Reaction of a Complexed Phosphinidene with 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene

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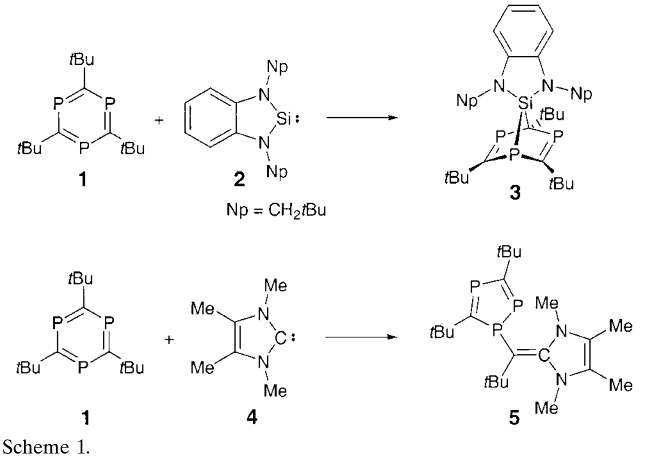
Dedicated to Professor Manfred Regitz on the occasion of his 65th birthday

Abstract: The terminal phosphinidene complex $PhPW(CO)_5$ reacts with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene to give two unexpected multicyclic organophosphorus compounds. One of them results from an initial 1,2-addition, followed by an intramolecular rearrangement. B3LYP/6–31G* calculations on simplified parent systems suggest that the reaction follows a unique concerted reaction pathway. The second, and major, product is a tetraphosphaquadricyclane derivative, which presumably results from an intramolecular [2+2] cycloaddition of an intermediate tetraphosphanorbornadiene complex. Single-crystal X-ray structures are presented for both products.

Keywords: cycloaddition · density functional calculations · electrophilic aromatic substitution · phosphinidene complex · triphosphabenzene

Introduction

The recent development of convenient synthetic routes to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**)[1] has encouraged a number of research groups to study its reactivity[2] and its structural[3] and ligating[4] properties. Previous work by two of us concerned reactions of **1** with silylene **2** and carbene **4**. The former gave a formal [1+4] cycloaddition product (**3**),[5] whereas the latter resulted in an ylide, which rearranged by contraction of the aromatic triphosphabenzene to give a five-membered ring structure (**5**) (Scheme 1).[6] These unusual results and the differences in reactivity between **2** and **4** motivated us to study the reactivity of **1** toward complexed phosphinidenes $RPW(CO)_5$, which are six-electron species analogous to silylenes and carbenes. The reactivity of these Fischer-carbene-like synthons toward a great variety of substrates has been studied,[7] but up to now only two reports have dealt with their reactivity toward aromatic compounds. Treatment of transient electrophilic phosphinidene complexes with ferrocene results in insertion into a C–H bond,[8] whereas a genuine [1+4] cycloaddition product is obtained from the reaction between $PhPW(CO)_5$ (**7**) and the aromatic [5]metacyclophane (**8**) (Scheme 2).[9] Treatment of **7** with a phosphaalkene gives a decomplexed diphosphirane.[10] Hence, formation of 1,2- and 1,4-addition products may be expected from the reaction between $PhPW(CO)_5$ and triphosphabenzene **1**.



Scheme 1.

Product isolation and characterization: Treatment of **1** with $PhPW(CO)_5$ (**7**), generated in situ by thermal decomposition

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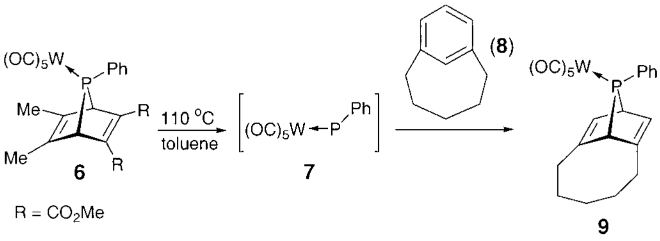
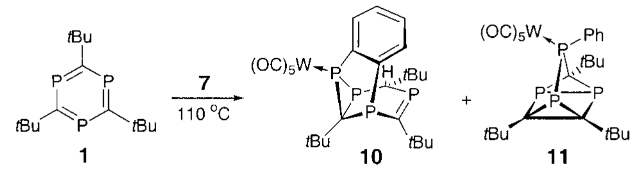


Scheme 2.

of **6** at 110 °C, gives two unexpected products in a ratio of roughly 1:2, as determined from integration of their ^{31}P NMR resonances. The ^{31}P NMR spectra are not in agreement with those expected for a 1,4-addition adduct similar to **3** or **9**, neither do they correspond to a 1,2-addition product. Instead, column chromatography afforded a mixture of compounds **10** and **11**, which were separated by fractional crystallization as yellow and colorless crystals in 25% and 39% yields, respectively (Scheme 3).



Scheme 3.

