J. Org. Chem. **1995**, *60*, 7439−7444 **7439**

Diels−Alder Reactions of Trichlorophosphaethene[1]

Herman T. Teunissen, Jan Hollebeek, Peter J. Nieuwenhuizen, Ben L. M. van Baar,
Frans J. J. de Kanter, and Friedrich Bickelhaupt*

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Received July 14, 1995®

The Diels−Alder reactions of trichlorophosphaethene (**3**), generated in situ from dichloro(dichloromethyl)phosphine (**2**), with 1-vinylnaphthalene (**6**), 1-(1-methylethenyl)cyclohexene (**4**), and 1-[1-(trimethylsiloxy)ethenyl]cyclohexene (**13**) at 60−75 °C, are described. The reactions of **3** with **4** and **6** afforded, after aromatization of the primary Diels−Alder adducts **5** and **8** under the influence of triethylamine, the 2-chlorophosphinines **9** and **11**, respectively. The reaction with **13**, however, led to the formation of the "double adduct" **16**, which could not be isolated in pure form. The formation of the "double adduct" is explained by a subsequent Diels−Alder reaction of **13** with dihydrophosphinine **15**, which is formed after HCl elimination from the primary Diels−Alder adduct **14**. The reaction of **13** with **23**, the pentacarbonyltungsten complex of **2**, furnished **27**, the pentacarbonyltungsten complex of **16**, which was isolated in pure form. The regiochemistry of the Diels−Alder reactions described above is discussed on the basis of MNDO/PM3 calculations of the frontier molecular orbital coefficients. The Diels−Alder reactions proceed with normal electron demand, and the experimentally observed regiochemistry is in accordance with theoretical predictions. The formation of the "double adducts" **16** and **27** is rationalized as a consequence of the high HOMO energy of **13** compared with that of **4**.

Introduction

During the last decade, the Diels−Alder reaction has become an important synthetic device for the preparation of functionalized phosphinines.[2] Among the published procedures, the Diels−Alder reaction of trichlorophosphaethene **3**, developed by Mathey *et al.* for the preparation of 2-chlorophosphinines,[3] has two attractive features. First, aromatization of the primary Diels−Alder adduct is easily achieved under the influence of excess triethylamine. Second, the procedure amounts to a one-pot synthesis which makes it practically useful. In so far as investigations into the synthetic utility of the Diels−Alder reactions of **3** have been limited to butadiene and its 2,3-dimethyl derivative as diene partners,[3] we investigated its reactions with 1-(1-methylethenyl)cyclohexene (**4**), 1-vinylnaphthalene (**6**), and 1-[1-(trimethylsiloxy)ethenyl]cyclohexene (**13**) with the aim of preparing annelated phosphinines.

Results and Discussion

Synthetic Aspects. The starting material for the preparation of the thermally unstable phosphaalkene **3** is dichloro(dichloromethyl)phosphine (**2**).[3] A procedure for the preparation of **2** has been reported,[4] but in view of its low yield (28%) we decided to search for a better route. The new approach consists of the alkylation of phosphorus trichloride with the carbenoid **1**[5] (Scheme 1).

Scheme 1

$$\underset{\mathbf{1}}{ClZnCHCl_2} \xrightarrow{PCl_3} \underset{\mathbf{2}}{Cl_2PCHCl_2}$$

Reaction of **1** with phosphorus trichloride for 30 h at room temperature gave **2** ($\delta(^{31}P)$ 145.5 ppm) in 48% isolated yield. Compound **2** (bp 150−151 °C) was 72% pure; the remaining 28% consisted of 1,4-dichlorobutane (bp 154 °C). Due to the similar boiling points, distillative separation proved to be impossible. This byproduct is presumably formed from THF under the influence of phosphorus trichloride and zinc chloride;[6] it was not detrimental in the subsequent chemistry of **2**.

Phosphaalkene **3** was generated in situ by dehydrohalogenation of **2** with triethylamine. The Diels−Alder reactions of **3** with dienes **4**[7] and **6**[8] are depicted in Scheme 2. In general, a solution of **2** with an excess of the diene (typically 3−7 equiv; this is necessary to avoid the formation of byproducts) was heated to 65−75 °C. Triethylamine then was added slowly to keep the concentration of **3** as low as possible in order to prevent a head-to-tail [2 + 2] cycloaddition leading to the formation of **7**. This dimerization is of preparative interest as **7** could be isolated in a yield of 72%.[9] After **2** had been consumed by conversion to **3** and, via subsequent Diels−Alder reactions, to the primary adducts, aromatization was achieved by heating with an excess of triethylamine.

With **4** (2.8 equiv), the Diels−Alder reaction with **3** was performed at 65 °C in THF. After reaction for 4.25 h with 4.6 equiv of triethylamine, **2** had reacted completely; Diels−Alder adduct **5** ($\delta(^{31}P)$ 72 ppm) as the main product and a minor amount of the tetrahydro-2-phosphanaph-

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® Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Part of this work has been reported at the XVth European Colloquium on Heterocyclic Chemistry, Noordwijkerhout 1992; see: Teunissen, H. T.; Bickelhaupt, F. *Bull. Soc. Chim. Belg.* **1992**, *101*, 609.

(2) Märkl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; pp 220−257.

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(4) Shokol, V. A.; Gamaleya, V. F.; Derkach, G. I. *Zh. Obshch. Khim.* **1969**, *39*, 856.

(5) Köbrich, G; Merkle, H. R. *Chem. Ber.* **1966**, *99*, 1782.

(6) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249. Peringer, P.; Winkler, P. P. *Inorg. Chim. Acta* **1986**, *118*, L1. Reppe, W. *Liebigs Ann. Chem.* **1955**, *596*, 1.

