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1,4-Addition of a Phosphinidene Complex to *Cisoid* 1,3-Dienes

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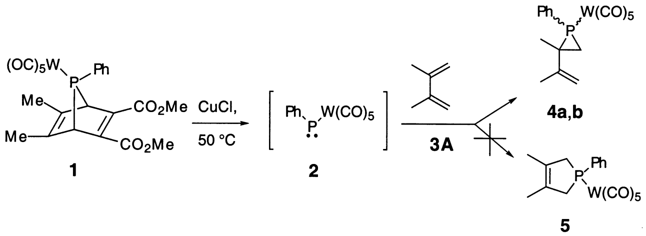
Abstract—The first genuine 1,4-additions of the terminal phosphinidene complex $PhPW(CO)_5$ (**2**) to 1,3-dienes **3** are reported. Two of the 1,4-adducts, **15** and **17**, were characterised by X-ray crystal structure determinations. A *cisoid* conformation, but *not* coplanarity, of **3** appears to be a prerequisite for the occurrence of a 1,4-addition. The reaction of **2** with the sterically hindered **3B** yields 66.5% of the 1,4-addition product **13**, the highest percentage of 1,4-addition thus far observed for the reaction of an electrophilic species with a 1,3-diene. The product composition is almost independent of the temperature, implying that the usual preference for the 1,2-mode is mainly entropy controlled. Steric factors appear to be the main cause of the higher tendency towards 1,4-addition of phosphinidines as compared to carbenes. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Initially considered as chemical curiosities, the monovalent phosphorus species R-P, the so-called phosphinidenes, have become well established.[1] In particular the discovery in the early 80's that the stability of phosphinidenes is increased by metal complexation and that the resulting complexes such as **2** are easily accessible via cheletropic cleavage from phosphanorbornadiene complexes **1**, gave tremendous impetus to the development of this type of chemistry.[2] In many regards, terminal phosphinidine complexes **2** are closely related to electrophilic carbenes.[3] Thus, they react with olefins to furnish phosphiranes, and with 1,3-dienes such as **3A**, they analogously afford the corresponding vinylphosphiranes **4**.[3,4]



Interestingly, even though orbital symmetry would allow for both 1,2- *and* 1,4-addition to a 1,3-diene, 1,4-additions are rare in the case of carbenes, while for phosphinidines, this mode of reaction (leading e.g. to **5**) has not been previously reported. This may seem paradoxical as the 1,4-addition of a carbene is a least-motion symmetry allowed process, and the 1,4-addition product of butadiene is at least 84 kJ mol^{-1} more stable than the corresponding 1,2-adduct.[5] In an early Extended Hückel study on the addition of methylene to butadiene, Hoffmann and Fujimoto concluded that 1,4-addition is discriminated against 1,2-addition due to excessive closed shell repulsion between the filled orbital π_1 of the diene and the carbene σ-orbital, which gives rise to an activation barrier of 96 kJ mol^{-1}.[5] A few years later Bauld and Wirth reported that the closed-shell repulsions to which the 1,4-barrier had been attributed, involve next-nearest neighbour (anti-aromatic) resonance interactions.[6] Nevertheless, several examples of 1,4-additions of carbenes are known. Apart from a few very special cases,[7] the first simple 1,4-addition to a 1,3-diene was that of dichlorocarbene to 1,2-dimethylenecycloheptane (**3C**), albeit in 1% yield.[8] Later these results were extended to other dienes and carbenes.[9] The highest yield for 1,4-addition to **3C** was found for dibromocarbene; it yielded 19% of **9**.[9b] Apparently, the 1,4-addition is promoted by the enforced *cisoid* conformation of the diene. Mayr and Heigl reported that dibromocarbene adds in a 1,4-mode to the diene **3B** in an even higher yield of 30% to give **7**.[9a] In this case the 1,2-addition is clearly hampered by the congesting methyl groups.

The only case of a genuine 1,4-addition of a phosphinidene complex reported so far is the selective addition of **2** to the highly strained benzene ring of [5]metacyclophane (**10**) under formation of **11**.[10] This stimulated us to search for

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Keywords: 1,3-dienes; phosphinidines; cheletropic cleavage.

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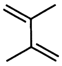
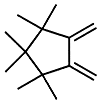
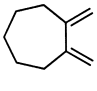
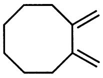
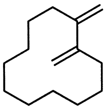
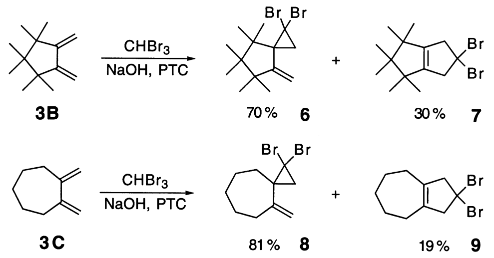
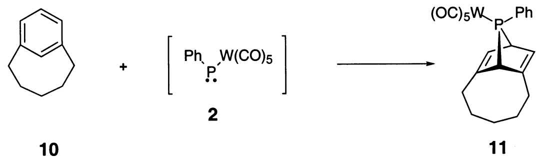
Table 1. Product formation from **1**, **3**, and CuCl in xylene (relative yields)