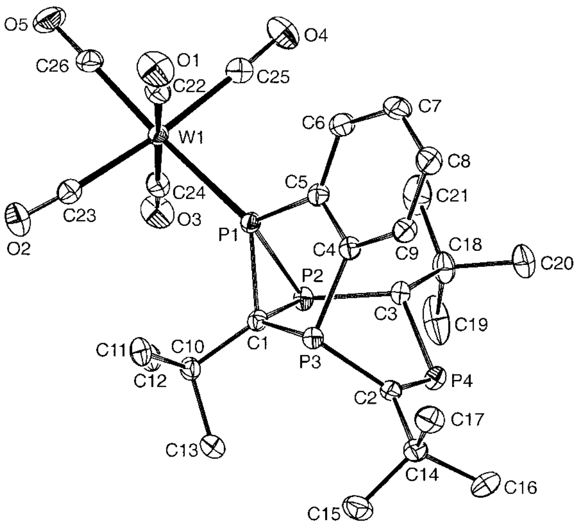


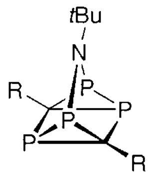
Figure 1. Displacement ellipsoid plot of **10** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles, and torsion angles [°]: W(1)−P(1) 2.5252(5), P(1)−C(1) 1.8698(19), P(1)−P(2) 2.1978(7), P(1)−C(5) 1.8144(19), P(2)−C(1) 1.8752(19), P(2)−C(3) 1.8614(19), P(3)−C(1) 1.8711(19), P(3)−C(2) 1.8603(19), P(3)−C(4) 1.8309(19), P(4)−C(2) 1.677(2), P(4)−C(3) 1.8544(19), C(4)−C(5) 1.400(3), P(1)-W(1)-C(2)6 176.39(6), W(1)-P(1)-P(2) 123.36(2), W(1)-P(1)-C(1) 137.99(6), P(2)-P(1)-C(1) 54.18(6), P(1)-P(2)-C(1) 53.95(6), P(1)-P(2)-C(3) 105.53(6), C(1)-P(2)-C(3) 105.56(8), C(1)-P(3)-C(2) 105.20(9), C(1)-P(3)-C(4) 96.52(9), C(2)-P(3)-C(4) 102.91(8), C(2)-P(4)-C(3) 105.12(9), P(1)-C(1)-P(2) 71.87(7), P(1)-C(1)-P(3) 109.60(9), P(2)-C(1)-P(3) 118.98(10), P(3)-C(2)-P(4) 126.29(11), P(2)-C(3)-P(4) 111.63(10), C(4)-P(3)-C(1)-P(1) −13.77(10), P(3)-C(4)-C(5)-P(1) −5.7(2), C(3)-P(2)-C(1)-P(3) −4.72(13), C(3)-P(4)-C(2)-P(3) 10.07(15).

Product 10: The ^{31}P NMR spectrum of compound **10** has four resonances with rather complicated coupling patterns, but with very characteristic chemical shifts. The presence of the diphosphirane unit is evident from the typical high-field resonances at $\delta = -94.3$ and -152.9, with a large ^{1}J(P,P) coupling constant of 192.4 Hz. The coordination to the W(CO)$_5$ group is clear from the ^{1}J(W,P) coupling constant of 249.1 Hz at the former resonance. The existence of the phosphaalkene part is confirmed by the characteristic low-field absorptions at $\delta = 319.3$ in the ^{31}P NMR spectrum and $\delta = 219.7$ in the ^{13}C NMR spectrum.[11] The ^{31}P NMR signal for the remaining phosphorus, P(3), is found at $\delta = -6.0$.

Ultimate proof for the structure of **10** was provided by a single-crystal X-ray analysis. The P−P bond of 2.1978(7) Å, the P=C bond of 1.677(2) Å, and the P−C bonds of 1.814(2) to 1.8752(19) Å are all of normal lengths (Figure 1).[11] The six-membered ring is fixed in an almost perfect boat conformation, due to the C=P double bond and the fusion with the three- and five-membered rings. Consequently, the proton at C(3) is located in the shielding cone of the phenyl ring, which explains its relatively high-field shift ($\delta = 0.47$) in the ^{1}H NMR spectrum.

Product 11: The structural composition of **11** is also readily derived from the spectroscopic data. The absence of P=C bonds is immediately evident from the lack of signals around $\delta = 300$ in the ^{31}P NMR spectrum and around $\delta = 200$ in the ^{13}C NMR spectrum. The bridgehead phosphorus is recognized in the ^{31}P NMR spectrum from the resonance at $\delta = 24.2$ with a ^{1}J(W,P) coupling constant of 222.6 Hz and a large ^{1}J(P,P) coupling constant of 257.4 Hz with the phosphirane phosphorus, which has a typical high-field shift at $\delta = -113.0$. The ^{31}P NMR resonances at $\delta = -122.8$ and -138.7 are characteristic of phosphorus atoms that constitute part of a diphosphirane ring, but their ^{1}J(P,P) coupling constant of only 47.1 Hz is very small for such a system.[12]

The intriguing and unique structure of **11** was confirmed by a single-crystal X-ray structure determination (Figure 2). The asymmetric unit contains two crystallographically independent molecules with a very similar geometry. The P(1)−P(2) bond length of 2.2060(9) Å, the P(3)−P(4) bond length of 2.1843(9) Å, the C−C bond length of 1.551(3) Å, and the P−C bond lengths of 1.835(3) – 1.901(3) Å are within the ranges generally observed for the separate three-, four-, and five-membered rings. There is very little precedence for structures like **11**. In fact, the only other quadricyclane derivatives containing two or more heteroatoms are compounds **12**. These are obtained by treatment of tBuN=VCl$_3\cdot$DME with excess phosphaalkyne R$-$C$\equiv$P.[1b] The crystal structure of the derivative with R = tBu shows a nonplanar 1,3-diphosphetane unit with C-P-C-P torsion angles of ≈13°. In