(7) Wharton, P. S.; Aw, B. T. *J. Org. Chem.* **1966**, *31*, 3787. For Wittig procedure see: Le, N. A.; Jones, M.; Bickelhaupt, F.; de Wolf, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 8491.

(8) Cohen, A.; Warren, F. L. *J. Chem. Soc.* **1937**, 1315.

(9) Prishchenko, A. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1981**, *51*, 2630.

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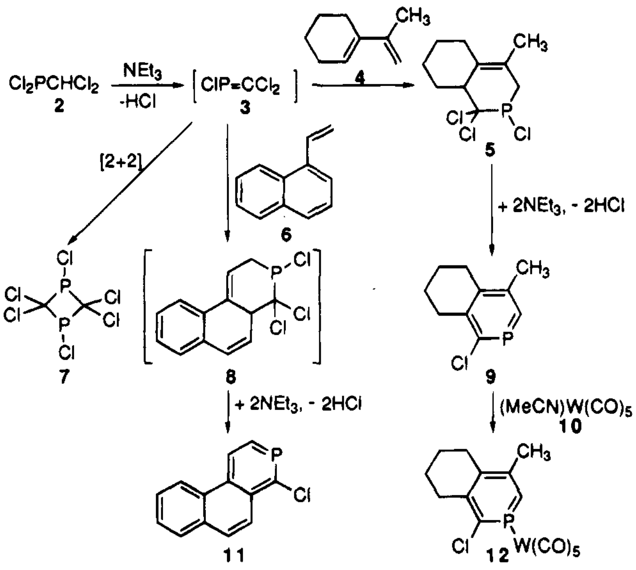
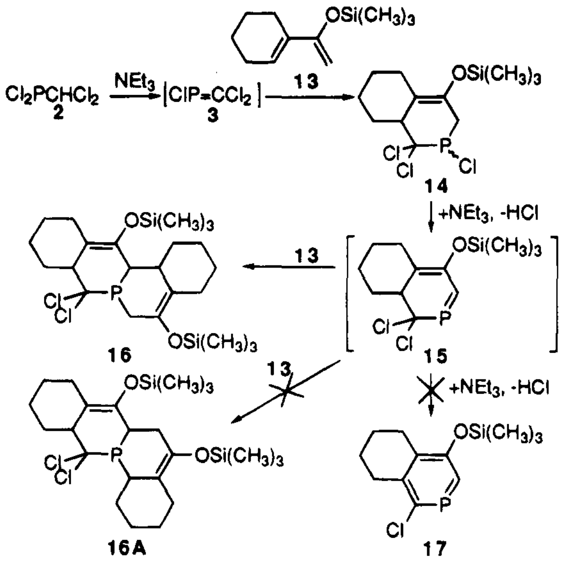
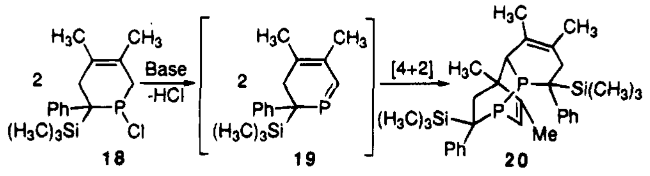
Scheme 2



Scheme 3



Scheme 4



thalene derivative **9** ($\delta(^{31}P)$ 181 ppm) were detected by ^{31}P NMR spectroscopy. The complete aromatization to **9** required 56 h at 55–65 °C and the addition of 23 equiv of triethylamine. The purification of **9** proved to be difficult (see Experimental Section); it gave a light brown sticky substance which according to ^1H NMR was nearly pure **9**. Therefore **9** was transformed to its pentacarbonyltungsten complex **12** ($\delta(^{31}P)$ 158.5 ppm, $^1J(PW) = 276$ Hz) with (acetonitrile)pentacarbonyltungsten **10**[10] in THF. Thus, pure **12** was isolated in a yield of 8% relative to **2**; in view of the numerous manipulations, this does not reflect the real yield of **9**.

With **6** (7.3 equiv), the Diels–Alder reaction was carried out at 75 °C in toluene. The formation of the primary adduct **8** was not observed; after 4 h heating in the presence of 8.2 equiv of triethylamine, only 1-chloro-2-phosphaphenanthrene **11** was detected by ^{31}P NMR spectroscopy ($\delta(^{31}P)$ 187 ppm). Product **11** is the first halogen-substituted phosphaphenanthrene; it was isolated in pure form in a yield of 14% relative to **2**. This successful Diels–Alder reaction showed that in the competition between [2 + 2] dimerization of **3** to **7** and Diels–Alder reaction with **6** (present in excess), **3** prefers to undergo the Diels–Alder reaction as **7** was not observed. Compared with the reported yield of **7** (72%)[9] the yield of **11** is rather low; this is probably due to polymerization of **3** and **6**.

Whereas the Diels–Alder reactions of **3** with **4** and **6** led to phosphaaromatic products in the expected fashion, the reaction with **13**[11] (6.9 equiv) took a strikingly different course (Scheme 3).

On reacting **2** and **13** for 0.45 h at 65 °C in the presence of 4.2 equiv of triethylamine, the primary adduct **14**, which apparently is formed as a mixture of diastereoisomers ($\delta(^{31}P)$ 76 and 73 ppm) in a ratio of 1:2, was obtained as the main product. Prolonged heating (4.5 h) did not result in aromatization as was the case with **4** and **6**, but led to the formation of **16** ($\delta(^{31}P)$ 1.5 ppm) as the only phosphorus-containing product. Apparently, the intermediate elimination product **15** is a reactive dienophile and is trapped at its P=C bond by a Diels–Alder reaction with diene **13** (present in excess); this generates the "double adduct" **16**.