Entry	Diene	T (°C)	1,2-Adducts (%)		1,4-Adduct (%)
1	 **3A**	55	66 **4a**	34 **4b**	–
2	 **3B**	55	33.5 **12**		66.5 **13**
3	 **3C**	22	53.0 **14a**	29.2 **14b**	17.8 **15**
4		45	55.5	27.2	17.3
5		50	53.6	27.6	18.8
6		60	53.2	28.4	18.3
7		65	53.3	29.0	17.7
8		70	53.8	28.1	18.1
9	 **3D**	50	51.2 **16a**	23.2 **16b**	25.6 **17**
10	 **3E**	50	66 **18a**	34 **18b**	



1,4-additions of **2** to 1,3-dienes, and in this paper we wish to demonstrate that this hitherto unknown addition mode does indeed occur with dienes possessing an enforced *cisoid* conformation.



Results

Adduct formation

In search of 1,4-additions of **2** to 1,3-dienes, we investigated the CuCl catalysed decomposition of **1**[2] in the presence of dienes **3**. In a typical experiment, a solution of **1** (approx. 0.10 M), an excess of **3** (1.5–10 equiv.) and a pinch of CuCl was prepared in xylene in an NMR tube, flushed with nitrogen, and tightly capped. The NMR tube was transferred to the pre-heated NMR probe and the progress of the reaction was followed by ^{31}P NMR spectroscopy at 50°C (Table 1; for further details, see Experimental). Taking **3C** as an example, directly after the start of the reaction, three new resonances emerged at $\delta=-136.1$, -132.2, and 2.8 ppm; the product composition was determined by integration of the ^{31}P NMR signals. The two strongly shielded signals are characteristic for phosphiranes and were therefore assigned to the two isomeric 1,2-adducts **14a**,**b**.[3a] An unambiguous assignment of their stereochemistry was not achieved, but it is likely that the major isomer **14a** ($\delta=-136.1$ ppm; 53.6%) has the bulky pentacarbonyltungsten group oriented *syn* to the vinyl substituent in order to minimise steric interactions. Much to our delight, the signal at 2.8 ppm could be assigned to the 1,4-adduct **15** on the basis of its spectral data and an X-ray crystal structure determination (vide infra).

Several observations exclude the possibility that **15** is a secondary product resulting from rearrangement of primarily formed **14a**,**b**. Firstly, within an experimental accuracy of about 2%, the average amount of **15** at 50°C (18.8%; Table 1) is constant during at least two half-lives of **1**. At temperatures higher than 50°C, the rearrangement of the primarily formed **14** contributes slightly to the amount of **15**. This was accounted for by plotting the fraction of **15** for the first two half-lives of **1** versus time and fitting these data with a straight line according to an unweighted least-mean square procedure; extrapolation to $t=0$ furnished the molar fraction of directly formed **15** corrected for its subsequent formation by rearrangement. At the highest temperature (70°C), the values obtained by this procedure differed less than 5% from the average value of **15** at all temperatures. Secondly, it should be pointed out that the rate of decomposition of **1** is about 30–70 times higher than the rate of rearrangement, depending on the excess of diene and the reaction temperature (50–70°C) (vide infra). In all cases the rearrangement of **14a** and **14b** accounts for less than 5% of the total amount of **15**. Finally, we reinvestigated the addition of **2** to **3A** at 50°C and confirmed that only the 1,2-adducts **4a**,**b** are formed; no 1,4-adduct could be detected, in agreement with a previous study by Marinetti and Mathey.[3a]

We next extended the scope of our study to the addition of **2** to **3B**, **3D** and **3E**. Key data are listed in Table 1. Only in the case of **3B**, 1,4-addition (66.5%) outweighs the otherwise