12 R = alkyl

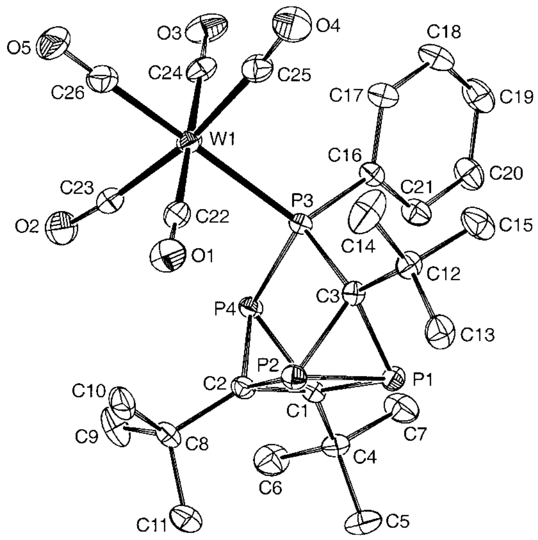
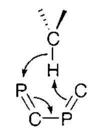


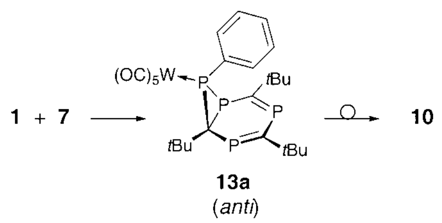
Figure 2. Displacement ellipsoid plot of **11** drawn at the 50% probability level. Only the first of two crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles, and torsion angles [°]; the values for the second molecule are in square brackets: W(1)–P(3) 2.5755(6) [2.5791(6)], P(1)–P(2) 2.2060(9) [2.2070(9)], P(1)–C(1) 1.890(2) [1.891(2)], P(1)–C(3) 1.876(2) [1.874(3)], P(2)–C(2) 1.901(3) [1.909(2)], P(2)–C(3) 1.865(2) [1.867(2)], P(3)–P(4) 2.1843(9) [2.1841(8)], P(3)–C(3) 1.854(2) [1.853(2)], P(3)–C(1)6 1.835(2) [1.835(2)], P(4)–C(1) 1.863(2) [1.863(2)], P(4)–C(2) 1.863(3) [1.862(2)], C(1)–C(2) 1.551(3) [1.549(3)], P(3)-W(1)-C(2)6 178.17(9) [177.19(9)], P(2)-P(1)-C(1) 79.95(8) [79.88(8)], P(2)-P(1)-C(3) 53.64(8) [53.71(7)], C(1)-P(1)-C(3) 97.73(11) [97.87(11)], P(1)-P(2)-C(2) 80.13(8) [80.15(8)], P(1)-P(2)-C(3) 54.11(8) [53.99(8)], C(2)-P(2)-C(3) 96.72(11) [96.68(10)], W(1)-P(3)-P(4) 106.07(3) [105.09(3)], W(1)-P(3)-C(3) 124.61(8) [124.18(8)], W(1)-P(3)-C(1)6 115.41(8) [116.54(8)], P(4)-P(3)-C(3) 96.27(8) [96.38(8)], P(4)-P(3)-C(1)6 104.19(8) [105.09(8)], C(3)-P(3)-C(1)6 106.66(11) [105.99(11)], P(3)-P(4)-C(1) 102.04(8) [102.17(8)], P(3)-P(4)-C(2) 97.58(8) [97.41(8)], C(1)-P(4)-C(2) 49.21(10) [49.15(10)], P(1)-C(1)-P(4) 115.84(12) [115.63(12)], P(1)-C(1)-C(2) 100.45(15) [100.78(15)], P(4)-C(1)-C(2) 65.41(13) [65.39(12)], P(2)-C(2)-P(4) 117.55(13) [117.43(12)], P(2)-C(2)-C(1) 99.40(16) [99.10(15)], P(4)-C(2)-C(1) 65.38(13) [65.46(12)], P(1)-C(3)-P(2) 72.25(9) [72.30(9)], P(1)-C(3)-P(3) 116.48(12) [116.61(13)], P(2)-C(3)-P(3) 112.46(12) [112.13(12)], P(1)-C(1)-C(2)-P(2) −2.33(15) [−2.69(14)], P(2)-P(1)-C(1)-C(2) 2.01(13) [2.34(12)].

contrast, the 1,2-diphosphetane ring of **11** is exceptionally planar, as is reflected in the very small torsion angles of −2.33(15)° for P(1)-C(1)-C(2)-P(2) and of 2.01(13)° for P(2)-P(1)-C(1)-C(2). Generally, 1,2-diphosphetanes are puckered, with P-C-C-P torsion angles between 18° and 42°.[13] We are aware of only one 1,2-diphosphetane with similarly small torsion angles of 4.9° and −4.1°.[14]

Reaction pathway: The unexpected formation of compounds **10** and **11** illustrates once again the rich chemistry of electrophilic phosphinidene complexes. But how are these products formed? And why is the reaction behavior in this case so different from that in the Arduengo carbenes and silylenes? Because the expected 1,2- and 1,4-addition products are not observed as such, we also wondered whether they are involved as intermediates.

Formation of 10: The presence of a three-membered ring in structure **10** suggests that $PhPW(CO)_5$ (**7**) initially adds to one of the P=C bonds of **1** to give **13** (Scheme 4). 1,2-Additions to aromatic compounds have not been reported yet, but they are well established for reactions with olefins[7] and heteroolefins such as C=O,[15] C=N,[16] C=S,[17] C=Si,[18] and C=P,[10] and usually give rise to two isomeric, three-membered ring products. Hence, the formation of two isomers (*syn* and *anti*) would also be expected for the 1,2-addition of **7** to **1**. The *syn* isomer **13b** may undergo a 1,3-sigmatropic rearrangement to give the formal 1,4-addition product **11** (vide infra). Instead product **10** may result, at least formally, from an *intra*-molecular electrophilic aromatic substitution of the *anti* isomer **13a**, which has the phenyl group above the ring, with replacement of an *ortho* hydrogen from the phenyl group for a phosphorus and a concurrent H-shift to C(3). However, the electrophilicity of the phosphorus of the phosphaalkene part appears to be relatively low for such a reaction pathway. On the other hand, related *intra*-molecular reactions between phosphaalkenes and olefins, together with P–C bond formation, are known from the phospha-Cope rearrangement.[11]





