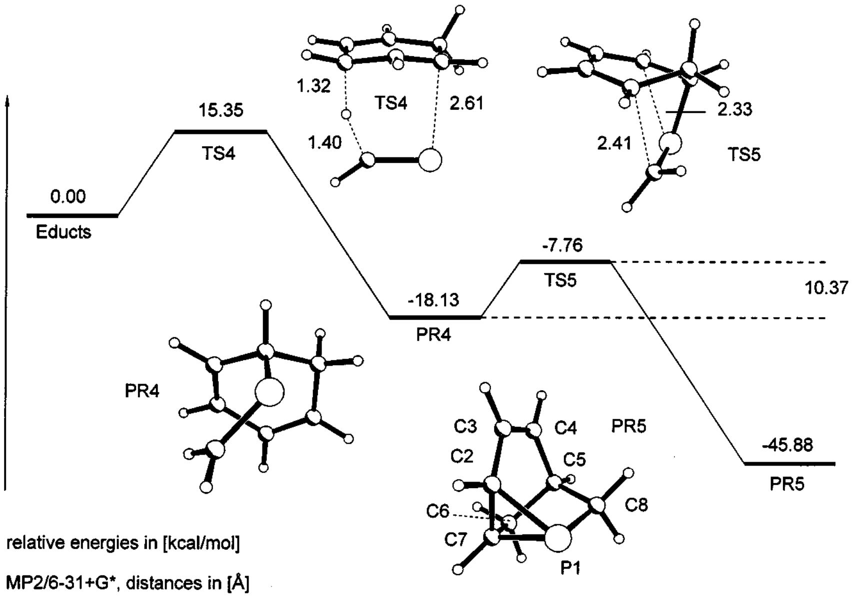
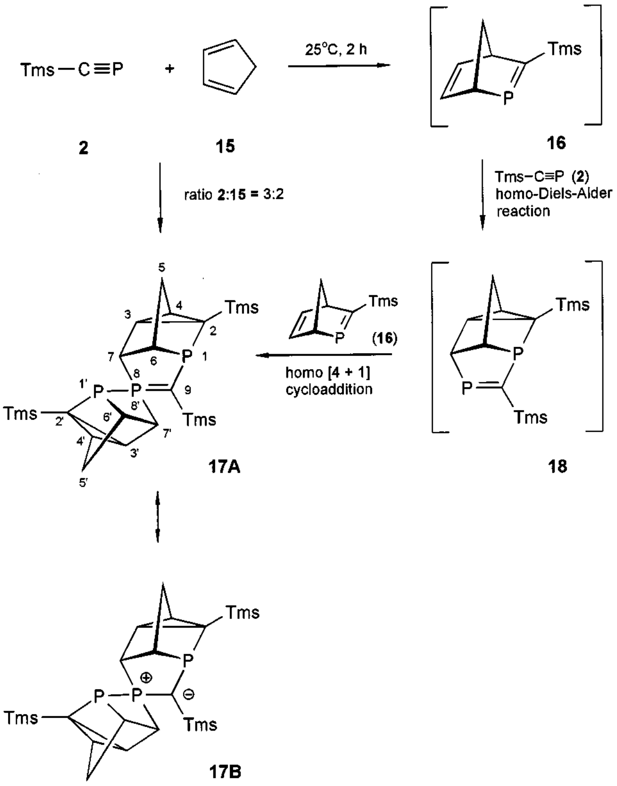


Figure 3. Energy profile of the reaction sequence between methylidynephosphane (**2**, H in place of Tms) and cyclohexa-1,4-diene; MP2/6−31+G* level of theory

are mixed in a 1:1 ratio and stirred for 2 hours at room temperature the phosphaalkyne **2** can no longer be detected in the reaction mixture by ^{31}P-NMR spectroscopy. Instead, it is found that a product containing three different phosphorus atoms per molecule has formed. Removal of all volatile materials under high vacuum and crystallization of the residue from *n*-pentane furnishes the spiro compound **17**, the structure of which was confirmed by X-ray crystallography.



