Polymerization of ADMR and ADBZR. High-vacuum technique was used for polymerization.[17] Monomer (0.2 g) was polymerized by cationic catalyst in 1 mL of methylene chloride. Syrupy monomer ADMR was transfered into the polymerization ampule by distillation under vacuum just before polymerization. After termination by the addition of methanol, polymers were purified by reprecipitations using chloroform-petroleum benzin several times and subsequent freeze-drying from benzene. Polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose was carried out by antimony pentachloride catalyst according to the previous paper.[8]

Debenzylation. To 60 mL of liquid ammonia containing 0.4 g of sodium, a solution of 0.5 g of 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan with $[\alpha]_D$ +148.4° in 20 mL of dimethoxyethane was added dropwise at −78 °C under nitrogen. After the mixture was stirred for 2 h, anhydrous ammonium chloride and a small amount of water were added. The aqueous solution was washed with methylene chloride and dialyzed with running water. The solution was concentrated and finally freeze-dried from water. The (1→5)-α-D-ribofuranan showed $[\alpha]^{25}_D$ +164.1° in water (yield about 50%). Debenzylidenation of 2,3-*O*-benzylidene-β-D-ribopyranan (0.39 g) was performed using the same method (yield 0.11 g (45%)).

Methylation of Free Polysaccharides. To a 3 mL of dimethyl sulfoxide solution containing (1→4)-β-D-ribopyranan (30 mg) was added a 3-mL portion of carbanion solution, which was prepared by reacting 5.7 g of sodium hydride with 50 mL of dimethyl sulfoxide for 3 h, followed by the addition of 3 mL of methyl iodide. After it had reacted overnight, the reaction mixture was worked up (yield 23.6 mg (65%)). When (1→5)-α-D-ribofuranan was methylated using the same procedure, the yield was over 100%, because it contained impurities that were distinguishable from the product by the NMR spectroscopy.

Measurements. 400-MHz ^{1}H and 100-MHz ^{13}C NMR spectra were measured on the solutions in $CDCl_3$ and CD_2Cl_2, respectively, by means of a JEOL GX-400 spectrometer. 25-MHz ^{13}C spectrum of a free polysaccharide was measured by means of a JEOL PS-100 spectrometer. The peak assignments of ^{1}H and ^{13}C spectra were performed by the decoupling method and the heterospin decoupling method, respectively. Specific rotations were measured by means of a Perkin-Elmer 241 polarimeter.

Acknowledgment. We thank Dr. K. Hatanaka and T. Kawamura of our department for their performances of NMR measurements.

Proton [1,5] Shifts in P-Unsubstituted 1*H*-Phospholes. Synthesis and Chemistry of 2*H*-Phosphole Dimers

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Abstract: The protonation of four representative phospholyl anions has been studied at low temperature. In each case, the primary protonation product is the P-unsubstituted 1*H*-phosphole. Among the products described is the parent phosphole C_4H_4PH. Between −70 °C and room temperature according to the substitution pattern, the 1*H*-phospholes rearrange through proton [1,5] shifts to give 2*H*-phospholes, which instantly dimerize. Such an evolution can be frozen out by P-complexation with $W(CO)_5$ in the case of 1,2,3,4-tetraphenyl-1*H*-phosphole. The 2*H*-phosphole dimers are generally [4 + 2] Diels-Alder endo dimers in which one 2*H*-phosphole unit acts as a diene and the other as a dienophile through its P=C double bond. In the case of 1,2,3,4-tetraphenyl-2*H*-phosphole, the dimerization takes another path, however. The P—H bond of the 1*H*-phosphole adds onto the P=C double bond of the 2*H*-phosphole to give a 1-phospholylphospholene, this type of dimerization being probably less sensitive to steric hindrance than the normal [4 + 2] dimerization. Around 100 °C, the [4 + 2] endo dimers give the more stable [4 + 2] exo dimers. At higher temperature, 1,1′-biphospholyls are obtained through loss of hydrogen. UV irradiation of the [4 + 2] endo dimers, on the other hand, gives pentacyclic cage compounds. Mixed [4 + 2] dimers are also described together with some reactions in which the 2*H*-phospholes act as dienes (with acetylenes) and as dienophiles (with conjugated dienes). A tentative theoretical explanation of the observed proton [1,5] shifts is presented; it relies on a σ(P–H)/π hyperconjugative interaction, which has been proposed previously by Schweig as one of the major stabilizing mechanisms within the phosphole nucleus.