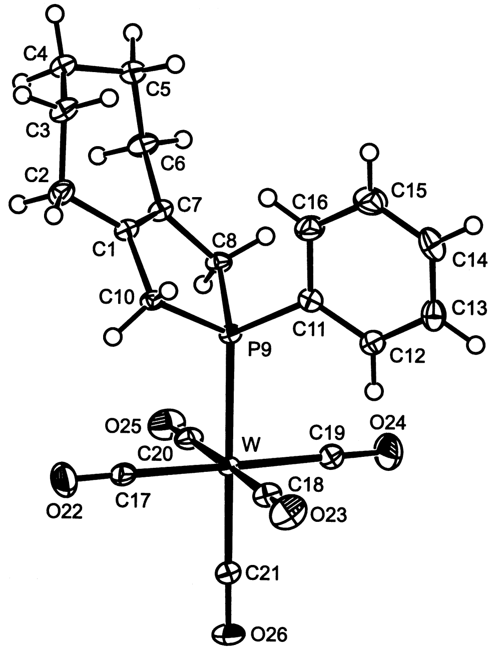


Figure 1. X-Ray crystal structure of **15**. Displacement ellipsoid plot of (**15**). Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): P(9)–W 2.5241(7), P(9)–C(8) 1.849(3), P(9)–C(10) 1.845(3), P(9)–C(11) 1.834(3), C(1)–C(2) 1.512(4), C(1)–C(7) 1.339(4),C(1)–C(10) 1.515(3), C(7)–C(6) 1.516(4), C(7)–C(8) 1.511(4), C(11)–P(9)–C(10) 102.83(12), C(11)–P(9)–C(8) 101.74(13), C(10)–P(9)–C(8) 93.46(12), C(11)–P(9)–W 118.49(9), C(10)–P(9)–W 117.38(9), C(8)–P(9)–W 118.85(8), C(7)–C(1)–C(2) 127.3(2), C(7)–C(1)–C(10) 116.3(2), C(2)–C(1)–C(10) 116.2(2), C(1)–C(2)–C(3) 117.7(2), C(1)–C(7)–C(8) 116.8(2), C(1)–C(7)–C(6) 126.8(2), C(8)–C(7)–C(6) 116.2(2), C(7)–C(8)–P(9) 106.33(16), C(1)–C(10)–P(9) 106.62(16).

predominant 1,2-addition. Contrary to the carbene additions, **3D** gives a higher yield of 1,4-addition (**17**: 25.6%) than **3C** (**15**: entry 5, 18.8%). Reaction of **2** with **3E**, which is assumed to adopt a *trans*-conformation,[11] results in 1,2-addition only. At this stage we may conclude that the *cisoid* conformation of the diene is indeed a prerequisite for the occurrence of 1,4-addition. In the case of **3C**, we have evaluated the dependence of the product ratio on the temperature (entries 3–8). It is obvious that this ratio is almost temperature independent.

Isolation and characterisation of the reaction products; X-ray crystal structure determination of 15 and 17

We have not succeeded in separating the 1,2- and 1,4-adducts. Therefore, the 1,2-adducts have only been identified on the basis of their ^{31}P NMR spectra and by means of HRMS. Prolonged heating of the reaction mixture at 90°C resulted in complete conversion of the 1,2-adducts to the 1,4-adduct; the latter was fully characterised. In the case of **15** and **17**, crystals were obtained, suitable for crystal structure determinations. They confirmed the identity of both compounds; the structures and essential data are presented in Figs. 1 and 2, respectively.

Kinetics of the thermolysis of 1 in the presence of 3C

According to a study by Mathey et al., the decomposition of **1** in the absence of CuCl follows clean first-order kinetics; the rate of decomposition was found to be independent on the nature and the concentration of the substrate.[12] We were able to reproduce these results using **3A** as a trapping reagent. However, several unexpected difficulties were encountered during our initial attempts to measure the rate of the CuCl catalysed decomposition of **1** in the presence of a large excess of **3C** at 50°C. The decomposition of **1** appeared to be accelerated with increasing diene concentration (0 equiv.: $k=1.1\times10^{-4}\ \text{s}^{-1}$; 1.5 equiv.: $k=1.5\times10^{-4}\ \text{s}^{-1}$; 10 equiv.: $k=6.0\times10^{-4}\ \text{s}^{-1}$), i.e. much less than would be expected if the reaction is first-order in the diene concentration; moreover, the reaction followed strict first-order kinetics at all diene concentrations. This suggests that the rate increase with increasing diene concentration must be attributed to a secondary effect, e.g. a solvent effect, rather than to participation of the diene in the rate-determining decomposition of **1**.

One may speculate that the diene increases the solubility of CuCl by complexation, thereby increasing the effective catalyst concentration and hence promoting the decomposition of **1**.

The temperature dependence for the decomposition of **1** in the presence of **3C** was investigated over a temperature range of 45–70°C. At constant diene concentration (3.0 equiv.), an Eyring plot was obtained (Fig. 3), from which the activation parameters $\Delta H^{\ddagger}=60.0\ \text{kJ mol}^{-1}$ and $\Delta S^{\ddagger}=-131\ \text{J K}^{-1}\text{mol}^{-1}$ were deduced. Contrary to what

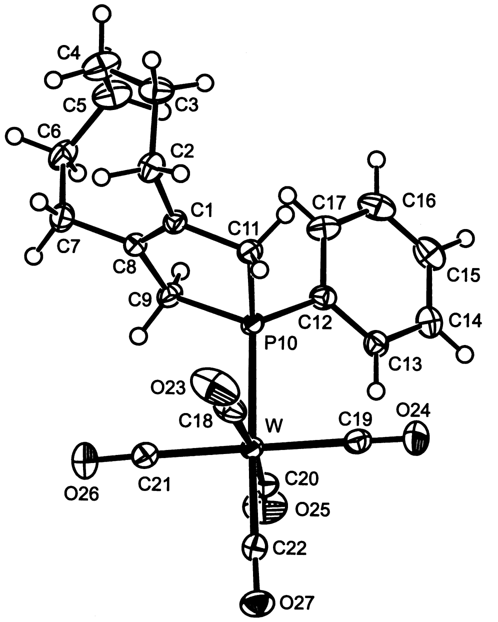


Figure 2. X-Ray crystal structure of **17**. Displacement ellipsoid plot of (**17**). Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): P(10)–W 2.5210(6), P(10)–C(9) 1.850(2), P(10)–C(11) 1.851(2), P(10)–C(12) 1.831(3), C(1)–C(8) 1.333(3), C(1)–C(2) 1.512(3), C(1)–C(11) 1.516(3), C(8)–C(7) 1.500(3), C(8)–C(9) 1.512(3), C(12)–P(10)–(9) 104.08(11), C(12)–P(10)–C(11) 103.84(11), C(9)–P(10)–C(11) 94.06(10), C(12)–P(10)–W 119.29(7), C(9)–P(10)–W 115.51(8), C(11)–P(10)–W 116.43(8), C(8)–C(1)–C(2) 124.8(2), C(8)–C(1)–C(11) 116.7(2), C(2)–C(1)–C(11) 118.49(19), C(1)–C(2)–C(3) 114.9(2), C(1)–C(8)–C(7) 124.0(2), C(1)–C(8)–C(9) 117.26(19), C(7)–C(8)–C(9) 118.39(19), C(8)–C(9)–P(10) 104.33(14), C(1)–C(11)–P(10) 104.59(14).