Scheme 5

^{1}H-NMR and mass spectral data of **17** indicate that the molecule must be built up from the starting materials **2** and **15** in a 3:2 stoichiometry. The ^{31}P-NMR spectrum provides information about the arrangement of the phosphorus atoms in the molecule: while the large coupling of 162.5 Hz is indicative of a direct bond between two of the phosphorus atoms, the small (22.8 Hz) and very small (4.4 Hz) coupling constants suggest an interaction between two phosphorus atoms through two and three bonds, respectively. The signals of P1′ and P1 appear as double doublets at a somewhat higher field ($\delta = 39.7$ and $\delta = 45.9$) than is expected for $\lambda^3\sigma^3$-phosphorus atoms in cyclophosphanes.[18] This reflects the shielding effects of the trimethylsilyl groups. As indicated in Scheme 5, product **17** possesses only a formal P/C double bond (**17A**) and has instead more the nature of a phosphorus ylid (**17B**). Thus the ^{31}P-NMR signal for the phosphorus atom P8/8′ is not found in the expected region for a normal phosphaalkene at around $\delta > 150$,[18] but rather at $\delta = 89.5$ as a double doublet. In comparison to peralkylated ylids[18] the signal is shifted to lower field which can be explained reasonably in terms of the deshielding effect of phosphorus atom P1′. In the ^{13}C-NMR spectrum the ylidic carbon atom C9 gives a triple doublet signal at $\delta = 18.6$. This signal at a much higher field than is expected for a normal sp^2 carbon atom indicates a high electron density at this atom and thus supports a significant proportion of the limiting form **17B** in the electronic state of the molecule.[19] The large $^1J_{C,P}$ coupling constant of 63.9 Hz must be attributed to an interaction with the ylidic phosphorus atom P8/8′ while a small $^1J_{C,P}$ and a $^2J_{C,P}$ coupling constant of 5.5 Hz each result from coupling with the other phosphorus atoms. The proton decoupled and coupled ^{13}C-NMR spectra provide the following additional information:

1. The molecule is completely unsymmetrical; a total of 16 signals are observed of which 13 can be assigned to skeletal carbon atoms which exhibit more or less large couplings with the phosphorus atoms.
2. There are two methylene units in the molecule which manifest as two triplets in the coupled ^{13}C-NMR spectrum ($\delta = 31.6, 36.9$).
3. On the basis of a $^1J_{C,H}$ coupling constant of ca. 175 Hz the signals at $\delta = 18.4, 21.4, 25.2$, and 25.4 are assigned to carbon atoms in three-membered rings.
4. The signals at $\delta = 11.3$ and $\delta = 17.2$ are assigned to trimethylsilyl-substituted carbon atoms on account of their chemical shifts and splitting patterns.

An X-ray crystallographic analysis was performed in order to confirm the structure of compound **17** (Figure 4). Suitable single crystals were obtained by allowing a solution of the compound in *n*-pentane to stand at −20°C for several days.

The spirocyclic structure of compound **17** is immediately apparent from Figure 4. The bonds of the two linked rings at spiro atom P8/8′ form a distorted tetrahedral environment. The bond angles are between 90.71° and 124.62°, with the smallest angle resulting from the presence of P8/8′ in the four-membered ring P8/8′−P1′−C6′−C7′. The separation between the two phosphorus atoms is *d*(P8/8′−P1′) = 225.8 pm, typical for a P/P single bond.[19] The distance between the atoms P8/8′ and C9, comprising the ylid unit, is *d*(P8/8′−C9) = 170.1 pm and thus about 15 pm shorter than a normal P/C single bond,[20] reflecting the unsaturated nature of this bond. Similar bond lengths have recently been reported for comparable phosphorus ylids.[21] When a least squares plane is defined by the four atoms P8/8′, C9, P1, and Si9, the average deviation from this plane is 0.26 pm. Together with the ideal angular sum of 360.0° at C9, this confirms the trigonal planar arrangement of the substituents and hence also the sp^2 hybridization of the ylid carbon atom. The two phosphorus atoms P1′ and P1 exhibit the typical bond angles of about 90° for $\lambda^3\sigma^3$ phosphorus atoms. The small angle of 74.03° at P1′ is again due to its incorporation in a four-membered ring while the large bond angle at P1 of 103.92° can be attributed to steric repulsion of the bulky trimethylsilyl groups at C2 and C9.

As far as the mechanism is concerned, the formation of **17** can be described by a three-step reaction sequence. The first step is the [4 + 2] cycloaddition of **2** to the cyclopen-