Precedent involving a dihydrophosphinine as a dienophile (and, incidentally, also as a diene) has been reported by Appel[12] and is shown in Scheme 4. Elimination of HCl from Diels–Alder adduct **18** under the influence of a base generated the intermediate dihydrophosphinine **19**, which dimerized in a Diels–Alder reaction to give a tricyclic compound **20**; however, the authors did not succeed in intercepting **19** with other dienes.

Compound **16** could not be isolated in pure form; its thermal lability as well as the excess of **13** were the main obstacles. However, the structural identification of **16** is reliable for three reasons. In the first place, a solution with **16** as the only phosphorus-containing compound (^{31}P NMR) was analyzed by GCMS, which was recorded with an increased solvent delay to prevent the entrance of the excess of **13** into the mass spectrometer. This analysis showed the presence of three components (Table 1; peaks 1, 2, and 6) which can be explained as being derived from **16**; together, they represented 90% of the TIC (total ion current). Three minor products (peaks 3, 4, and 5) represented 10% of the TIC and were not identified. The interpretation of the GCMS results is shown in Table 1 and the rationalization of the fragmentations is presented in Scheme 5.

It is necessary to emphasize that all reactions depicted in Scheme 5 are thermally induced and have presumably occurred in the injector which operated at 288 °C; otherwise, clear separation of components on the GC column would not have been observed. The formation of the first component (**22**) is quite remarkable and not well understood. In contrast, the formation of **17** is easily rationalized as a retro-Diels–Alder reaction of **21** with

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[10] Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.

[11] Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1977**, *42*, 1051.

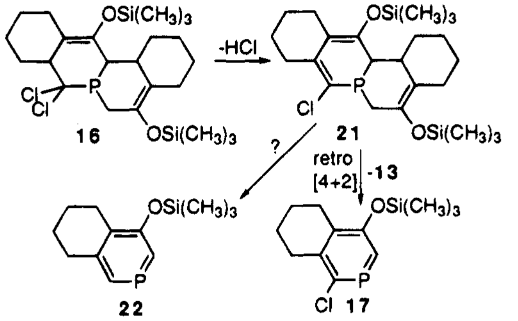
[12] Appel, R.; Knoch, F.; Zimmermann, R. *Chem. Ber.* **1985**, *118*, 814.

Table 1. GCMS Data of Crude 16 in 13

peak no.	retention time, min	relative abundance, %	MS (EI), *m/z* (relative intensity)[a]	assignment
1	12.48	8.57	238 ($[\mathrm{M}]^{\bullet+}$, 52), 223 ($[\mathrm{M}-\mathrm{CH_3}]^+$, 27) 148 ($[\mathrm{M}-\mathrm{HOSi(CH_3)_3}]^{\bullet+}$, 27) 73 ($\mathrm{Si(CH_3)_3}^+$, 100)	$\mathrm{C_{12}H_{19}OPSi}$ (**22**)
2	13.95	78.42	272 ($[\mathrm{M}]^{\bullet+}$, 94), 257 ($[\mathrm{M}-\mathrm{CH_3}]^+$, 14) 73 (Si(CH3)3+, 100)	$\mathrm{C_{12}H_{18}ClOPSi}$ (**17**)
6	22.18	2.63	468 ($[\mathrm{M}^{\bullet+}]$, 12), 433 ($[\mathrm{M}-\mathrm{Cl}]^+$, 9) 73 ($\mathrm{Si(CH_3)_3}^+$, 100)	$\mathrm{C_{23}H_{38}ClO_2PSi_2}$ (**21**)

[a] Where relevant, the expected isotope pattern characteristic for Cl was experimentally observed.

Scheme 5

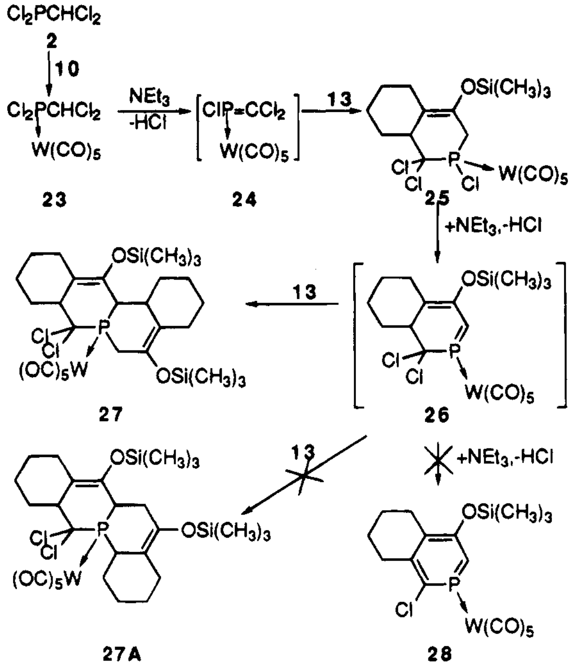


loss of **13**. Finally, the formation of **21** is caused by HCl elimination from **16**; note that **16** itself was not detected in the GCMS analysis. It is remarkable that the mass spectrum of **21** does not show a retro-Diels–Alder reaction as a fragmentation process. Apparently, in this case the retro-Diels–Alder reaction is more favorable thermally (from **21**) than under mass spectrometer conditions, i.e. from **21**$^{\bullet+}$.

Further support for the assigned structure of **16** (or **21**) is the retro-Diels–Alder reaction mentioned above, which was also achieved in solution by heating crude **16** for 1.5 h at 80 °C and 2×10^{-5} mbar. This procedure resulted to a large extent in decomposition; 31P NMR spectroscopy, however, indicated a signal in the phosphaaromatic region:[13] ($\delta(^{31}\mathrm{P})$ 182 ppm) with J(PH) = 33.8 Hz. This signal is only compatible with the structure of **17** (Scheme 3), because a coupling of 33.8 Hz is characteristic of ^2J(PH) in phosphinines. Even though **17** could not be isolated from this reaction mixture in pure form, this observation establishes the regiochemistry in the Diels–Alder reaction of **3** with **13** as indicated by the structure of the primary adduct **14** (Scheme 3).