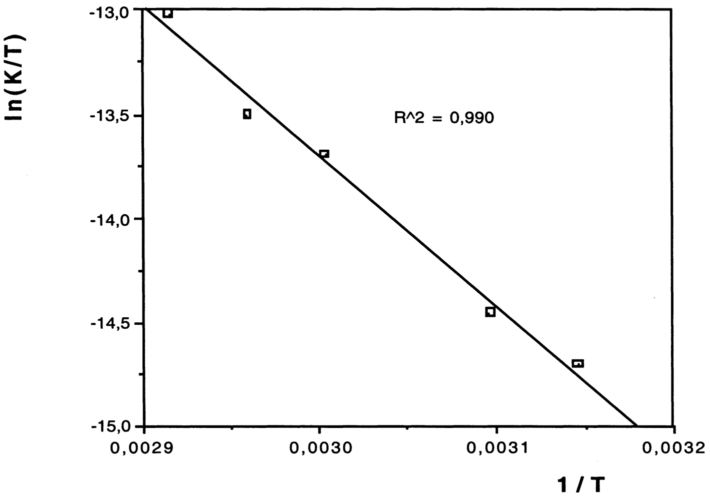


Figure 3. Eyring plot for the CuCl catalysed decomposition of **1** in the presence of **3C**.

one would expect for a concerted cheletropic elimination reaction of **1**, the activation entropy has a strongly negative value. At this moment we are unable to provide a satisfactory explanation; it may indicate the formation, in a low steady state concentration, of a complex between Cu(I) and **1**, followed by its decomposition in the rate determining step. From the Arrhenius equation, an activation energy (ΔE) of 62.6 kJ mol^{-1} is derived, which is considerably lower than that for the uncatalysed decomposition of **1**, i.e. 138 kJ mol^{-1}.[12]

Competition experiments

Competition experiments were carried out by performing the thermolysis of **1** with CuCl at 50°C in the presence of a 7–10 fold excess of a 1:1 mixture of two dienes; in all cases the ratio of 1,2-adducts and 1,4-adducts was the same as that obtained with **3B**, **3C** and **3D** separately (Table 1). It appears that **2** has only a slight preference for addition to **3C** over addition to **3D** (Σ(**14**+**15**)=53%; Σ(**16**+**17**)=47%, respectively). However, when **2** was reacted with a mixture of **3B** and **3C**, only the latter gave adducts; the accuracy of the NMR measurements would have allowed the detection of 1% of **12**.

Discussion

Before discussing the results of the additions of phosphinidene complexes, it is useful to consider the corresponding carbene reactions. Firstly, it has been established that the amount of 1,4-adduct does not strongly depend on the mode of carbene generation, which implies that free carbenes are involved.[13] Secondly, deuteration experiments have shown that the 1,4-addition of dibromocarbene to **3C** proceeds in a concerted disrotatory fashion with a stereoselectivity of at least 70%.[14] One may safely assume that the same applies to the terminal phosphinidene complexes in general and for **2** in particular. Extensive evidence has been gathered during the past decade which strongly suggests that phosphinidene complexes, generated thermally from a phosphanorbornadiene precursor, are truly free phosphinidene complexes with a singlet ground state.[3] Therefore, we may exclude a stepwise 1,4-addition via a triplet state of **2**.

The close resemblance between **2** and singlet electrophilic carbenes is corroborated by their similar behaviour towards exocyclic dienes. In the case of **3C** (entries 3–8), the molar fraction of the 1,4-adduct **15** (18±2%) is practically identical to that of the dibromocarbene adduct **9** (19%),[9b] whereas for **3B** (entry 2), 1,4-addition prevails over 1,2-addition by a factor of 2 for obvious steric reasons. The amount of the 1,4-adduct **13** (66.5%) is significantly higher than in the corresponding addition of dibromocarbene (30%)[9a] making this the highest yielding 1,4-addition reported thus far for an electrophilic species. The higher preference for 1,4-addition of **2** as compared to dibromocarbene may be explained by the difference in size of the two electrophilic species.