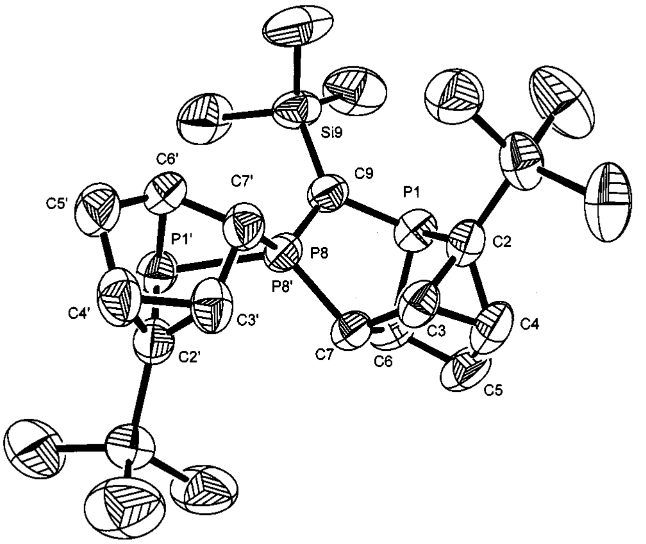


Figure 4. Molecular structure of **17**. Hydrogen atoms are omitted for reasons of clarity (displacement ellipsoids at the 50% probability level); selected bond lengths [Å] and angles [°]: P8/8′−P1′ 2.2582(10), P8/8′−C9 1.701(3), P8/8′−C7′ 1.845(3), P8/8′−C7 1.826(3), P1′−C2′ 1.851(3), P1′−C6′ 1.900(3), P1−C9 1.793(3), P1−C6 1.865(3), P1−C2 1.877(3); C9−P8/8′−C7 101.60(12), C9−P8/8′−C7′ 124.62(14), C7−P8/8′−C7′ 109.74(13), C9−P8/8′−P1′ 122.11(10), C7−P8/8′−P1′ 122.92(9), C7′−P8/8′−P1′ 75.53(9), C2′−P1′−C6′ 83.8(2), C2′−P1′−P8/8′ 90.71(9), C6′−P1′−P8/8′ 74.03(9), C9−P1−C6 97.71(13), C9−P1−C2 103.92(12), C2−P1−C6 83.70(14)

tadiene **15** with formation of the phosphanorbornadiene **16** which then participates in a homo-Diels−Alder reaction with a further equivalent of **2** (formation of **18**). This type of reaction is rare in organic chemistry but plays a major role for the construction of cage compounds in the chemistry of low-coordinated phosphorus.[22−24] According to Woodward and Hoffmann[13] this transannular reaction in which three π-bonds are converted to three σ-bonds with formation of two new rings belongs to the thermally allowed [$\pi^2{}_s + \pi^2{}_s + \pi^2{}_s$] processes. The conspicuously mild reaction conditions under which the sequence proceeds again emphasize the increased dienophilicity of trimethylsilylphosphaacetylene in comparison to the *t*Bu derivative. When the *tert*-butylphosphaalkyne (**2**, *t*Bu in place of Tms) is allowed to react with the cyclopentadiene **15**, the reaction proceeds slowly at room temperature but comes to a standstill at the stage of the phosphanorbornadiene (**16**, *t*Bu in place of Tms). Pyrolysis at 180°C is necessary to initiate the homo-Diels−Alder reaction and thus construction of the tetracyclic species **18** (*t*Bu in place of Tms).[22] Although this species is the final product of the reaction of *tert*-butylphosphaacetylene (**2**, *t*Bu in place of Tms), in the case of the more reactive Tms derivative a subsequent homo [4 + 1] cycloaddition with an equivalent of the phosphanorbornadiene **16** occurs. Reports on homo [4 + 1] cycloadditions of this type are rather scarce and mostly concern the additions of carbenes to norbornadiene derivatives.[25] Since, in this reaction sequence the first step directly leads to the second which, in turn, makes the third step possible it seems justified to refer to the process as a tandem Diels−Alder/homo-Diels−Alder/homo [4 + 1] cycloaddition reaction.

Experimental Section

General: All reactions were performed under argon in previously evacuated and baked out reaction vessels. The solvents were dried according to standard procedures, distilled, and stored under argon prior to use. − Column chromatography was performed in water-cooled glass tubes. Silica gel was heated for 3 h in vacuum and then deactivated with 4% of degassed water (Brockmann activity II). − Bulb-to-bulb distillation: Büchi GKR 50; the temperatures stated are oven temperatures. − Melting points: Mettler FP 61; heating rate 3°C/min; not corrected. − NMR: Bruker AMX 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, and 162 MHz for ^{31}P) and Bruker AC 200 spectrometers (81 MHz for ^{31}P); chemical shifts (ppm) are relative to internal TMS or solvent (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). − MS: Finnigan MAT 90 (70 eV). − IR: Perkin Elmer 16 PC FT. − Trimethylsilylphosphaacetylene (**2**) was prepared according to a published method.[8] The quantity of the phosphaalkyne obtained was determined with the help of the ^{1}H-NMR spectroscopy. All other starting materials were obtained from commercial sources and used without further purification.