The third and most important piece of evidence for the structural assignment of **16** came from the Diels–Alder reaction of **13** with **24**, the pentacarbonyltungsten complex of **3**, which was prepared *in situ* from **23** by analogy to the transformation of **2** from **3** (Scheme 6). Compound **23** was obtained by a reaction of **2** with **10** in THF at 40–50 °C; **23** was isolated in pure form in a disappointingly low yield of 13%. When **24** was generated *in situ* with triethylamine (5 equiv) in the presence of **13** (10 equiv), Diels–Alder adduct **25** ($\delta(^{31}\mathrm{P})$ 12 ppm) was formed stereoselectively after 1 h at 60–70 °C. Prolonged heating resulted in transformation of **25**, presumably via **26**, to **27**, whereas aromatization to **28** was not observed. Compound **27** ($\delta(^{31}\mathrm{P})$ 48.7 ppm, ^1J(PW) = 262.4 Hz) was isolated in a yield of 22% relative to **23** and fully characterized by NMR and MS spectroscopy and by elemental analysis.

Scheme 6



The regiochemistry of the second Diels–Alder reaction involving **26** and **13** was established by NOE NMR spectroscopy; the formation of **27A** could thus be excluded. Compound **27** was also observed as the main product when crude **16** was reacted with **10**. A ^{31}P NMR spectrum of this reaction mixture showed, besides many other peaks, a prominent signal at 49.5 ppm (^1J(PW) = 263 Hz), which is, apart from a small solvent effect, equal to the value measured for **27** obtained according to Scheme 6. Thus, a connection was made for **27** formed either directly via the reaction depicted in Scheme 6 or via **16**. As the regiochemistry of the Diels–Alder reaction of **15** with **13** is the same as that of **26** and **13**, the formation of **16A** (Scheme 3) can be excluded as well.

In conclusion, Diels–Alder reactions of **3** (and **24**) with dienes **6** and **4** show interesting features and open perspectives for the preparation of new annelated 2-chlorophosphinines, although in moderate yield. The "double" Diels–Alder reaction with **13** is mechanistically interesting and unprecedented in Diels–Alder reactions of *P*-chlorophosphaalkenes.[2,3,12]

Regiochemical Aspects of the Diels–Alder Reactions of Phosphaalkenes. The regiochemistry of the Diels–Alder reactions of **3** is expected to be governed by frontier molecular orbital interactions.[14] Therefore, the HOMO and LUMO energies of several reactants were

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(13) Märkl, G. In *Multiple bonds and low coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; p 233.

(14) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976; pp 110–140.

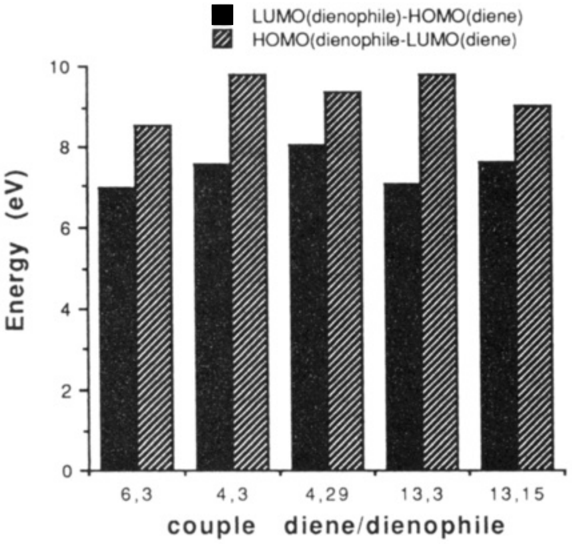
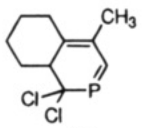


Figure 1. HOMO–LUMO energy differences of diene–dienophile couples.

Table 2. HOMO and LUMO Energies of Dienophiles (3, 15, and 29) and Dienes (6, 4, and 13) Calculated by MNDO/PM3

MO	3	15	29	6	4	13
HOMO, eV	−9.155	−8.365	−8.703	−8.599	−9.213	−8.704
LUMO, eV	−1.636	−1.071	−1.173	−0.629	0.666	0.658

calculated by the MNDO/PM3 method.[15] The geometries of the dienophiles were assumed to be of C_{2v} symmetry, with all atoms lying in the *xy* plane. The geometries of the dienes were optimized for the s-cis conformation which was found to be completely planar for diene **6**. In contrast, dienes **4** and **13** were substantially twisted around the central single bond by 54.2° and 50.3°, respectively. The results of these calculations are presented in Table 2. Compound **29** is the product of HCl elimination of **5** and as such the analog of **15**.



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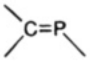
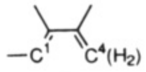
The energy differences LUMO(dienophile)–HOMO(diene) and HOMO(dienophile)–LUMO(diene) were calculated for several diene–dienophile couples. These results are shown in Figure 1.

It is clear from Figure 1 that the energy gap between LUMO(dienophile) and HOMO(diene) ($\Delta E = 6.962-8.040$ eV) is significantly smaller than that between HOMO(dienophile) and LUMO(diene) ($\Delta E = 8.527-9.822$ eV). Therefore, the Diels–Alder reactions considered here proceed with normal electron demand which is in accordance with the conclusions of Pen'kovskii *et al.*[16] and Carrié *et al.*[17]

In an attempt to understand the regiochemistry of the Diels–Alder reactions, we calculated the frontier molecular orbital coefficients of the dienes (**4**, **6**, **and 13**) and the dienophiles (**3**, **15**, and **29**) by MNDO/PM3; they are presented in Table 3. The LUMO of the dienophiles and the HOMO of the dienes are the relevant orbitals for Diels–Alder reactions with normal electron demand (*vide supra*).