The synthesis and properties of phosphaalkenes are currently under active investigation in many laboratories working on organophosphorus chemistry.[1] The stability of phosphaalkenes is generally achieved through steric crowding or cyclic delocalization. In both cases, the reactivity of the P=C double bond is significantly reduced. For instance, Diels-Alder reactions in which P=C double bonds act as dienophiles remain scarce in the literature.[2] We have recently shown that 2*H*-phosphole [4 + 2] dimers can be easily obtained by protonation of phospholyl anions.[3,4] These dimers can yield monomeric 2*H*-phospholes by heating at moderate temperatures (~100 °C). The 2*H*-phospholes thus obtained are stabilized neither by steric crowding nor by cyclic delocalization. They appear to be very reactive both as dienes and dienophiles. Therefore, we decided to perform a thorough study of these species. The results of this study are described hereafter.

Results and Discussion

Protonation of Phospholyl Anions at Low Temperature. Synthesis of P-Unsubstituted 1*H*-Phospholes. Theoretical investigations[5-7] on the phospholyl anion have established that it is fully aromatic as the isoelectronic thiophene. As a consequence, the initial protonation site could be either phosphorus or α- or β-carbons. Thus, we decided to perform a ^{31}P NMR study of this protonation at very low temperature in order to observe the

(1) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731-744.

(2) As far as we know, the reaction of hexachlorocyclopentadiene with 1,2,3-diazaphospholes is the only Diels-Alder reaction so far described in the literature that involves a P=C double bond as the dienophile if we except similar reactions with 2*H*-phospholes: Arbuzov, B. A.; Dianova, E. N., international Conference on Phosphorus Chemistry, Halle, 1979, abstracts of papers, p 51. For such reactions with 2*H*-phospholes, see ref 3, 4, and 13.

(3) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 511-514.

(4) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1272-1273.

(5) Kaufmann, G.; Mathey, F. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 231-235.

(6) Guimon, C.; Pfister-Guillouzo, G.; Mathey, F. *Nouv. J. Chim.* **1979**, *3*, 725-729.

(7) Kostic, N. M.; Fenske, R. F. *Organometallics* **1983**, *2*, 1008.

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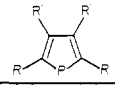
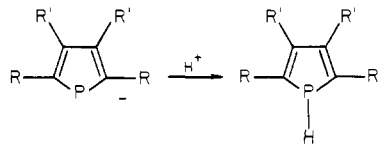
Table I. ^{31}P NMR Data on Phospholyl Anions, 1*H*-Phospholes, and 2*H*-Phosphole Dimers[a]

	phospholyl anions[b]	protonation conditions	1*H*-phospholes	dimers
R = R′ = H	**1**, δ_P +76.6	CF_3CO_2H, −100 °C	**5**, δ_P −49.2, $^1J_{PH}$ = 234	**9**, δ_P −35.5 and −49.1, $^1J_{PP}$ = 193
R = H, R′ = Me	**2**, δ_P +58.9	CF_3CO_2H, −100 °C	**6**, δ_P −59.4, $^1J_{PH}$ = 217	**10**, δ_P −24.1 and −63.1, $^1J_{PP}$ = 185
R = Ph, R′ = H	**3**, δ_P +78.7	CF_3CO_2H, −60 °C	**7**, δ_P −54.2, $^1J_{PH}$ = 232	**11**, δ_P +17.1 and −25.9, $^1J_{PP}$ = 200
R = R′ = Ph	**4**, δ_P +98.8	CH_3CO_2H, +30 °C	**8**, δ_P −40.9, $^1J_{PH}$ = 218	**12**, δ_P + 28.7 and −1.7, $^1J_{PP}$ = 370