2,8-Bis(trimethylsilyl)-1,7-diphosphatricyclo[3.2.1.0^{2,7}]oct-3-ene (8a): The solution of phosphaalkyne **2** (0.16 g, 1.4 mmol) and buta-1,3-diene (**6a**) (1.00 g, 18.5 mmol) in diethyl ether (2 mL) was stirred at room temperature for 2 h and evaporated at 25°C/3·10^{-2} mbar. Bulb-to-bulb distillation of the residue at 120°C/3·10^{-2} mbar afforded 0.20 g (50%) **8a** as colorless crystals; m.p. 112°C. − IR (KBr): $\tilde{\nu}$ = 2954, 2898, 1654, 1500, 1250, 1174, 978, 893 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.02 [s, 9 H, $Si(CH_3)_3$], 0.03 [d, $^{4}J_{H,P}$ = 0.7 Hz, 9 H, $Si(CH_3)_3$], 0.68 (d, $^{3}J_{H,H}$ = 4.2 Hz, 1 H, 8-H), 0.96 (ddd, $^{2}J_{H,H}$ = 13.5 Hz, $^{2}J_{H,P}$ = 5.8 Hz, $^{3}J_{H,P}$ = 4.8 Hz, 1 H, 6-H), 1.22 (ddd, $^{2}J_{H,H}$ = 13.5 Hz, $^{2}J_{H,P}$ = 10.5 Hz, $^{3}J_{H,H}$ = 4.8 Hz, 1 H, 6-H), 3.09−3.16 (m, 1 H, 5-H), 5.73 (pt, $^{3}J_{H,H}$ = 8.5 Hz, $^{3}J_{H,H}$ = 8.7 Hz, 1 H, 4-H), 6.01 (dt, $^{3}J_{H,H}$ = 8.5 Hz, $^{3}J_{H,P}$ = 2.4 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = −2.4 [t, $^{3}J_{C,P}$ = 3.7 Hz, 2-$Si(CH_3)_3$], 0.0 [d, $^{3}J_{C,P}$ = 3.0 Hz, 8-$Si(CH_3)_3$], 15.8 (dd, $^{1}J_{C,P}$ = 57.8 Hz, $^{1}J_{C,P}$ = 55.8 Hz, C2), 32.1 (dd, $^{1}J_{C,P}$ = 60.8 Hz, $^{2}J_{C,P}$ = 3.0 Hz, C8), 33.5 (s, C5), 34.3 (dd, $^{1}J_{C,P}$ = 48.9 Hz, $^{2}J_{C,P}$ = 2.3 Hz, C6), 125.1, 127.1 (each s, C3 and C4). − ^{31}P NMR ($CDCl_3$): δ = −201.8 (d, $^{1}J_{P,P}$ = 178.3 Hz, P7), −186.5 (d, $^{1}J_{P,P}$ = 178.3 Hz, P1). − MS (EI, 70 eV); *m/z* (%): 286 [M^+] (100), 271 [$M^+ - CH_3$] (26), 241 (43), 170 (19), 153 (93), 73 [$Si(CH_3)_3{}^+$] (87).

4,5-Dimethyl-2,8-bis(trimethylsilyl)-1,7-diphosphatricyclo[3.2.1.0^{2,7}]oct-3-ene (8b): Analogously to **8a** (see above), phosphaalkyne **2** (0.10 g, 0.9 mmol) and buta-1,3-diene **6b** (0.9 g, 10 mmol) afforded 0.16 g (55%) of **8b** as a colorless oil; b.p. 125°C/3·10^{-2} mbar. − ^{1}H NMR ($CDCl_3$): δ = 0.05 [pt, $^{4}J_{H,P}$ = 2.2 Hz, $^{4}J_{H,P}$ = 1.1 Hz, 9 H, 2-$Si(CH_3)_3$], 0.06 [s, 9 H, 8-$Si(CH_3)_3$], 0.93 (ddd, $^{2}J_{H,H}$ = 13.6 Hz, $^{2}J_{H,P}$ = 11.0 Hz, $^{3}J_{H,P}$ = 5.1 Hz, 1 H, 6-H), 1.17 (dd, $^{2}J_{H,P}$ = 18.8 Hz, $^{3}J_{H,P}$ = 1.9 Hz, 1 H, 8-H), 1.27 (dd, $^{2}J_{H,H}$ = 13.6 Hz, $^{2}J_{H,P}$ = 10.2 Hz, 1 H, 6-H), 1.38 (s, 3 H, 5-CH_3), 1.79 (d, $^{5}J_{H,P}$ = 1.4 Hz, 3 H, 4-CH_3), 5.75 (s, 1 H, 3-H). − ^{13}C NMR (C_6D_6): δ = −2.1 [s, 2-$Si(CH_3)_3$], −0.6 [d, $^{3}J_{C,P}$ = 6.3 Hz, 8-$Si(CH_3)_3$], 18.3 (pt, $^{1}J_{C,P}$ = 55.7 Hz, $^{1}J_{C,P}$ = 53.2 Hz, C2), 19.7 (s, 5-CH_3), 25.7 (s, 4-CH_3), 39.2 (d, $^{1}J_{C,P}$ = 59.7 Hz, C8), 43.0 (s, C5), 44.5 (d, $^{1}J_{C,P}$ = 45.6 Hz, C6), 120.7 (d, $^{2}J_{C,P}$ = 1.7 Hz, C3), 136.6 (s, C4). − ^{31}P NMR ($CDCl_3$): δ = −205.0 (d, $^{1}J_{P,P}$ = 169.0 Hz, P7), −167.0 (d, $^{1}J_{P,P}$ = 169.0 Hz, P1). − MS (EI, 70 eV); *m/z* (%): 314 [M^+] (40), 299 [$M^+ - CH_3$] (11), 269 (62), 180 (100), 150 (15), 73 [$Si(CH_3)_3{}^+$] (87).