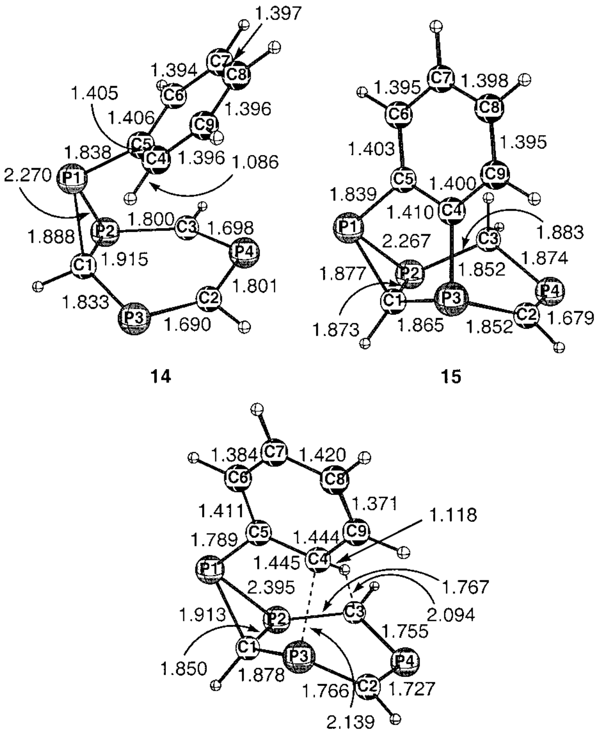
Scheme 4.

We resorted to DFT calculations at the B3LYP/6–31G* level of theory to verify the postulated reaction pathway. The $W(CO)_5$ group was eliminated from the calculations and the *tert*-butyl substituents were replaced by hydrogens to keep the calculations within manageable proportions. The B3LYP/6–31G*-optimized geometries for the simplified *syn*-1,2-addition adduct **14**, product **15**, and transition structure **16** are depicted in Figure 3, together with their main geometrical parameters. Their absolute and relative energies are summarized in Table 1.

The two phosphaalkene parts of the initially formed *syn*-1,2-adduct **14** are significantly conjugated, as is evident from the relatively long P=C bonds of 1.698 Å [P(4)–C(3)] and 1.690 Å [P(3)–C(2)] and from the relatively short connecting P(4)–C(2) bond of 1.801 Å. Apparently, the stabilization gained from this conjugation is insufficient to prevent the conversion to the global minimum **15**, which is a considerable 20.3 kcal mol^{-1} more stable. This energy gain is readily

Table 1. Absolute (in a.u.) and Relative B3LYP/6–31G* Energies (in kcal mol^{-1}) of **14–16**

Structures	Energies	
	Absolute	Relative
14	−1713.11677	0.0
15	−1713.14918	−20.3
16	−1713.08376	20.7

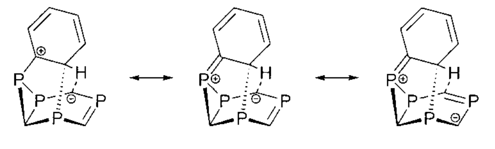


14 **15** **16**

Figure 3. B3LYP/6-31G*-optimized geometries of **14**, **15**, and **16**.

attributable to the loss of a weak C=P π-bond and the formation of a relatively strong C–P σ-bond. The computed geometry of **15** is in good agreement with the experimentally determined molecular structure of **10** in the crystal, taking into account the thermal motion in the crystal structure and the absence of the $W(CO)_5$ and the *tert*-butyl substituents in the computed structure, which result in a slight elongation of most of the P–C bonds and a widening of the endocyclic angles at the carbon centers.

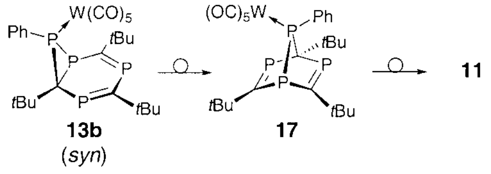
Typically, electrophilic aromatic substitutions involve very strong (ionic) electrophiles and follow a two-step reaction pathway; intermediate products (Wheland intermediates) have even been characterized. However, we found no other minima along the reaction coordinate and located only a single transition structure (**16**); this indicated a concerted process. A vibrational frequency analysis giving one and only one negative eigenvalue, corresponding to the formation of the new P(3)–C(4) and C(3)–H bonds and the concurrent breaking of the C(4)–H bond, confirmed it to be a true transition structure. The small imaginary frequency of TS**16**, 118.5 cm^{-1}, indicates a flat potential energy surface around the saddle. Consequently, an IRC calculation connecting TS**16** with the final product **15** was not successful, but the reaction coordinate could be followed back to the *syn*-1,2-adduct **14**.



Scheme 5.