Table 3. Frontier Molecular Orbital Coefficients of the HOMO of Dienes (6, 4, and 13) and the LUMO of Dienophiles (3, 15, and 29)

	LUMO			HOMO	
	C	P		C1	C4
3	−0.6366	0.7156	**6**	−0.3223	0.3272
15	−0.5187	0.6210	**4**	0.3296	−0.4224
29	0.5064	−0.6147	**13**	−0.2155	0.6528

The calculations show that with all dienophiles, the larger coefficient is located at phosphorus and the smaller one at carbon. The larger coefficients of the dienes **4**, **6**, and **13** are located at C4. The difference Δ between the coefficients on C1 and C4 is small in the case of **6** (Δ = 0.0049) and large in the case of **13** (Δ = 0.4373). The experimentally observed (Schemes 2 and 3) and the theoretically predicted (Table 3) regioselectivities of the Diels–Alder reactions of **3** with **4**, **6**, and **13** show excellent agreement.

The same holds for the Diels–Alder reaction of **13** with **15**, which gives the "double adduct" **16**, and not **16A** (Scheme 3). Moreover it is possible to understand why intermediate **15** underwent a Diels–Alder reaction with **13** to give "double adduct" **16** (Scheme 3) whereas the analogous intermediate **29** did not undergo a Diels–Alder reaction with **4** to give a comparable "double adduct", but instead aromatized with formation of phosphinine **9** (Scheme 2). The electron donating potential of the $OSi(CH_3)_3$ group is substantially higher than that of the CH_3 group,[18] which is reflected in the energy of the HOMO of **13** (−8.704 eV) being higher than that of **4** (-9.213 eV). For the (observed) Diels–Alder reaction involving **13** and **15**, the energy gap between the HOMO of **13** and the LUMO of **15** is 7.633 eV, while the corresponding energy difference for the (not observed) Diels–Alder reaction of **4** and **29** is 8.04 eV. The energy difference between the respective HOMO/LUMO gaps (0.407 eV = 9.4 kcal mol^{-1}) might be the reason why **13** formed a "double adduct" **16** (with **15**), whereas **4** (with **29**) did not. Apparently, for the couple **15/13**, the Diels–Alder reaction is fast enough to proceed under the reaction conditions to furnish **16**, whereas in the case of **29/4**, it is much slower, so that it cannot compete with the second elimination of hydrogen chloride leading to the aromatic phosphinine **9**. This argument is valid provided that the sequence of HCl eliminations in **5** and **14** is the same, i.e. the HCl elimination of the CH_2-PCl moiety of **5** precedes that of the $CH-CCl_2$ moiety.

Experimental Section

General comments. All reactions with oxygen and/or water-sensitive compounds were carried out under dry nitrogen with oven-dried glassware and oxygen-free, dry solvents. THF was distilled first from NaH and finally from Na/benzophenone. Pentane was distilled from $LiAlH_4$, and CH_2Cl_2 was distilled from P_2O_5. Triethylamine was distilled from CaH_2, toluene was distilled from Na. PCl_3 and $ClSi(CH_3)_3$ were distilled before use. Zinc chloride was heated under reflux with thionyl chloride and dried under vacuum. The starting compounds 1-(1-methylethenyl)cyclohexene,[7] 1-vinyl-

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[15] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

[16] Pen'kovskii, V. V.; Kharchenko, V. I.; Alekseiko, L. N. *Teor. Eksp. Khim.* **1991**, *27*, 462.

[17] Abbari, M.; Cosquer, P.; Tonnard, F.; Yeung Lam Ko, Y. Y. C.; Carrié, R. *Tetrahedron* **1991**, *47*, 71.

[18] See ref 14, pp 47–48.

naphthalene,[8] (acetonitrile)pentacarbonyltungsten,[10] and 1-[1-(trimethylsiloxy)ethenyl]cyclohexene[11] were prepared according to reported procedures. NMR,[19] GCMS,[19] and HRMS[20] equipment has been described previously. In the mass spectra, the appropriate isotope pattern was observed unless otherwise stated. Elemental analysis were carried out by Micro Analytisches Labor Pascher in Remagen (Germany). Melting points (uncorrected) were determined with the melting point equipment of Pleuger after Dr. Tottoli.

Dichloro(dichloromethyl)phosphine (2). A solution of CH_2Cl_2 (7.10 mL, 110 mmol) in THF (200 mL) was cooled to −95 °C. Under mechanical stirring, 1.6 M *n*-BuLi (68.75 mL, 110.0 mmol) was added during 45 min. The reaction mixture was then stirred for 2.5 h, maintaining the temperature between −80 and −95 °C. After the mixture was cooled to −95 °C, a solution of $ZnCl_2$ (14.80 g, 108.5 mmol) in THF (200 mL) was added dropwise during 2 h. The temperature was allowed to rise slowly to rt. The very light yellow solution was transferred to a dropping funnel and added at −20 °C during 0.5 h to a solution of PCl_3 (100 mL, 1.15 mol) in THF (100 mL). After warming up to rt, the reaction mixture was stirred for 30 h, and then evaporated under reduced pressure to a volume of 40 mL. Extraction was carried out five times with pentane (100 mL). After removal of the pentane at atmospheric pressure, distillation of the residue under reduced pressure afforded **2** (72% pure) (bp 79 °C, 80 mbar) in a yield of 48% (13.6 g, 52.7 mmol) relative to dichloromethane. The distillate contained 28% 1,4-dichlorobutane as evidenced by the ^{13}C NMR data.[21] **2**: NMR (C_6D_6) δ(^{1}H) 5.05 (d, ^2J(PH) = 12.3 Hz); δ(^{13}C) 73.2 (dd, ^1J(PC) = 71.4 Hz, ^1J(CH) = 181.3 Hz); δ(^{31}P) 145.5; the data are in agreement with those reported.[9] 1,4-Dichlorobutane: δ(^{1}H) 1.4 (m, 4H), 2.9 (m, 4H); δ(^{13}C) 29.9 (t, ^1J(CH) = 129.3 Hz), 44.1 (t, ^1J(CH) = 149.8 Hz).