2,8-Bis(trimethylsilyl)-1,7-diphosphatricyclo[3.2.1.0^{2,7}]oct-3-ene-7-tetracarbonyliron (10a): To a suspension of nonacarbonyl diiron (0.33 g, 0.9 mmol) in *n*-pentane (6.5 mL) was added a solution of the diphosphatricyclooctene **8a** (0.20 g, 0.7 mmol) in *n*-pentane (1 mL) and the mixture was stirred for 12 h at room temperature. Filtering over Celite, removal of the solvent at 25°C/$3\cdot10^{-2}$ mbar, and column chromatography (1 × 15 cm) on silica gel with *n*-pentane as eluent yielded 0.08 g (26%) **10a** as red brown crystals (from *n*-pentane at −78°C); ≥120°C dec. − IR (*n*-pentane): ṽ = 2054, 1984, 1976, 1958 cm^{-1} (CO). − ^{1}H NMR (C_6D_6): δ = −0.12 [s, 9 H, Si(CH_3)$_3$], 0.22 [s, 9 H, Si(CH_3)$_3$], 0.26 (d, *J* = 12.1 Hz, 1 H, 6-H or 8-H), 1.23 (br, s, 2 H, 6-H or 8-H), 2.37−2.45 (m, 1 H, 5-H), 5.39 (dt, $^{3}J_{H,H}$ = 8.3 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 1 H, 4-H), 5.78 (d, $^{3}J_{H,H}$ = 8.3 Hz, 1 H, 3-H). − ^{13}C NMR (C_6D_6): δ = −1.4 [d, $^{3}J_{C,P}$ = 5.1 Hz, Si(CH_3)$_3$], −0.4 [d, $^{3}J_{C,P}$ = 3.4 Hz, Si(CH_3)$_3$], 16.5 (dd, $^{1}J_{C,P}$ = 44.9 Hz, $^{1}J_{C,P}$ = 29.7 Hz, C2), 31.2 (d, $^{1}J_{C,P}$ = 62.7 Hz, C8), 35.0 (d, $^{2}J_{C,P}$ = 6.8 Hz, C5), 39.9 (d, $^{1}J_{C,P}$ = 15.3 Hz, C6), 125.4 (d, $J_{C,P}$ = 7.6 Hz, C3 or C4), 129.2 (d, $J_{C,P}$ = 8.5 Hz, C3 or C4), 214.9 (d, $^{2}J_{P,C}$ = 17.8 Hz, CO). − ^{31}P NMR (C_6D_6): δ = −195.0 (d, $^{1}J_{P,P}$ = 210.1 Hz, P1), −76.9 (d, $^{1}J_{P,P}$ = 210.1 Hz, P7). − MS (EI, 70 eV); *m/z* (%): 454 [M$^+$] (2), 426 [M$^+$ − CO] (3), 398 [M$^+$ − 2 CO] (4), 370 [M$^+$ − 3 CO] (47), 342 [M$^+$ − 4 CO] (100), 286 [M$^+$ − Fe(CO)$_4$] (11), 224 (21), 153 (17), 73 [Si(CH_3)$_3{}^+$] (50). − HRMS: $C_{16}H_{24}FeO_4P_2Si_2$: calcd. 454.0038; found 454.0053.