The conversion of **14** to **15** appears to represent a unique nonionic unimolecular electrophilic aromatic substitution, as TS**16** closely resembles a Wheland intermediate.[19] The barrier to this conversion, 20.7 kcal mol^{-1}, is relatively low due to significant resonance stabilization (Scheme 5). TS**16** most closely resembles resonance structures **16B** and **16C**, and illustrates attack by the electropositive phosphorus of the P(3)=C(2) bond onto the *ortho* carbon of the phenyl group; this results in pyramidalization of C(4) and alternating C–C bond lengths within the phenyl group. Subsequently, the *ortho* hydrogen shifts to C(3); the H ··· C(3) length of 2.094 Å falls well within their van der Waals radii. The concertedness of the reaction pathway is further reflected in the simultaneous conversion of the 1,3-diphosphabutadiene part of **14** to a single phosphaalkene unit, as is evident from the elongation of the two P=C bonds by ≈0.06 Å and the shortening of the P(4)–C(2) bond by ≈0.07 Å to 1.727 Å in TS**16**. That the reaction proceeds readily, despite the low electrophilicity of the phosphorus, may be attributed to the fact that the three reaction centers are part of the same molecule. Moreover, the electrophilic center [P(3)], the *ortho* hydrogen, which is activated by the P-substituent at the benzene ring, and the base [C(3)] are all positioned in such a way that only very small geometrical changes of the conformation in **14** are needed to bring them together. Because the structural differences between 1,2-adduct **14**, TS**16**, and product **15** are only modest, we believe that the $W(CO)_5$ and *tert*-butyl substituents, which are located at the periphery of the structures, will not significantly affect the reaction pathway.

Formation of 11: For the formation of **11**, an *intra*molecular [2+2] cycloaddition between the two P=C units of an initially formed tetraphosphanorbornadiene complex **17** seems more likely (Scheme 6). Indeed, both *inter*- and *intra*molecular head-to-head dimerizations of phosphaalkenes to give 1,2-diphosphetanes are well established.[20] It is noteworthy that compound **12** is believed to result from an *intra*molecular head-to-tail dimerization of the phosphaalkene parts of a transiently formed norbornadiene derivative,[1b] and a similar head-to-head dimerization has been proposed in a rearrangement reaction of a 1,3,5-triphospha-7-hafnanorbornadiene complex.[21] If **17** is an intermediate, we should consider two reaction pathways for its transient formation: 1) 1,2-addition followed by rearrangement, similar to the 1,3-sigmatropic shift usually observed for vinylphosphiranes,[22] or 2) a direct 1,4-addition, similar to the reaction between $PhPW(CO)_5$ and [5]metacyclophane **8**.[9] However, the formation of **10**, as described above, suggests that the former reaction pathway is more plausible. Whereas complex **10** is obtained from an



Scheme 6.

intermediate *anti*-1,2-adduct (**13a**), compound **11** may result from rearrangement of the *syn*-1,2-addition product (**13b**).

Origin of the differences in reactivity: The major difference between the reactivities of the silylene **2** and the carbene **4**, and the complexed phosphinidene $PhPW(CO)_5$ (**7**) is, of course, their electrophilic or nucleophilic natures. Complexed phosphinidenes $RPW(CO)_5$ are electrophilic, as is evident from the Hammett reaction constants of -0.76,[23] -0.60,[24] and -0.55[25] for cycloadditions to styrenes of $PhPW(CO)_5$, $MePW(CO)_5$, and $MeOPW(CO)_5$, respectively. Silylenes and carbenes of the Arduengo type, typified by silylene **2** and carbene **4**, are, on the other hand, strongly nucleophilic.[26] Indeed, computational analysis of the reaction between carbene **4** and **1** showed that the first step of the reaction is the nucleophilic attack of **4** at a carbon of the triphosphabenzene to give a C–C ylide.[6] The electrophilic $PhPW(CO)_5$ is more likely to attack a phosphorus, as is illustrated by its reactions with phosphanes, yielding phosphoranylidene phosphine complexes.[27]

Computational Section: All electronic structure calculations were carried out using the Gaussian 98 suite of programs (G98).[28] For the density functional theory (DFT) calculations we used Becke's three-parameter hybrid-exchange functional,[29] combined with the Lee–Yang–Parr correlation functional,[30] denoted as B3LYP. The 6–31G* basis set was employed throughout for the geometry optimizations. First and second order energy derivatives were computed to confirm the nature of the minima and transition structures. Intrinsic reaction coordinate calculations (IRC) were performed to establish connections between transition structures and minima.

Experimental Section

The experiment was performed under an atmosphere of dry nitrogen. Solids were dried in vacuo, and liquids were distilled (under N_2) prior to use. Solvents were used as purchased, except for toluene, which was distilled over sodium. NMR spectra were recorded on Bruker AC200 (^{1}H, ^{13}C) and Avance250 spectrometers (^{31}P) with $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) on a Finnigan Mat 90 spectrometer.

Treatment of 1 with PhPW(CO)$_5$ (7): Complex **6** (0.32 g, 0.49 mmol) and **1** (0.15 g, 0.50 mmol) were heated under reflux in toluene (5 mL) for 6.5 h. Evaporation to dryness and chromatography of the residue over silica with pentane/dichloromethane (9:1) as eluent gave a mixture of **10** and **11**. Fractional crystallization from a hexane/dichloromethane mixture afforded **10** as yellow crystals and **11** as colorless crystals.