1-Chloro-2-phosphaphenanthrene (11). A solution of **2** (72% pure (*vide supra*), 1.09 g, 4.22 mmol) and 1-vinylnaphthalene (**6**)[8] (4.75 g, 30.8 mmol) in toluene was heated to 75 °C. NEt_3 (4.80 mL, 34.5 mmol) was then added dropwise during 25 min. The solution turned from colorless to dark brown, and a brown precipitate formed. Stirring was continued for 3.5 h after which time the reaction mixture was evaporated under reduced pressure. The residue was extracted three times with pentane (20 mL). Crystallization by cooling the extract to −70 °C furnished pure **11** as colorless crystals (mp 143 °C) in a yield of 14% (0.14 g, 0.61 mmol) relative to Cl_2PCHCl_2. This compound was unambiguously characterized by HH COSY, CH COSY, and NOE experiments. **11**: NMR ($CDCl_3$) δ(^{1}H) 7.57–7.66 (m, 2H, H6,7), 7.85 (d, ^3J(HH) = 5.2 Hz, 1H, H8), 7.85 (dd, ^5J(PH) = 2.2 Hz, ^3J(HH) = 9.3 Hz, 1H, H9), 8.36 (d, ^3J(HH) = 9.3 Hz, 1H, H10), 8.50 (dd, ^2J(PH) = 40.4 Hz, ^3J(HH) = 11.0 Hz, 1H, H3), 8.68 (d, ^3J(HH) = 8.1 Hz, 1H, H5), 9.18 (t, ^3J(PH) = 10.3 Hz, ^3J(HH) = 11.0 Hz, 1H, H4); δ(^{13}C) 121.4 (d, ^3J(PC) = 5.4 Hz, C10), 123.2 (d, ^5J(PC) = 2.2 Hz, C5), 127.6 (d, J(PC) = 1.6 Hz), 127.9 (d, J(PC) = 2.5 Hz), 128.7 (d, ^2J(PC) = 12.7 Hz, C4), 128.8 (d, ^6J(PC) = 1.8 Hz, C8), 129.7 (d, ^4J(PC) = 3.4 Hz, C9), 131.0 (d, J(PC) = 5.1 Hz), 132.0 (d, J(PC) = 4.3 Hz), 133.1 (d, J(PC) = 12.8 Hz), 134.1 (d, J(PC) = 12.7 Hz), 147.1 (d, ^1J(PC) = 50.2 Hz, C3), 166.3 (d, J(PC) = 50.8 Hz); δ(^{31}P) 187.7; HRMS (EI) calcd for $C_{13}H_8{}^{35}ClP$ 230.0052, found 230.0037; MS (EI) *m/z* (relative intensity) 230 ($[M]^{\bullet+}$, 100), 195 ($[M - Cl]^+$, 28), 194 ($[M - HCl]^{\bullet+}$, 47). Anal. Calcd for $C_{13}H_8ClP$: C, 67.7; H, 3.50. Found: C, 66.71; H, 3.47.