4,5-Dimethyl-2,8-bis(trimethylsilyl)-1,7-diphosphatricyclo-[3.2.1.0^{2,7}]oct-3-ene-7-tetracarbonyliron (10b): Analogously to **10a** (see above) nonacarbonyldiiron (0.33 g, 0.9 mmol) and diphosphatricyclooctene **8b** (0.22 g, 0.7 mmol) yielded 0.07 g (21%) **10b** as red brown crystals (from *n*-pentane at −78°C); ≥ 123°C dec. − IR (*n*-pentane): ṽ = 2054, 1982, 1976, 1958 cm^{-1} (CO). − ^{1}H NMR (C_6D_6): δ = −0.02 [d, $^{4}J_{H,P}$ = 1.1 Hz, 9 H, Si(CH_3)$_3$], 0.16 (d, *J* = 3.4 Hz, 1 H, 8-H), 0.31 [s, 9 H, Si(CH_3)$_3$], 0.86 (d, $^{4}J_{H,P}$ = 1.3 Hz, 3 H, 5-CH_3), 1.20 (dd, $^{2}J_{H,H}$ = 14.1 Hz, *J* = 3.4 Hz, 1 H, 6-H), 1.35 (dd, $^{2}J_{H,H}$ = 14.1 Hz, *J* = 2.6 Hz, 1 H, 6-H), 1.46 (dd, *J* = 3.7 Hz, *J* = 1.7 Hz, 3 H, 4-CH_3), 5.71 (d, $^{3}J_{H,P}$ = 7.1 Hz, 1 H, 3-H). − ^{13}C NMR (C_6D_6): δ = −1.2 [d, $^{3}J_{C,P}$ = 4.0 Hz, Si(CH_3)$_3$], 0.6 [d, $^{3}J_{C,P}$ = 7.2 Hz, Si(CH_3)$_3$], 18.1 (dd, $^{1}J_{C,P}$ = 43.0 Hz, $^{1}J_{C,P}$ = 28.5 Hz, C2), 19.7 (s, 4-CH_3), 24.1 (d, $^{3}J_{C,P}$ = 12.9, 5-CH_3), 38.0 (d, $^{1}J_{C,P}$ = 61.0 Hz, C8), 44.5 (d, $^{2}J_{C,P}$ = 7.2 Hz, C5), 48.8 (d, $^{1}J_{C,P}$ = 17.7 Hz, C6), 120.5 (d, $^{3}J_{C,P}$ = 7.2 Hz, C3), 139.4 (s, C4), 214.9 (d, $^{2}J_{P,C}$ = 19.3 Hz, CO). − ^{31}P NMR (C_6D_6): δ = −176.8 (d, $^{1}J_{P,P}$ = 202.5 Hz, P1), −80.5 (d, $^{1}J_{P,P}$ = 202.5 Hz, P7). − MS (EI, 70 eV); *m/z* (%): 482 [M$^+$] (3), 454 [M$^+$ − CO] (3), 426 [M$^+$ − 2 CO] (2), 398 [M$^+$ − 3 CO] (57), 370 [M$^+$ − 4 CO] (100), 314 [M$^+$ − Fe(CO)$_4$] (11), 269 (18), 252 (42), 73 [Si(CH_3)$_3{}^+$] (57).

2,8-Bis(trimethylsilyl)-1,7-diphosphatricyclo[3.2.1.0^{2,7}]oct-3-ene-7-pentacarbonyltungsten (11): A water-cooled solution of hexacarbonyltungsten (0.21 g, 0.6 mmol) in THF (50 mL) was irradiated for 15 min. Then a solution of the diphosphatricyclooctene **8a** (0.17 g, 0.6 mmol) in THF (1 mL) was added and the mixture was stirred for 12 h at room temperature. After removal of the solvent at 25°C/$3\cdot10^{-2}$ mbar, the residue was dissolved in *n*-pentane and purified by flash column chromatography (1 × 5 cm) on silica gel using *n*-pentane as eluent. Unreacted hexacarbonyltungsten was removed by sublimation (60°C/$3\cdot10^{-2}$ mbar). Crystallization from *n*-pentane at −20°C gave 0.05 g (13%) **11** as yellow crystals; ≥ 127°C dec. − IR (*n*-pentane): ṽ = 2074, 1952, 1946 cm^{-1} (CO). − ^{1}H NMR (C_6D_6): δ = −0.10 [s, 9 H, Si(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$], 0.40 (s, 1 H, 8-H), 1.22−1.31 (m, 2 H, 6-H), 2.40−2.55 (m, 1 H, 5-H), 5.50 (dt, $^{3}J_{H,H}$ = 8.4 Hz, $^{3}J_{H,H}$ = 3.7 Hz, 1 H, 4-H), 5.73−5.77 (m, 1 H, 3-H). − ^{13}C NMR (C_6D_6): δ = −1.5 [d, $^{3}J_{C,P}$ = 3.4 Hz, Si(CH_3)$_3$], 0.3 [d, $^{3}J_{C,P}$ = 3.4 Hz, Si(CH_3)$_3$], 15.0 (dd, $^{1}J_{C,P}$ = 50.0 Hz, $^{1}J_{C,P}$ = 32.2 Hz, C2), 31.7 (d, $^{1}J_{C,P}$ = 62.7 Hz, C8), 35.4 (d, $^{2}J_{C,P}$ = 5.9 Hz, C5), 41.9 (d, $^{1}J_{C,P}$ = 11.9 Hz, C6), 125.0 (d, $^{3}J_{C,P}$ = 5.9 Hz, C4), 129.3 (d, $^{2}J_{C,P}$ = 4.2 Hz, C3), 196.4 (d, $^{2}J_{C,P}$ = 7.6 Hz, CO_{eq}), 197.5 (d, $^{2}J_{C,P}$ = 29.7 Hz, CO_{ax}). − ^{31}P NMR (C_6D_6): δ = −191.0 (d, $^{1}J_{P,P}$ = 196.1 Hz, P1), −155.6 (d, $^{1}J_{P,P}$ = 196.1 Hz, $^{1}J_{P,W}$ = 196.1 Hz, P7). − MS (EI, 70 eV); *m/z* (%): 610 [M$^+$] (8), 582 [M$^+$ − CO] (11), 554 [M$^+$ − 2 CO] (34), 496 [M$^+$ − 4 CO] (45), 468 [M$^+$ − 5 CO] (38), 286 [M$^+$ − W(CO)$_5$] (5), 153 (11), 73 [Si(CH_3)$_3{}^+$] (100). − HRMS: $C_{17}H_{24}O_5P_2Si_2W$: calcd. 610.0148; found 610.0148.