[a] δ in ppm, J in Hz; δ + ve for downfield shifts, H_3PO_4 as external reference, THF solution for **1-8**, $CDCl_3$ solution for **9-12**.
[b] Counterion: Li^+ for **1-3**, K^+ for **4**. PhM also present in the solutions.

transient protonation products. The results are collected in Table I. In all the cases studied, the primary protonation products are the P-unsubstituted 1*H*-phospholes. (The parent phosphole

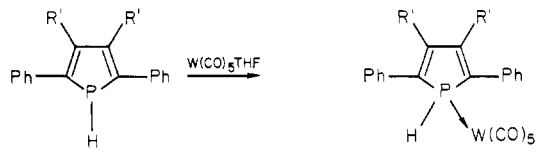


1, R = R′ = H — **5**
2, R = H; R′ = Me — **6**
3, R = Ph; R′ = H — **7**
4, R = R′ = Ph — **8**

C_4H_4PH is observed here for the first time.) The ^1J(P–H) coupling constants for classical secondary phosphines vary between 155 and 235 Hz.[8] Thus, it appears that the ^1J(P–H) coupling constants for 1*H*-phospholes fall in the upper part of that range. According to recent theoretical calculations,[9] it means probably that the s character of the P–H bond of **5–8** is low, suggesting a high s character for the lone pair and a weak cyclic delocalization within the ring.

While measuring the ^1J(P–H) coupling constant of **8** in THF, we discovered that it was notably temperature dependent. We obtained the following results: ^1J(P–H) = 224.4 ± 0.5 Hz (173 K); 218.2 ± 0.5 Hz (300 K); 216 ± 0.5 Hz (323 K). One of the referees suggested that this phenomenon was perhaps solvent dependent. Thus, additional measurements were made in toluene and showed no variation of ^{1}J(P–H) with the temperature in the range −75 to +25 °C (^1J(P–H) = 221 Hz). (2,2′,3,3′,4,4′,5,5′-Octaphenyl-1,1′-biphospholyl (**28**) was cleaved by sodium in boiling toluene. The reaction was very slow (complete in ca 3 days). The anion **4** was then protonated by a stoichiometric amount of CF_3CO_2H.) Our interpretation is as follows: due to the strong electronic stabilization of the corresponding anion **4**, the phosphole **8** shows some tendency to ionize according to **8** ⇄ **4** + H^+. This dissociation does not take place in toluene but appears in basic solvents such as THF. The corresponding equilibrium is displaced to the right when the temperature is raised. If we suppose that this reversible dissociation is fast on the NMR time scale, then we can explain the observed decrease of ^1J(P–H) when the temperature increases.

In order to more fully characterize these P–H phospholes, we attempted to stabilize the least unstable among them by P-complexation. In situ treatment of **7** and **8** by $W(CO)_5THF$ afforded the complexes **13** and **14**, respectively. A sizable stabilizing effect

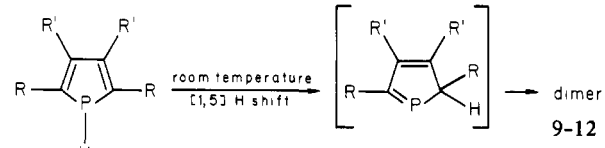


7, R′ = H
8, R′ = Ph

13, R′ = H; δ_P −39, ^1J(P–H) 342, ^1J(P–^{183}W) 215 (C_6D_6)
14, R′ = Ph; δ_P −22.7, ^1J(P–H) 338, ^1J(P–^{183}W) 217 (C_6D_6)

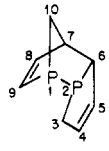
was observed but only complex **14** was sufficiently stable to allow its complete characterization. The ^1J(P–H) and ^1J(P–W) coupling constants recorded in both cases are close to those observed in the ^{31}P NMR spectrum of $(Ph_2PH)W(CO)_5$, i.e., 344.9 and 229.6 Hz, respectively,[10] suggesting no peculiarity for the phosphole ring.