1-Chloro-4-methyl-5,6,7,8-tetrahydro-2-phosphanaphthalene (9) and (η^1-1-Chloro-4-methyl-5,6,7,8-tetrahydro-2-phosphanaphthalene)pentacarbonyltungsten (12). A mixture of **2** (72% pure (*vide supra*), 1.6 g, 6.2 mmol) and 1-(1-methylethenyl)cyclohexene (**4**)[7] (2.10 g, 17.2 mmol) was heated to 60 °C. NEt_3 (1.0 mL, 7.2 mmol) was then added dropwise during 15 min. After 35 min, magnetic stirring became difficult due to the formation of a white precipitate; therefore THF (8 mL) was added. The addition of NEt_3 (1.0 mL, 7.2 mmol each time) was repeated after 45, 65, and 195 min. Stirring was continued for altogether 4.25 h, while the temperature was maintained between 55–65 °C. The reaction mixture was then evaporated under reduced pressure; to the residue were added NEt_3 (8.0 mL, 58 mmol) and THF (15 mL). Heating was continued for 56 h at 55–65 °C. Additional NEt_3 was added after 23.5 (2.0 mL, 14.4 mmol), 26.5 (10 mL, 72 mmol) and 33.75 h (10 mL, 72 mmol). At this stage aromatization had occurred for about 90%. The reaction mixture was evaporated, and the residue was extracted six times with pentane (30 mL). Cooling the combined extracts to −80 °C gave a small amount of almost colorless solid which after decantation of solvent and warming to rt became an inhomogeneous sticky oil which was nearly pure **9**. The ^{1}H NMR spectrum showed some impurities. This compound was characterized by CH COSY and NOE experiments. **9**: NMR ($CDCl_3$) δ(^{1}H) 1.6–1.8 (m, 4H), 2.25 (s, 3H, 4-CH_3), 2.6 (m, 2H, 5-CH_2), 2.85 (m, 2H), 8.06 (d, ^2J(PH) = 39.1 Hz, 1H, H3); δ(^{13}C) 22.2 (s), 22.3 (s), 23.6 (d, ^3J(PC) = 3.9 Hz, 4-CH_3), 29.5 (d, J(PC) = 4.4 Hz), 29.5 (s, C5), 141.6 (d, J(PC) = 9.3 Hz), 141.9 (d, J(PC) = 8.7 Hz), 142.6 (d, J(PC) = 14.0 Hz), 152.7 (d, ^1J(PC) = 46.2 Hz, C3), 162.0 (d, J(PC) = 49.6 Hz); δ(^{31}P) 179.7; HRMS (EI) calcd for $C_{10}H_{12}{}^{35}ClP$ 198.0365, found 198.0344; MS (EI) *m/z* (relative intensity) 198 ($[M]^{\bullet+}$, 100), 163 ($[M - Cl]^+$, 27), 131 ($[M - C_5H_7]^+$, 49). To obtain a pure derivative of **9**, the crude product was transformed into its pentacarbonyltungsten complex by a reaction with **10** in THF (10 mL). Addition of **10** (0.33 g, 2.00 mmol) was followed by heating for 12 h at 40–50 °C. After evaporation of the dark green reaction mixture, the residue was extracted three times with pentane (15 mL). Crystallization by cooling the extract to −70 °C was achieved first from THF: pentane (1:4) and finally from pentane to give pure **12** as yellow crystals (dec 131 °C). The yield was 8% (0.26 g, 0.50 mmol) relative to Cl_2PCHCl_2. This compound was characterized by CH COSY and NOE experiments. **12**: NMR (C_6D_6) δ(^{1}H) 1.2–1.3 (m, 4H), 1.63 (s, 3H, 4-CH_3), 1.92–2.02 (m, 2H, 5-CH_2), 2.45–2.57 (m, 2H), 7.60 (d, ^2J(PH) = 25.7 Hz, 1H, H-3). δ(^{13}C) 22.0 (d, J(PC) = 1.9 Hz), 23.1 (d, ^3J(PC) = 10.6 Hz, 4-CH_3), 29.0 (d, ^4J(PC) = 3.6 Hz, C-5), 30.2 (s), 30.6 (d, J(PC) = 3.0 Hz), 139.0 (d, J(PC) = 23.4 Hz), 145.9 (d, J(PC) = 16.9 Hz), 146.0 (d, J(PC) = 10.4 Hz), 147.7 (d, ^1J(PC) = 22.1 Hz, C-3), 155.5 (d, J(PC) = 30.6 Hz), 194.6 (d, ^2J(PC) = 9.5 Hz, CO [cis]), 198.8 (d, ^2J(PC) = 31.8 Hz, CO [trans]). δ(^{31}P) 158.5 ^1J(PW) = 276 Hz; HRMS (EI) calcd for $C_{15}H_{12}{}^{35}ClO_5P^{182}W$ 519.9594, found 519.960; MS (EI) *m/z* (relative intensity) 522 ($[M]^{\bullet+}$, 38), 466 ($[M - 2CO]^{\bullet+}$, 52), 382 ($[M - 5CO]^{\bullet+}$, 85). Anal. Calcd for $C_{15}H_{12}ClO_5PW$: C, 34.48; H, 2.32. Found: C, 32.87; H, 2.19.

7,7-Dichloro-5,12-bis(trimethylsiloxy)-1,2,3,4,6,6a,7,-7a,8,9,10,11,12a,12b-tetradecahydro-6a-phosphabenz[*a*]-anthracene (16). A mixture of **13** (4.9 g, 25 mmol) and **2** (72% pure (*vide supra*), 0.93 g, 3.60 mmol) was heated under stirring to 65 °C. NEt_3 (2.1 mL, 15 mmol) was then added dropwise during 45 min. The reaction mixture became yellow and a brown precipitate was formed. Heating was continued for 4.5 h after which the dark red reaction mixture was evaporated under vacuum. The residue was extracted three times with pentane (10 mL). The combined extracts were evaporated under vacuum and the residues dissolved in THF. Attempts to purify this compound by means of crystallization by cooling the extract to −70 °C, or by complexation with **10** failed. A ^{31}P NMR spectrum of the complexation reaction of **16** with **10** showed, besides many other peaks a prominent signal at 49.5 ppm (^1J(PW) = 263 Hz), which is, apart from a small solvent effect, equal to the value measured for **27** (*vide infra*). **16**: NMR (THF) δ(^{31}P) 1.5. For the GCMS analysis see Table 1.

1-Chloro-4-(trimethylsiloxy)-5,6,7,8-tetrahydro-2-phosphanaphthalene (17). The pentane extract containing **16** (*vide supra*) was evaporated under vacuum and the residue heated to 80 °C under vacuum (2 × 10^{-5} mbar) for 1.5 h. The reaction mixture became a gray black solid which was dissolved in THF. Subsequent ^{31}P NMR measurements indicated the presence of a phosphaaromatic compound with a charac-

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teristic two bond proton coupling of 33.8 Hz. **17**: NMR (THF) $\delta(^{31}P)$ 182.0 ($^2J(PH) = 33.8$ Hz). For GCMS analysis see Table 1.

(η^1-Dichloro(dichloromethyl)phosphine)pentacarbonyltungsten (23). A solution of **2** (72% pure (*vide supra*), 1.15 g, 4.46 mmol) and **10** (1.4 g, 3.8 mmol) in THF (8 mL) was stirred for 41 h at rt. As the conversion to **23** was slow, the mixture was heated to 45–50 °C for 17.5 h. After 7.5 h, **10** (0.28 g, 0.8 mmol) was added to drive the complexation to completion. The resulting dark green heterogeneous reaction mixture was evaporated under reduced pressure and the residue extracted with pentane (50 mL). Crystallization by cooling the extract to −70 °C furnished pure **23** as light yellow crystals (mp 68–69 °C) in a yield of 13% (0.30 g, 0.59 mmol). **23**: NMR (C_6D_6) $\delta(^1H)$ 5.01 (d, $^2J(PH) =$ 1.4 Hz); $\delta(^{13}C)$ 78.3 (dd, $^1J(PC) = 8.1$ Hz, $^1J(CH) = 183.6$ Hz, C1), 193.6 (d, $^2J(PC) = 8.1$ Hz, CO [cis]), 196.0 (d, $^2J(PC) =$ 51.3 Hz, CO [trans]); $\delta(^{31}P)$ 124.9 ($^1J(PW) = 369.5$ Hz); HRMS (EI) calcd for $C_6H^{35}Cl_4O_5P^{182}W$ 505.7798, found 505.779; MS (EI) *m/z* (relative intensity) 510 ($[M]^{\bullet+}$, 76), 475 ($[M - Cl]^+$, 25), 398 ($[M - 4CO]^{\bullet+}$, 45). Anal. calcd for $C_6HC_{14}O_5PW$: C, 14.14; H, 0.20. Found: C, 15.03; H, 0.26.