Table 1 reveals that 1,4-additions do not occur in those cases where the *trans*-conformation of the diene is favoured (entries 1 and 10). It appears that the *cisoid* conformation is a prerequisite for 1,4-addition, but coplanarity is not required and may in fact even be detrimental as can be illustrated by the following example. According to MNDO calculations, the torsion angle in exocyclic dienes increases with increasing ring size (**3B**: 0°, **3C**: 79°).[15] However, addition of dibromocarbene to 1,2-bismethylenecyclopentane affords only 2% of the 1,4-adduct, while the highest yield of 1,4-addition product (19%) is observed for **3C**. For **2** the highest yield of 1,4-product is observed for **3D**, not considering **3B** because in this case the 1,2-addition is hampered by the steric bulk of the methyl groups. The data in Table 1 give rise to three related issues. First, why is coplanarity not essential? Secondly, why is 1,4-addition of **2** to **3D** slightly more favourable than that to **3C**? Thirdly, why do carbenes and phosphinidene complexes behave differently?

To address these issues we start with a theoretical evaluation. As noted, a considerable barrier of 96 kJ mol^{-1} (MNDO) has been reported for the 1,4-addition of methylene to *cis*-butadiene under C_s-symmetry constraints.[5] However, at more sophisticated levels of theory

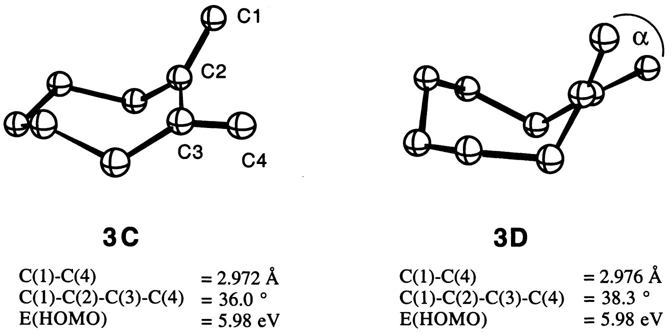


Figure 4. Lowest energy conformers of **3C** and **3D** at the B3LYP/6-31G* level of theory.

(RMP2/6-31G*), but without considering the effects of solvation, this barrier virtually disappears (2.5 kJ mol^{-1})[16] in agreement with preliminary DF calculations.[17] Several pieces of evidence suggest that a small but distinct activation enthalpy is associated with the 1,4-addition (vide infra). Interestingly, MNDO calculations suggest that the barrier for 1,4-addition is in part caused by the required distortion of the diene:[6] in order to facilitate the σ-approach of the carbene, the dihedral angle of the diene has to increase considerably. This requirement is of course already partially fulfilled when the diene unit is non-coplanar as in **3C** and **3D**, which is reflected in the lower activation energies.

Next, we must take a closer look at the factors which control the addition. Both structural and electronic factors are expected to play a role. Both the dihedral angle α (Fig. 4) and the distance between the termini of the diene unit (C1–C4) may be crucial. The electronic factor will be largely governed by the interaction between the HOMO of the diene and the LUMO of the electrophile. A detailed knowledge of the geometry and the electronic structure of the dienes **3C** and **3D** is clearly essential. Because of the limited accuracy of the MNDO calculations[15] we performed ab initio calculations at the B3LYP/6-31G* level of theory.[18]

The deviations between the optimised geometries and those previously reported are large. Although the MNDO calculations[15] appear to strongly overestimate both the dihedral angles (**3C**: 79°; **3D**: 82°) and the distance between the diene termini (**3C**: 3.25 Å; **3D**: 3.25 Å), this study confirms that these angles and distances are almost identical for **3C** and **3D**; the same applies for the HOMO energies (5.98 eV). The observed similarities are surprising in light of the different ring sizes.

Addressing the differences in product formation between **3C** and **3D**, it is evident that they cannot be explained by the nearly identical steric and electronic properties of the diene subunits; hence differences of the rings attached at the 2,3-positions must be decisive. When attempting to explain them one should keep in mind that the differences in yield are small; in terms of energy, they amount to less than 4 kJ mol^{-1}. Nevertheless, if one corrects the ratios of the 1,2-adducts and the 1,4-adducts from both dienes (Table 1) for the overall rates from the competition experiments (total product formation is 53:47, respectively), the differences are reduced even further, and the formation of 1,4-adduct (**15**) from **3C** turns out to be only about 20% slower than that of **17** from **3D**, while the relative rate of formation of the 1,2-adducts **14** and **16**, respectively, is *faster* by the same fraction; in other words, the variations in yield of 1,4-adducts are to a considerable extent determined by the different relative rates for the two dienes in the classical 1,2-addition.

With regard to the third question concerning the higher tendency towards 1,4-addition of **2** as compared to carbenes, we feel that here, too, size is the most important factor; the larger phosphorus is better able to bridge between the more distant 1- and 4-position of the diene. In this context, it should be mentioned that whereas **2** adds to **10** under formation of the 1,4-adduct **11** (vide supra), preliminary results show that dichlorocarbene adds to **10** exclusively by 1,2-addition.[17]

The entries for **3C** in Table 1 suggest that the 1,4-addition of **2** is temperature independent. This can be quantified by plotting the molar ratio of **14a** divided by **15** against the reciprocal temperature according to expression 1 which has been derived by combining the Eyring equations for the formation of **14a** and **15**.

$$\ln\left(\frac{\mathbf{14a}}{\mathbf{15}}\right) = \frac{(\Delta S^{\ddagger}_{\mathbf{14a}} - \Delta S^{\ddagger}_{\mathbf{15}})}{R} - \frac{(\Delta H^{\ddagger}_{\mathbf{14a}} - \Delta H^{\ddagger}_{\mathbf{15}})}{R}\left(\frac{1}{T}\right) \qquad (1)$$