8-Trimethylsilyl-1-phosphatricyclo[3.2.1.0^{2,7}]oct-3-ene (14): The solution of phosphaalkyne **2** (0.46 g, 4.0 mmol) and cyclohexa-1,4-diene (**12**) (1.71 g, 21.3 mmol) in diethyl ether (5 mL) was stirred at room temperature for 4 d. An additional amount of **12** (1.71 g, 21.3 mmol) was added and after renewed stirring for 4 d the solvent was removed at 25°C/$3\cdot10^{-2}$ mbar. The residue was purified by bulb-to-bulb distillation to afford 0.08 g (10%) **14** as a colorless oil; b.p. 90°C/$3\cdot10^{-2}$. − IR (film): ṽ = 3040, 2954, 2848, 1614, 1250, 842 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −0.06 [s, 9 H, Si(CH_3)$_3$], 0.74 (pt, *J* = 4.2 Hz, *J* = 4.0 Hz, 1 H, 8-H), 1.10−1.24 (m, 2 H, 6-H), 1.92−2.08 (m, 2 H, 2-H and 7-H), 2.70−2.90 (m, 1 H, 5-H), 5.60 (pt, $^{3}J_{H,H}$ = 8.3 Hz, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, 4-H), 6.00 (pt, $^{3}J_{H,H}$ = 8.3 Hz, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = −0.3 [s, Si(CH_3)$_3$], 19.9 (d, $^{1}J_{C,P}$ = 39.2 Hz, C2 or C7), 20.6 (d, $^{1}J_{C,P}$ = 39.3 Hz, C2 or C7), 27.9 (d, $^{1}J_{C,P}$ = 51.0 Hz, C8), 33.5 (d, $^{2}J_{C,P}$ = 3.7 Hz, C6), 34.4 (s, C5), 123.7, 125.0 (each s, C3 and C4). − ^{31}P NMR ($CDCl_3$): δ = −226.2 (s). − MS (EI, 70 eV); *m/z* (%): 196 [M$^+$] (32), 181 [M$^+$ − CH_3] (8), 147 (25), 118 (13), 73 [Si(CH_3)$_3{}^+$] (100), 59 (14), 45 (22).