(η^1-7,7-Dichloro-5,12-bis(trimethylsiloxy)-1,2,3,4,6,6a,7,7a,8,9,10,11,12a,12b-tetradecahydro-6a-phosphabenz[a]anthracene)pentacarbonyltungsten (27). A solution of **23** (0.30 g, 0.59 mmol) and **13** (1.17 g, 5.97 mmol) in THF (1.2 mL) was heated to 60–70 °C. NEt_3 (0.31 g, 3.06 mmol) was then added during 1 h. The reaction mixture turned from light yellow to black. This mixture was heated at 60–70 °C for 7 h. After 3.25 h, NEt_3 (0.50 mL, 3.59 mmol) was added to drive the elimination toward completion. The reaction mixture was evaporated under reduced pressure and the residue extracted with pentane (60 mL). After concentration, crystallization by cooling the extract to −70 °C furnished pure **27** as colorless crystals (mp 128 °C) in a yield of 22% (0.11 g, 0.13 mmol) relative to **23**. Compound **27** was unambiguously characterized by HH COSY, CH COSY, DEPT, and NOE experiments. **27**: NMR (C_6D_6) $\delta(^1H)$ 0.08 (s, 5-OSi($CH_3)_3$), 0.18 (s, 12-OSi($CH_3)_3$), 1.21 (m, H9), 1.24 (m, H10), 1.27 (m, H10), 1.30 (m, H2), 1.35 (m, H3), 1.50 (m, H9), 1.60 (m, H3), 1.62 (m, H8), 1.75 (m, H1), 1.76 (m, H2), 1.90 (m, H4), 2.05 (m, H11), 2.15 (m, H8), 2.23 (m, H11), 2.35 (m, H1), 2.59 (m, H4), 2.65 (m, H12b), 2.95 (m, H7a), 3.05 (m, H6), 3.15 (m, H6), 3.22 (m, H12a); $\delta(^{13}C)$ 0.40 (q, $^1J(CH) = 118.79$, 5-OSi($CH_3)_3$), 0.75 (q, $^1J(CH) = 118.77$ Hz, 12-OSi($CH_3)_3$), 21.61 (t, $^1J(CH) = 129.4$ Hz, C10), 21.65 (dt, $^2J(PC) = 1.37$ Hz, $^1J(CH) = 129.4$ Hz, C3), 21.92 (t, $^1J(CH) = 130.3$ Hz, C9), 22.44 (dt, $^4J(PC) = 1.70$ Hz, $^1J(CH) = 126.6$ Hz, C4), 22.54 (t, $^1J(CH) = 126.6$ Hz, C2), 25.33 (dt, $^2J(CH) = 3.16$ Hz, $^1J(CH) = 128.2$ Hz, C11), 26.03 (t, $^1J(CH) = 130.9$ Hz, C8), 28.23 (dt, $^3J(PC) = 10.46$ Hz, $^1J(CH) =$ 125.91 Hz, C1), 36.28 (ddt, $^1J(PC) = 14.38$ Hz, $^3J(CH) = 3.46$ Hz, $^1J(CH) = 131.56$ Hz, C6), 40.28 (t, $^1J(CH) = 127.57$ Hz, C12b), 47.38 (dt, $^2J(PC) = 2.36$ Hz, $^1J(CH) = 131.01$ Hz, C7a), 48.25 (dt, $^1J(PC) = 23.22$ Hz, $^1J(CH) = 133.52$ Hz, C12a), 94.76 (d, $J(PC) = 15.65$ Hz), 119.75 (d, $J(PC) = 5.03$ Hz), 120.59 (s), 139.99 (d, $J(PC) = 9.41$ Hz), 141.38 (d, $J(PC) = 3.92$ Hz), 197.02 (d, $^2J(PC) = 7.02$ Hz, $^1J(WC) = 126.08$ Hz, CO [cis]), 198.36 (d, $^2J(PC) = 27.67$ Hz, $^1J(WC) = 142.91$ Hz, CO [trans]), $\delta(^{31}P)$ 48.7 ($^2J(PW) = 262.4$ Hz); HRMS (EI) calcd for $C_{28}H_{39}{}^{35}Cl_2O_7P^{28}Si_2{}^{182}W$ 826.0831, found 826.082; MS (EI) *m/z* (relative intensity) 830 ($[M]^{\bullet+}$, 1), 634 ($[M - C_{11}H_{20}OSi]^{\bullet+}$, 14), 273 ($[M - C_{11}H_{20}OSi - W(CO)_6 - Cl]^+$, 100); Anal. Calcd for $C_{28}H_{39}C_{12}O_7PSi_2W$: C, 40.54; H, 4.74. Found: C, 40.73; H, 4.81.

MNDO/PM3 Calculations. Fully optimized geometries were obtained using the semiempirical MNDO/PM3 method.[15] This method is implemented as a part of the VAMP package, version 4.30, at the CAOS/CAMM center of the KUN, Nijmegen, The Netherlands.

JO951270G