A linear least-square fit to the data provided the following values: $\Delta\Delta H^{\ddagger}(\mathbf{14a}-\mathbf{15})=0.25\pm0.95$ kJ mol^{-1}, $\Delta\Delta S^{\ddagger}(\mathbf{14a}-\mathbf{15})=8.3\pm3.0$ J K^{-1}mol^{-1}. The low value of $\Delta\Delta H^{\ddagger}$ is in good agreement with preliminary high-level calculations[17] from which it was concluded that no barrier exists for the 1,2-addition. For the 1,4-addition, a small barrier (±1 kJ mol^{-1}) has been calculated. Thus, the observed preference for the 1,2-addition of **2** is essentially entropy controlled; a similar conclusion has been reached for the analogous carbene additions.[9b] These findings also explain why 1,4-addition is normally not observed. Entropically, formation of a five-membered ring is much less favourable than that of a three-membered ring. When, however, the diene is conformationally locked in a *cisoid* conformation, the degree of freedom has already been limited. Hence, the loss of entropy in formation of the five-membered ring will be smaller, which manifests itself in a less negative activation entropy.

From the remarkable selectivity displayed by **2** in the reaction with a mixture of **3B** and **3C**, we are again led to conclude that the rate determining step (formation of **2**) is succeeded by a second step in which **2** is able to distinguish between **3B** and **3C**. The observed selectivity (>99%) implies that in the case of **3B**, the barrier associated with this second step is at least 12.3 kJ mol^{-1} higher than for **3C** assuming that the entropies of activation of **3B** and **3C** are equal. The existence of a second, product determining step is also indicated by the findings of Lammertsma et al. who derived a Hammett reaction constant of −0.76 for the addition of **2** to substituted styrenes.[4a]

Conclusions

It has been established that terminal phosphinidene complexes such as **2** can add in a 1,4-fashion to 1,3-dienes. An enforced *cisoid* conformation appears to be an essential because it reduces the loss of entropy associated with the formation of a five-membered ring. Coplanarity of the diene system appears to be unimportant and may even be detrimental. Several observations suggest that a small activation energy exists for both the 1,2- and the 1,4-addition. It is argued that the non-coplanarity of the diene reduces the enthalpy barrier for the 1,4-addition. Thus, the normally unfavourable 1,4-addition becomes more feasible for both entropic and enthalpic reasons.

Experimental

General

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker MSL 400 spectrometer at 400.13, 100.32 and 162.0 MHz, respectively. ^{1}H NMR spectra were referenced to CHCl$_3$ (δ(7.27 ppm), ^{13}C NMR spectra to CDCl$_3$ (δ 77.0 ppm) and ^{31}P NMR spectra to external H$_3$PO$_4$. High resolution mass spectrometry (HRMS) was performed on a Finnigan MAT-90 mass spectrometer operating at an ionization potential of 70 eV. Melting points were measured on samples in unsealed capillary tubes and are uncorrected. Microanalyses were performed by Microanalytisches Labor Pascher. Xylene (mixture of isomers) was purchased from Aldrich, distilled from sodium and stored on sodium under nitrogen. CuCl (99.99% purity) was purchased from Acros and stored under nitrogen use. Preparative thick layer chromatography was carried out on alumina plates. Compound **1** was prepared according to a procedure by Mathey et al.[2] Dienes **3C** and **3D** were prepared by a procedure as previously described.[19] Diene **3B** was prepared according to a procedure by Mayr and Heigl.[20]

Synthesis and isolation of 1,4-adducts

[9-Phenyl-9-phosphabicyclo[5.3.0]dec-1(7)-ene]pentacarbonyltungsten (15). A solution of **1** (197 mg, 0.30 mmol) and **3C** (43.9 mg, 0.36 mmol) in xylene (2.5 mL) was purged with nitrogen (5 min), CuCl (10 mg) was added and the mixture was heated under nitrogen for 3 h at 60°C. At this stage ^{31}P NMR revealed the presence of a mixture of **14a**,**b** and **15**. Subsequently, the reaction mixture was heated for 18 h at 90°C. Aliquots were taken in order to monitor the progress of the rearrangement by ^{31}P NMR spectroscopy. The mixture was allowed to cool down and the solvent was removed in vacuo. The residue was subjected to preparative thick-layer chromatography (Al$_2$O$_3$/pentane) to give **15** as a white solid which was recrystallised from pentane. Yield: 148 mg (89%, 0.267 mmol). R_f (Al$_2$O$_3$/pentane)=0.62; m.p. 129°C; ^{31}P NMR (162.0 MHz, CDCl$_3$, 298 K): δ 2.8 (^{1}J(P,W)=227 Hz); ^{1}H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 7.57–7.36 (m, 5H), 3.30–3.10 (m, 4H), 2.24–2.14 (m, 4H), 1.79–1.47 (m, 6H); ^{13}C NMR (100.64 MHz, CDCl$_3$, 298 K): δ 199.8 (d, ^{2}J(C,P)=20.6 Hz, *trans* CO), 196.9 (dt, ^{1}J(C,W)=62.6 Hz, ^{2}J(C,P)=7.2 Hz, *cis* CO); 137.8 (d, ^{1}J(C,P)=34.6 Hz, *i*-Ar); 136.7 (s, C1, C7), 129.7 (d, ^{4}J(C,P)=1.8 Hz, *p*-Ar); 129.4 (d, ^{2}J(C,P)=10.6 Hz, *o*-Ar); 128.2 (d, ^{3}J(C,P)=9.7 Hz, *m*-Ar); 45.9 (d, ^{1}J(C,P)=27.5 Hz, C8, C10), 31.4 (d, ^{3}J(C,P)=7.0 Hz, C2, C6), 30.7 (s, C4), 26.2 (s, C3, C5); HRMS: Calcd for C$_{20}$H$_{19}$O$_5$PW 554.0480, Found 554.0481±0.0005; Anal. Calcd for C$_{20}$H$_{19}$O$_5$PW: C, 43.35; H, 3.46; P, 5.59. Found: C, 44.09; H, 3.56; P, 5.36.