1*H*- to 2*H*-Phosphole Conversion at Room Temperature and Dimerization. In a previous paper,[11] Braye described 1*H*-phospholes **7** and **8** as stable species that were isolable at room temperature. The characterization of **7** and **8** was minimal. In fact, all the 1*H*-phospholes **5–8** are unstable at room temperature and are converted more or less rapidly into 2*H*-phosphole dimers.

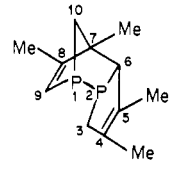


5-8 — **5a-8a** — **9-12**

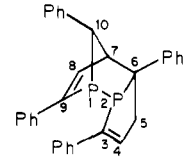
The ^{31}P NMR data of these dimers are given in Table I. Dimer **9** is extremely reactive, is not very stable, and has been characterized only by ^{31}P NMR spectroscopy. Therefore, its precise structure is not established with certainty. However, the ^{31}P NMR data suggest a formula similar to that of dimer **10**, which has been fully characterized by X-ray crystal-structure analysis.[4] Dimers **10** and **11** have been described in some detail previously,[3,4] and



9 (proposed formula with endo junction)



10 (endo junction)

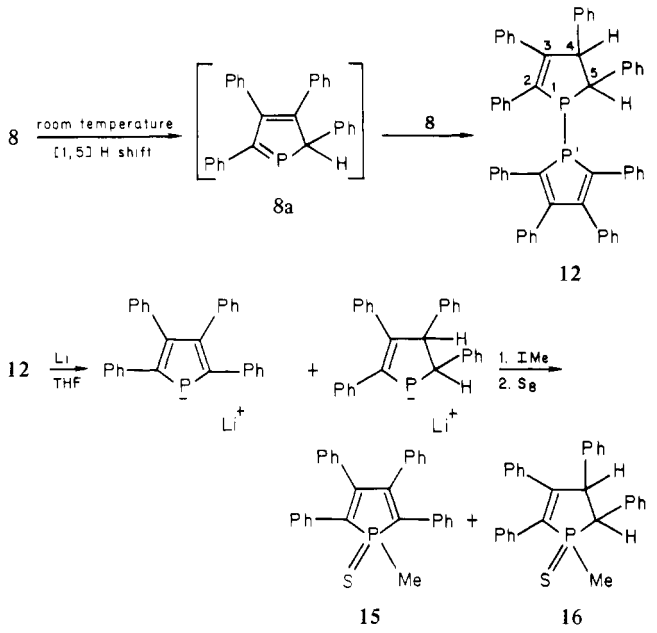


11 (endo junction, the stereochemistry at the bridge carbon is only postulated)

we give for them some additional spectroscopic data in the Experimental Section. The case of dimer **12** is entirely different. In our preliminary communication,[3] we proposed for **12** a formulation similar to those of **10** and **11** on the sole basis of ^{31}P NMR spectroscopy. However, the ^1J(P–P) coupling constant is abnormally large in **12** if its structure is similar to those of **10** and **11**. Therefore, we investigated more completely the structure of **12** by mass and ^1H and ^{13}C NMR spectroscopies. The only formula compatible with all the spectroscopic data incorporates P–P-linked phosphole and phospholene rings. In that respect, the

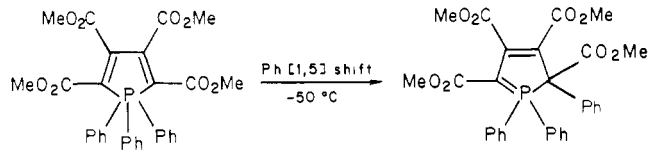
(8) Brazier, J. F.; Houalla, D.; Koenig, M.; Wolf, R. *Top. Phosphorus Chem.* **1976**, *8*, 99–192.
(9) Goetz, H.; Frenking, G.; Marschner, F. *Phosphorus Sulfur* **1978**, *4*, 309–310.
(10) Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638–2641.
(11) Braye, E. H.; Caplier, I.; Saussez, R. *Tetrahedron* **1971**, *27*, 5523–5537.