Compound 10: Yield: 0.09 g (25%); m.p. 180–182 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.3-7.7$ (m, 4H; Ph), 1.59 (d, $^{4}J(P,H) = 2.3$ Hz, 9H; $P=C\text{-}C(CH_3)_3$), 1.25 (s, 9H; $P_3CC(CH_3)_3$), 1.08 (s, 9H; $HCC(CH_3)_3$), 0.47 (ddd, $^{2}J(P,H) = 15.8$ Hz, $^{2}J(P,H) = 10.6$ Hz, $^{2}J(P,H) = 1.1$ Hz, 1H; PCH); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 219.7$ (ddd, $^{1}J(P,C) = 65.5$, $^{1}J(P,C) = 60.1$ Hz, $^{2}J(P,C) = 5.5$; P=*C*), 197.9 (d, $^{2}J(P,C) = 32.5$ Hz, *trans* CO), 196.5 (dd, $^{2}J(P,C) = 7.6$ Hz, $^{3}J(P,C) = 1.1$ Hz, $^{1}J(W,C) = 127.9$ Hz, *cis* CO), 145.1 (m, *ipso* Ph), 144.2 (m, *ipso* Ph), 132.8 (d, $^{2}J(P,C) = 22.8$ Hz, Ph), 131.2 (dd, $^{3}J(P,C) = 5.8$ Hz, $^{4}J(P,C) = 2.5$ Hz, Ph), 128.6 (m, Ph), 128.4 (dd, $^{2}J(P,C) = 25.7$ Hz, $^{3}J(P,C) = 6.2$ Hz, Ph), 49.3 (ddd, $^{1}J(P,C) = 64.8$ Hz, $^{1}J(P,C) = 56.1$ Hz, $^{2}J(P,C) = 2.5$ Hz, P*C*H), 45.8 (dd, $^{2}J(P,C) = 29.3$ Hz, $^{2}J(P,C) = 20.8$ Hz $P=C\text{-}C(CH_3)_3$, 35.7 (ddd, $^{2}J(P,C) = 22.0$ Hz, $^{2}J(P,C) = 14.8$ Hz, $^{2}J(P,C) = 1.8$ Hz, $P_3CC(CH_3)_3$), 33.9 (dd, $^{2}J(P,C) = 16.5$ Hz, $^{2}J(P,C) = 16.1$ Hz, $HCC(CH_3)_3$), 33.3 (dd, $^{3}J(P,C) = 16.7$ Hz, $^{3}J(P,C) = 9.4$ Hz, $P=C\text{-}C(CH_3)_3$, 31.8 (m, $P_3CC(CH_3)_3$), 30.6 (dd, $^{3}J(P,C) = {}^{3}J(P,C) = 9.7$ Hz, $HCC(CH_3)_3$); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 319.3$ (m, P=C), -6.0 (ddd, $^{2}J(P,P) = 14.4$ Hz, $^{2}J(P,P) = 8.1$ Hz, $^{2}J(P,P) = 3.1$ Hz, *P*-C=P), -94.3 (ddd, $^{1}J(P,P) = 192.4$ Hz, $^{2}J(P,P) = 14.4$ Hz, $^{3}J(P,P) = 6.4$ Hz, $^{1}J(W,P) = 249.1$ Hz, W-*P*-P), -152.9 (m, $^{1}J(P,P) = 192.4$ Hz, W–P–*P*); IR (CH_2Cl_2): $\tilde{\nu} = 1914$ cm^{-1} (s), 2074 cm^{-1} (w) (C=O); HR-MS: calcd. for $C_{26}H_{32}P_4O_5W$: 732.07098; found 732.07656.

Compound 11: Yield: 0.14 g (39%); m.p. 176–177 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 8.0$ (m, 2H; Ph), 7.5 (m, 3H; Ph), 1.40 (s, 9H; CH_3), 1.37 (s, 9H; CH_3), 1.06 (s, 9H; CH_3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 198.3$ (d, $^{2}J(P,C) = 24.2$ Hz, *trans* CO), 198.1 (dd, $^{2}J(P,C) \approx {}^{3}J(P,C) \approx 5.7$ Hz, $^{1}J(W,C) = 126.7$ Hz, *cis* CO), 135.3 (ddd, $^{2}J(P,C) = 8.8$ Hz, $^{3}J(P,C) = 3.2$ Hz, $^{4}J(P,C) = 2.6$ Hz, *o*-Ph), 133.3 (dd, $^{1}J(P,C) = 20.1$ Hz, $^{2}J(P,C) = 3.3$ Hz, *ipso*-Ph), 131.5 (d, $^{4}J(P,C) = 2.1$ Hz, *p*-Ph), 128.8 (d, $^{3}J(P,C) = 9.2$ Hz, *m*-Ph), 71.7 (dddd, $^{1}J(P,C) = 63.6$ Hz, $^{1}J(P,C) = 58.6$ Hz, $^{1}J(P,C) = 22.8$ Hz, $^{2}J(P,C) = 3.0$ Hz, CP_3), 56.5 (dddd, $^{1}J(P,C) = 54.2$ Hz, $^{1}J(P,C) = 31.6$ Hz, $^{2}J(P,C) \approx {}^{2}J(P,C) \approx 4.3$ Hz, CP_2), 47.7 (ddd, $^{1}J(P,C) = 48.6$ Hz, $^{1}J(P,C) = 29.5$ Hz, $^{2}J(P,C) = 3.9$ Hz, CP_2), 37.8 (dt, $^{2}J(P(1),C) \approx {}^{2}J(P(2),C) \approx 13.1$ Hz, $^{2}J(P,C) = 2.8$ Hz, $C(CH_3)_3$), 35.9 (dd, $^{2}J(P,C) = 18.6$ Hz, $^{2}J(P,C) = 8.2$ Hz, $C(CH_3)_3$), 35.4 (ddd, $^{2}J(P,C) = 12.4$ Hz, $^{2}J(P,C) = 9.1$ Hz, $^{3}J(P,C) = 3.0$ Hz, $C(CH_3)_3$), 33.7 (ddd, $^{3}J(P,C) \approx {}^{3}J(P,C) \approx 10.4$ Hz, $^{3}J(P,C) = 3.2$ Hz, CH_3), 31.9 (dd, $^{3}J(P,C) = 10.4$ Hz, $^{3}J(P,C) = 5.3$ Hz, CH_3), 31.1 (dd, $^{3}J(P,C) = 11.7$ Hz, $^{3}J(P,C) = 6.7$ Hz, CH_3); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 48.9$ (dd, $^{1}J(P,P) = 278.9$ Hz, $^{2}J(P,P) = 19.0$ Hz, $^{1}J(W,P) = 232.0$ Hz, W–*P*–P), -113.0 (d, $^{1}J(P,P) = 278.9$ Hz, W–P–*P*), -122.8 (dd, $^{1}J(P,P) = 47.1$ Hz, $^{2}J(P,P) = 19.0$ Hz), -138.7 (d, $^{1}J(P,P) = 47.1$ Hz, P); IR (CH_2Cl_2): $\tilde{\nu} = 1937$ cm^{-1} (s), 2070 cm^{-1} (w) (C=O); HR-MS: calcd. for $C_{26}H_{32}P_4O_5W$: 732.07098; found 732.06725.