[10-Phenyl-10-phosphabicyclo[6.3.1]undec-1(8)-ene]-pentacarbonyltungsten (17). Prepared from **1** and **3D** as described for **15**. Yield: 120 mg (72%, 0.216 mmol). R_f (Al$_2$O$_3$/pentane)=0.75; m.p. 72°C; ^{31}P NMR (162.0 MHz, CDCl$_3$, 298 K): δ 0.8 (^{1}J(P,W)=227 Hz); ^{1}H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 7.57–7.37 (m, 5H), 3.28–3.09 (m, 4H), 2.27–2.21 (m, 4H), 1.54–1.30 (m, 8H); ^{13}C NMR (100.64 MHz, CDCl$_3$, 298 K): δ 199.8 (d, ^{2}J(C,P)=20.5 Hz, *trans* CO), 196.7 (d, ^{2}J(C,P)=7.1 Hz, *cis* CO); 137.7 (d, ^{1}J(C,P)=34.7 Hz, *i*-Ar); 134.8 (s, C1, C8), 129.6 (d, ^{4}J(C,P)=2.0 Hz, *p*-Ar); 129.0 (d, ^{2}J(C,P)=10.5 Hz, *o*-Ar); 128.5 (d, ^{3}J(C,P)=9.1 Hz, *m*-Ar); 43.0 (d, ^{1}J(C,P)=27.3 Hz, C9, C11), 28.7 (d, ^{3}J(C,P)=6.9 Hz, C2, C7), 28.2 (s, C4, C5), 25.8 (s, C3, C6); HRMS: Calcd for C$_{21}$H$_{21}$O$_5$PW 568.0637, Found 568.0632±0.0005; Anal. Calcd for C$_{21}$H$_{21}$O$_5$PW: C, 44.39; H, 3.73; P, 5.45. Found: C, 44.32; H, 3.76; P, 4.92.

[3-Phenyl-3-phospha-6,6,7,7,8,8-hexamethylbicyclo-[3.3.0]oct-1(5)ene]pentacarbonyltungsten (13). Prepared from **1** and **3B** by the same procedure as used for **3C**. **13** was obtained as a pale yellow oil. Yield: 70% (79 mg, 0.140 mmol); R_f (Al$_2$O$_3$/pentane)=0.65; ^{31}P NMR (162.0 MHz, CDCl$_3$, 298 K): δ 24.0 (^{1}J(P,W)=229 Hz); ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.55–7.40 (m, 5H), 2.98 (m, 4H), 1.02 (s, 6H), 0.89 (s, 6H), 0.88 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100.64 MHz, CDCl$_3$, 298 K): δ 199.8 (d, ^{2}J(C,P)=20.7 Hz, *trans* CO), 196.8 (d, ^{2}J(C,P)=7.1 Hz, *cis* CO), 145.3 (s, C1, C5), 138.2 (d, ^{1}J(C,P)=33.8 Hz, *i*-Ar), 129.6 (d, ^{4}J(C,P)=2.1 Hz, *p*-Ar), 129.2 (d, ^{2}J(C,P)=10.5 Hz, *o*-Ar), 128.6 (d, ^{3}J(C,P)=9.1 Hz, *m*-Ar), 50.8 (s, C7), 46.7 (d, ^{3}J(C,P)=4.7 Hz, C6, C8), 34.3 (d, ^{1}J(C,P)=26.9 Hz, C2, C4), 23.8 (s, 2C), 23.5 (s, 2C), 21.9 (s), 21.6 (s); HRMS: Calcd for C$_{24}$H$_{27}$O$_5$PW 610.1106, Found 610.1105±0.0005; Anal. Calcd for C$_{24}$H$_{27}$O$_5$PW: C, 47.23; H, 4.46; P, 5.08. Found: C, 47.15; H, 4.40; P, 5.40.

Characterisation of 1,2-adducts

The 1,2-adducts were obtained as an inseparable mixture with the corresponding 1,4-adduct. Their identity has been confirmed by ^{31}P NMR spectroscopy and in the case of **18**, where the isomeric 1,4-adduct was not obtained, by HRMS.