appearance of an AB system centered at 4.38 and 4.69 ppm (2 protons) with a coupling constant $^3J(H-H) = 9$ Hz in the $\{^{31}P\}^1H$ NMR spectrum of **12** is particularly significant. The formula of **12** was definitively established by cleavage of the P–P bond with lithium. After reaction with methyl iodide and sulfur, the phosphole sulfide **15** and the phospholene sulfide **16** were obtained in equimolecular amounts and completely characterized. In the

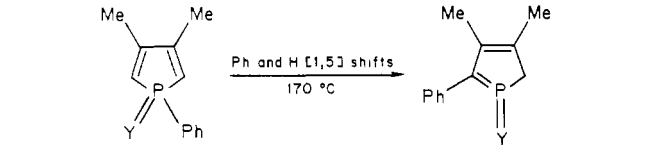


case of **8**, the conversion of the 1*H*-phosphole into the 2*H*-phosphole remains slow even at room temperature. Thus, during a rather long period of time, both the concentrations of **8** and **8a** are sufficiently high in the reaction medium so that they can react together. Instead of the classical [4 + 2] Diels–Alder dimerization observed with **5a–7a**, an addition of the P—H bond of **8** onto the P=C bond of **8a** takes place and yields **12**. Obviously, this type of dimerization is less sensitive to steric hindrance than the classical Diels–Alder dimerization.

General Comments on the [1,5] Shifts in the Phosphole Nucleus. The proton [1,5] shifts described here are, by no means, the first such phenomena encountered in phosphole chemistry. More than ten years ago, it was established that the pentacoordinate phosphole **17** isomerized even at −50 °C to give the corresponding 2*H*-phosphole **18** through a phenyl [1,5] shift:[12]



Some time ago, it was discovered in our laboratory[13] that the phenyl group could also migrate in tervalent phospholes such as **19** to give the 2*H*-phosphole **21** around 170 °C:



19, Y = lone pair
20, Y = S

21 (100%)
22 (30%)

A similar phenomenon was also noted with phosphole sulfide **20** but the migration appeared to be far more difficult in that case.

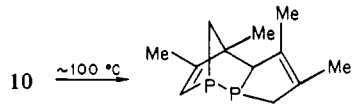
From all these data, we can draw a first conclusion: the coordination state of phosphorus has a drastic influence on the migratory aptitude of its substituents; this aptitude decreases in the order pentacoordinate P >> tricoordinate P > tetracoordinate P.

It is not very surprising to note that the nature of the migrating group also has an influence on the phenomenon. It was recently discovered that stable pentacoordinate 1*H*-phospholes could be prepared when alkoxy groups were bonded to phosphorus.[14-16] Thus, from these results and from our own results on P-phenyl and P-unsubstituted tervalent phospholes, we can draw a second conclusion: the migratory aptitude decreases in the following (and quite logical) order H >> Ph >> OR. The low migratory aptitude of the alkoxy group is very probably connected with the very high strength of the P–O bond.

For such widely studied fluxional molecules as cyclopentadienylsilanes, it is well established now that the driving force of the silyl migrations is a hyperconjugative interaction between the σ(C–Si) bond and the π-dienic system.[17] A similar hyperconjugative interaction $\sigma(P-R)/\pi$ has been proposed as one of the major stabilizing mechanism in pyramidal tervalent phospholes,[18] and we see no reason why it would not be still operative in pentavalent phospholes. A key parameter governing this hyperconjugation in phospholes is the P–R out-of-plane angle. When this angle is close to 90°, the $\sigma(P-R)/\pi$ overlap probably reaches its maximum[19] and the migration of R becomes very easy. On this basis, it is possible to rationalize the trends noted above. In a pentacoordinate phosphole, the ring probably occupies an apical–equatorial position in the classical trigonal-bipyramidal arrangement[16] in order to minimize its strain (intracyclic CPC angle is close to 90°[20]). However, through an easy pseudorotation, it can reach the diequatorial position. In that situation, the P–R(axial) out-of-plane angle is precisely 90°, and the migration of the axial substituent becomes extremely easy. In tervalent phospholes, typical P–R out-of-plane angles are close to 67°,[20] and thus, the migration of R is far more difficult. The classical opening of the CPC angles upon oxidation or sulfurization of a tervalent phosphorus compound probably leads to even smaller P–R out-of-plane angles in tetracoordinate phospholes with a concomitant decrease of the migratory aptitude of R. The overall trend is thus explained.