Crystal structure determinations: X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150 K. The structures were solved with automated Patterson methods (DIRDIF97[31]) and refined with SHELXL-97[32] against F^2 of all reflections up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined freely with isotropic displacement parameters (compound **10**) or as rigid groups (compound **11**). Molecular illustrations, structure checking, and calculations were performed with the PLATON package[33]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 155694 (compound **10**) and 165695 (compound **11**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Compound **10**: $C_{26}H_{32}O_5P_4W$, Fw = 732.25, yellow block, 0.50 × 0.20 × 0.08 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 10.4859(1)$, $b = 15.2912(2)$, $c = 20.6734(2)$ Å, $\beta = 116.2453(7)°$, $V = 2973.09(6)$ Å^3, $Z = 4$, $\rho = 1.636$ g cm^{-3}. 59052 measured reflections, of which 6816 were unique ($R_{int} = 0.049$). Absorption correction based on multiple measured reflections with the program PLATON[33] ($\mu = 4.133$ mm^{-1}, 0.51–0.83 transmission). 453 refined parameters, 0 restraints. R values [$I > 2\sigma(I)$]: $R1 = 0.0181$, $wR2 = 0.0425$. R values [all reflections]: $R1 = 0.0206$, $wR2 = 0.0435$. $S = 1.068$. Rest electron density between -0.82 and 0.91 e Å^{-3}.

Compound **11**: $C_{26}H_{32}O_5P_4W$, Fw = 732.25, yellow needle, 0.36 × 0.15 × 0.12 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 20.3148(3)$, $b = 13.8535(2)$, $c = 23.2691(3)$ Å, $\beta = 117.1720(5)°$, $V = 5825.93(14)$ Å^3, $Z = 8$, $\rho = 1.670$ g cm^{-3}. 95608 measured reflections, of which 13336 were unique ($R_{int} = 0.059$). Absorption correction based on multiple measured reflections with the program PLATON[33] ($\mu = 4.219$ mm^{-1}, 0.46–0.63 transmission). 667 refined parameters, 0 restraints. R values [$I > 2\sigma(I)$]: $R1 = 0.0234$, $wR2 = 0.0494$. R values [all refl.]: $R1 = 0.0292$, $wR2 = 0.0513$. $S = 1.050$. Rest electron density between -0.96 and 0.68 e Å^{-3}.

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[1] a) P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411–2414; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227–2230; b) F. Tabellion, A. Nachbauer, S. Leininger, C. Peters, M. Regitz, F. Preuss, *Angew. Chem.* **1998**, *110*, 1318–1321; *Angew. Chem. Int. Ed.* **1998**, *37*, 1233–1235.

[2] a) S. M. Bachrach, P. Magdalinos, *J. Mol. Struct. (Theochem.)* **1996**, *368*, 1–6; b) P. Binger, S. Stutzmann, J. Bruckmann, C. Krüger, J. Grobe, D. Le Van, T. Pohlmeyer, *Eur. J. Inorg. Chem.* **1998**, 2071–2074; c) F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. J. Wilson, *Organometallics* **2000**, *19*, 219–220; d) M. Krein, U. Bergsträßer, C. Peters, S. G. Ruf, M. Regitz, *Chem. Commun.* **2000**, 2015–2016.

[3] a) R. Gleiter, H. Lange, B. Binger, J. Stanneck, C. Kruger, J. Bruckmann, U. Zenneck, S. Kummer, *Eur. J. Inorg. Chem.* **1998**, 1619–1621; b) M. Hofmann, P. v. R. Schleyer, M. Regitz, *Eur. J. Inorg. Chem.* **1999**, 3291–3303.

[4] a) P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, *J. Am. Chem. Soc.* **1996**, *118*, 7630–7631; b) S. B. Clendenning, P. B. Hitchcock, J. F. Nixon, *Chem. Commun.* **1999**, 1377–1378; c) P. Binger, S. Stutzmann, J. Stannek, B. Gabor, R. Mynott, *Eur. J. Inorg. Chem.* **1999**, 83–86; d) S. B. Clendenning, J. C. Green, J. F. Nixon, *J. Chem. Soc. Dalton Trans.* **2000**, 1507–1512.

[5] S. B. Clendenning, B. Gehrhus, P. B. Hitchcock, J. F. Nixon, *Chem. Commun.* **1999**, 2451–2452.

[6] S. B. Clendenning, P. B. Hitchcock, J. F. Nixon, L. Nyulaszi, *Chem. Commun.* **2000**, 1305–1306.

[7] a) F. Mathey, *Angew. Chem.* **1987**, *99*, 285–296; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 275–286; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.

[8] J. Svara, F. Mathey, *Organometallics* **1986**, *5*, 1159–1161.

[9] M. J. van Eis, C. M. D. Komen, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, M. Lutz, A. L. Spek, *Angew. Chem.* **1998**, *110*, 1656–1659; *Angew. Chem. Int. Ed.* **1998**, *37*, 1547–1550.