2,2′,9-Tris(trimethylsilyl)-*spiro*{1,8-diphosphatetracyclo-[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,8′-1′,8′-diphosphatetracyclo-[4.2.0.0$^{2′,4′}$.0$^{3′,7′}$]octane} (17): To a solution of phosphaalkyne **2** (0.41 g, 3.5 mmol) in diethyl ether (8 mL) was added freshly distilled cyclopentadiene (**15**) (0.23 g, 3.5 mmol), and the mixture was stirred at room temperature for 2 h. After evaporation of the solvent at 25°C/$3\cdot10^{-2}$ mbar, crystallization of the residue from *n*-pentane at −20°C gave 1.21 g (72%) **17** as yellow crystals; ≥ 240°C, dec. − ^{1}H NMR (C_6D_6): δ = 0.06 [s, 9 H, Si(CH_3)$_3$], 0.23 [s, 9 H, Si(CH_3)$_3$], 0.59 [d, $^{4}J_{H,P}$ = 0.8 Hz, 9 H, Si(CH_3)$_3$], 0.97−0.99 (m, 1 H), 1.12−1.42 (m, 5 H), 1.46−1.54 (m, 1 H), 1.75−1.84 (m, 2 H), 2.66−2.69 (m, 1 H), 2.79−2.87 (m, 2 H). − ^{13}C NMR (C_6D_6): δ = −1.0 [s, Si(CH_3)$_3$], −0.4 [s, Si(CH_3)$_3$], 3.9 [d, $^{3}J_{C,P}$ = 5.7 Hz, Si(CH_3)$_3$], 11.3 (dd, $^{1}J_{C,P}$ = 54.8 Hz, $J_{C,P}$ = 2.4 Hz, PCTms), 17.2 (dd, $^{1}J_{C,P}$ = 50.1 Hz, $J_{C,P}$ = 6.2 Hz, PCTms), 18.4 (d, $^{1}J_{C,H}$ = 176.4 Hz, $J_{C,P}$ = 7.6 Hz, cyclopropane-C), 18.6 (dt, $^{1}J_{C,P}$ = 63.9 Hz, $^{1}J_{C,P}$ = 5.5 Hz, $^{2}J_{C,P}$ = 5.5 Hz, C9), 21.4 (d, $^{1}J_{C,H}$ = 179.3 Hz, $J_{C,P}$ = 6,7 Hz, cyclopropane-C), 25.2 (d, $^{1}J_{C,H}$ = 171.7 Hz, $J_{C,P}$ = 20.0 Hz, cyclopropane-C), 25.4 (dd, $^{1}J_{C,H}$ = 172.6 Hz, $J_{C,P}$ = 9.5 Hz, $J_{C,P}$ = 5.7 Hz, cyclopropane-C), 31.6 (dd, $J_{C,P}$ = 16.2 Hz, $J_{C,P}$ = 11.5 Hz, CH_2), 33.3 (dd, $J_{C,P}$ = 6.7 Hz, $J_{C,P}$ = 2.7 Hz), 36.9 (dd, $J_{C,P}$ = 20.0 Hz, $J_{C,P}$ = 6.7 Hz, CH_2), 40.7 (dd, $J_{C,P}$ = 18.0 Hz, $J_{C,P}$ = 7.6 Hz), 50.4 (dd, $J_{C,P}$ = 45.8 Hz, $J_{C,P}$ = 7.6 Hz), 57.5 (dd, $J_{C,P}$ = 31.5 Hz, $J_{C,P}$ = 2.7 Hz). − ^{31}P NMR (C_6D_6): δ = 39.7 (dd, $^{1}J_{P,P}$ = 162.5 Hz, $^{3}J_{P,P}$ = 4.4 Hz, P1′), 45.9 (dd, $^{2}J_{P,P}$ = 22.8 Hz, $^{3}J_{P,P}$ = 4.4 Hz, P1), 89.5 (dd, $^{1}J_{P,P}$ = 162.5 Hz, $^{2}J_{P,P}$ = 22.8 Hz, P8/8′). − MS (EI, 70 eV); *m/z* (%): 480 [M$^+$] (50), 465 [M$^+$ − CH_3] (5), 407 [M$^+$ − Si(CH_3)$_3$] (19), 73 [Si(CH_3)$_3{}^+$] (100). − HRMS: $C_{22}H_{39}P_3Si_3$: calcd. 480.1572; found 480.1567.

X-ray Structural Analysis of 17:[26] A bright yellow prism of **17**, $C_{22}H_{39}P_3Si_3$, was grown from an *n*-pentane solution of the compound at −20°C; crystal size 0.50 × 0.30 × 0.25 mm^3; *a* = 11.872(2) Å, *b* = 12.544(3) Å, *c* = 19.674(4) Å, *β* = 101.61(3)°; *V* = 2870.0(10) Å^3; *Z* = 4; $D_{calcd.}$ = 1.113 Mg/m^3; *μ* = 0.340 mm^{-1}; $F_{(000)}$ = 1032; monoclinic space group $P2_{(1)}/n$. Graphite monochromated Mo-K_α radiation; Imaging Plate Diffraction System (IPDS−STOE); θ = 2.22 − 26.00°; temperature: 293 K; 18279 reflections, 5428 independent ($R_{\text{int}} = 0.0772$), 4293 observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using the SHELXTL-PLUS program system[27] and refined by full-matrix least-squares techniques against F^2 with SHELXL-93[28]. Hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 0.960$ Å) and all other atoms were refined anisotropically. The final refinement with 268 parameters converged with $R1 = 0.0626$, $wR2 = 0.1376$ (observed data) and $R1 = 0.0772$, $wR2 = 0.1464$ (all data) with $w^{-1} = [\sigma^2(F_o^2) + (0.003P)^2]$ and $P = [\max(F_o^2,0) + 2\,F_c^2]/3$; residual electron density 470 e nm^{-3} and -496 e nm^{-3} ; *GOF* on F^2 1.210.

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