[4-Methylene-5,5,6,6,7,7-hexamethyl-2-phenyl-2-phosphaspiro[2.4]heptane]pentacarbonyltungsten (12)

^{31}P NMR (162.0 MHz, xylene, 298 K): δ −134.8 (^1J(P,W)=250 Hz).

[4-Methylene-2-phenyl-2-phosphaspiro[2.6]nonane]pentacarbonyltungsten (14). (**14a**) (major isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −136.1 (^1J(P,W)=250 Hz). (**14b**) (minor isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −132.3 (^1J(P,W)=260 Hz).

[4-Methylene-2-phenyl-2-phosphaspiro[2.7]decane]pentacarbonyltungsten (16). (**16a**) (major isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −134.0 (^1J(P,W)=250 Hz). (**16b**) (minor isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −127.3 (^1J(P,W)=260 Hz).

[4-Methylene-2-phenyl-2-phosphaspiro[2.11]tetradecane]pentacarbonyltungsten (18). (**18a**) (major isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −134.4 (^1J(P,W)=256 Hz). (**18b**) (minor isomer): ^{31}P NMR (162.0 MHz, xylene, 298 K): δ −140.1 (^1J(P,W)=251 Hz); HRMS: Calcd for $C_{23}H_{25}O_5PW$ 596.0949, Found 596.0938±0.0008.

Kinetic measurements

A representative procedure is as follows. A solution of **1** (39.49 mg, 0.060 mmol), **3C** (14.64 mg, 0.012 mmol) and a pinch of CuCl in xylene was prepared in a 5 mm NMR tube. The NMR tube was flushed with nitrogen and tightly capped. After wrapping the cap with teflon tape, the tube was introduced into the preheated (45–70°C) NMR probe. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. Spectra were acquired at 20–60 min intervals depending on the temperature at which the reaction was performed. Normally 10–30 data points were collected. ^{31}P NMR spectra of **1**, **14a**, **14b** and **15** were recorded separately in unlocked mode with a SW of 4000 Hz and decoupling only during acquisition. Multipulse decoupling with WALTZ-16 has been applied in order to suppress heating effects during acquisition. In each case 32 transients were acquired over 5 min (pulse repetition time 9.5 s, acquisition time 2.05 s, relaxation delay 7.5 s). After careful phasing, signal intensities were accurately integrated for (relative) product composition. The temperature of the NMR probe was calibrated using the standard ethylene glycol method of Geet[21] before acquisition. Temperatures were shown to vary by no more than 0.1°C during the course of each experiment, within an overall accuracy of ca. 1°C. First-order rate constants were obtained from the slope of a plot of the natural logarithm of the integral versus time. The observed rate constants were reproducible within 10%. Errors for each rate determination were obtained from standard unweighted linear least-square analysis and correspond to one standard deviation. The rearrangement of **14a**,**b** was studied from 45 to 70°C. A plot of the natural logarithm of the rate constant divided by the temperature versus the reciprocal temperature showed good linearity. Linear regression analysis was used to extract the activation parameters from the Eyring plot. Quoted errors correspond to one standard deviation.

Competition experiments

Competition experiments were performed as described for the kinetic experiments; a 1:1 mixture of two dienes both in large excess (7–10 equiv.) was used.

Crystal structure determinations

Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo-K$_\alpha$, λ=0.71073 Å) at a temperature of 150 K. The structures were solved with the program DIRDIF97[22] and refined with the program SHELXL97[23] against F^2 of all reflections up to a resolution of $(\sin\vartheta/\lambda)_{max}$=0.65 Å^{-1}. Non hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The drawings, absorption correction, and checking for higher symmetry were performed with the program PLATON.[24]

Structure of (15)

$C_{20}H_{19}O_5PW$, M_r=554.17 g mol^{-1}, colourless block, 0.31×0.31×0.25 mm^3, triclinic, $P\bar{1}$, a=9.8765(1) Å, b=11.0811(2) Å, c=11.1535(2) Å, α=68.9599(6)°, β=64.0347(8)°, γ=67.3639(8)°, V=985.86(3) Å^3, Z=2, ρ=1.867 g cm^{-3}, 15213 measured reflections, 4502 unique reflections (R_{int}=0.0604), R ($I>2\sigma(I)$): $R1$=0.0214, $wR2$=0.0546. R (all data): $R1$=0.0216, $wR2$=0.0547. S=1.124, absorption correction (MULABS, μ=5.967 mm^{-1}, 0.16–0.25 transmission).

Structure of (17)

$C_{21}H_{21}O_5PW$, M_r=568.20 g mol^{-1}, colourless block, 0.41×0.25×0.25 mm^3, triclinic, $P\bar{1}$, a=10.0413(1) Å, b=10.9070(1) Å, c=11.3312(2) Å, α=71.2557(7)°, β=69.9508(6)°, γ=67.2992(8)°, V=1049.58(2) Å^3, Z=2, ρ=1.798 g cm^{-3}, 20563 measured reflections, 4802 unique reflections (R_{int}=0.0519), R ($I>2\sigma(I)$): $R1$=0.0165, $wR2$=0.0435. R (all data): $R1$=0.0169, $wR2$=0.0437. S=1.153, absorption correction (DELABS, μ=5.607 mm^{-1}, 0.29–0.73 transmission).

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