[10] R. Streubel, N. H. T. Huy, F. Mathey, *Synthesis* **1993**, 763–764.

[11] R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme Medical, New York, **1990**, pp. 157–219, and references therein.

[12] F. Mathey, *Chem. Rev.* **1990**, *90*, 997–1025.

[13] a) B. Geißler, S. Barth, U. Bergsträßer, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. R. Schleyer, M. Regitz, *Angew. Chem.* **1995**, *107*, 485–488; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484–487; b) B. Breit, U. Bergsträßer, G. Maas, M. Regitz, *Angew. Chem.* **1992**, *104*, 1043–1046; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1055–1058; c) M. Julino, M. Slany, U. Bergsträßer, F. Mercier, F. Mathey, M. Regitz, *Chem. Ber.* **1995**, *128*, 991–997; d) W. Fiedler, O. Löber, U. Bergsträßer, M. Regitz, *Eur. J. Org. Chem.* **1999**, *64*, 363–371; e) B. Breit, R. Boese, M. Regitz, *J. Organomet. Chem.* **1994**, *464*, 41–45; f) R. Appel, F. Knoch, H. Kunze, *Chem. Ber.* **1984**, *117*, 3151–3159; g) W. Brieden, T. Kellersohn, *Chem. Ber.* **1993**, *126*, 845–847; h) R. Appel, C. Casser, F. Knoch, B. Nieman, *Chem. Ber.* **1986**, *119*, 2915–2920; i) N. H. T. Huy, L. Ricard, F. Mathey, *Organometallics* **1991**, *10*, 3958–3959; j) A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, V. P. Kukhar, J. V. Shevchenko, O. I. Kolodyazhnyi, I. E. Boldeskul, *Zh. Strukt. Khim.* **1984**, *25*, 122–130; k) L. Weber, M. Frebel, R. Boese, *Chem. Ber.* **1990**, *123*, 733–738; l) R. Appel, V. Barth, M. Halstenberg, G. Huttner, J. Seyerl, *Angew. Chem.* **1979**, *91*, 935–936; *Angew. Chem. Int. Ed. Eng.* **1979**, *18*, 872–873; m) G. Becker, W. Becker, O. Mundt, *Phosphorus Sulfur* **1983**, *14*, 267–283.

[14] L. Weber, M. Frebel, A. Müller, H. Bögge, *Organometallics* **1991**, *10*, 1130–1135.

[15] R. Streubel, A. Kusenberg, J. Jeske, P. G. Jones, *Angew. Chem.* **1994**, *106*, 2564–2566; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2427–2428.

[16] a) R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske, P. G. Jones, *Angew. Chem.* **1997**, *109*, 409–413; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 378–382; b) M. J. M. Vlaar, P. Valkier, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, A. L. Spek, M. Lutz, K. Lammertsma, *Chem. Eur. J.* **2001**, *7*, 3551–3557.

[17] R. Streubel, C. Neumann, *Chem. Commun.* **1999**, 499–500.

[18] M. J. M. Vlaar, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, A. L. Spek, M. Lutz, N. Sigal, Y. Apeloig, K. Lammertsma, *Angew. Chem.* **2000**, *112*, 4296–4299; *Angew. Chem. Int. Ed.* **2000**, *39*, 4127–4130.

[19] Alternatively, the six-electron process may be considered a transition structure for an unusual ene reaction, although the plane of the phenyl ring in TS**16** is positioned orthogonally to that of the ring containing the three phosphorus atoms.

[20] a) G. Becker, W. Becker, G. Uhl, W. Uhl, H.-J. Wessely, *Phosphorus Sulfur* **1983**, *18*, 7–10; b) N. H. T. Huy, L. Ricard, F. Mathey, *Organometallics* **1988**, *7*, 1791–1795. See also ref. [13 a,f,h,l,m].

[21] P. Binger, S. Leininger, K. Günther, U. Bergsträßer, *Chem. Ber./Recueil* **1997**, *130*, 1491–1494.

[22] a) K. Lammertsma, J.-T. Hung, P. Chand, G. M. Gray, *J. Org. Chem.* **1992**, *57*, 6557–6560; b) J.-T. Hung, K. Lammertsna, *J. Org. Chem.* **1993**, *58*, 1800–1803; c) B. Wang, C. H. Lake, K. Lammertsma, *J. Am. Chem. Soc.* **1996**, *118*, 1690–1695; d) M. J. van Eis, T. Nijbacker, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *J. Am. Chem. Soc.* **2000**, *13*, 3033–3036.

[23] K. Lammertsma, P. Chand, S.-W. Yang, J.-T. Hung, *Organometallics* **1988**, *7*, 1875–1876.

[24] J.-T. Hung, K. Lammertsma, *Organometallics* **1992**, *11*, 4365–4366.

[25] B. Wang, K. Lammertsma, *J. Am. Chem. Soc.* **1994**, *116*, 10486–10488.

[26] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91, and references therein.

[27] a) P. Le Floch, A. Marinetti, L. Ricard, F. Mathey, *J. Am. Chem. Soc.* **1990**, *112*, 2407–2410; b) M. J. M. Vlaar, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Organomet. Chem.* **2001**, *617–618*, 311–317.

[28] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

[29] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[30] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[31] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, The DIRDIF97 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen (The Netherlands) **1997**.

[32] G. M. Sheldrick, SHELXL-97. Program for crystal structure refinement. University of Göttingen (Germany) **1997**.

[33] A. L. Spek, PLATON. A multipurpose crystallographic tool. Utrecht University (The Netherlands) **2000**.

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