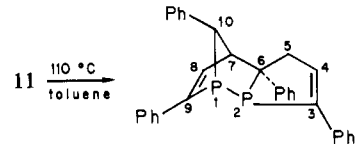
Thermal Evolution of 2*H*-Phosphole Dimers. In previous papers,[21,22] we have shown that 2*H*-phospholes, when generated at high temperature, gave interesting P–P bonded 1*H*-phosphole dimers and tetramers by loss of hydrogen. Therefore, it was tempting to study the thermal evolution of our 2*H*-phosphole dimers to see whether or not they would generate similar structures. When heating **10** to around 100 °C, we observed that it was converted into another dimer **23** (δ_P +17.8 and −56.4 ppm, $^1J(P-P) = 185$ Hz), which was not isolated in the pure state but whose structure was probably that of another [4 + 2] Diels–Alder dimer according to the analysis of its ^{13}C NMR spectrum. We were unable to assign an unambiguous formula to **23** but it seemed likely to have an exo junction. A similar transformation occurred

(12) Waite, N. E.; Allen, D. W.; Tebby, J. C. *Phosphorus Relat. Group V Elem.* **1971**, *1*, 139–143.
(13) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595–4597.
(14) Tebby, J. C.; Willetts, S. E.; Griffiths, D. V. *J. Chem. Soc., Chem. Commun.* **1981**, 420–421.
(15) Burgada, R.; Leroux, Y.; El Khoshnieh, Y. O. *Tetrahedron Lett.* **1981**, *22*, 3533–3536.
(16) Bkouche-Waksman, I.; L'Haridon, P.; Leroux, Y.; Burgada, R. *Acta Crystallogr., Sect. B*, **1982**, *B38*, 3024–3028.
(17) Cradock, S.; Findlay, R. H.; Palmer, M. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1650–1654.
(18) Schäfer, W.; Schweig, A.; Mathey, F. *J. Am. Chem. Soc.* **1976**, *98*, 407–414.
(19) For similar discussions on the relationship between conformation and hyperconjugation in vinyl- and allylphosphines, see: Schmidt, H.; Schweig, A.; Mathey, F.; Muller, G. *Tetrahedron* **1975**, *31*, 1287–1294.
(20) Coggon, P; Mc Phail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888–1891.
(21) Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077–2079.
(22) Charrier, C.; Bonnard, H.; Mathey, F. *J. Org. Chem.* **1982**, *47*, 2376–2379.



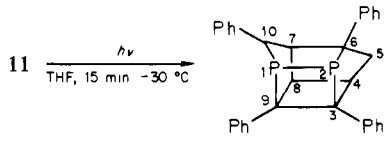
23 (exo junction, tentative formulation)

when heating **11** in boiling toluene for 2.5 h. In that case, we were able to isolate **24** in the pure state, and its exo structure was



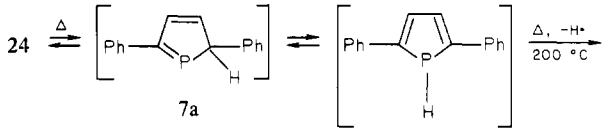
24

established unambiguously. The ^1H, ^{13}C and ^{31}P NMR spectra of **11** and **24** are, of course, very similar. However, two experimental evidences support the endo formulation for **11** and the exo formulation for **24**. When irradiated under UV, **11** gives the cage compound **25** through a [2 + 2] intramolecular cycloaddition of its two double bonds. Under strictly identical conditions, **24** does not react.

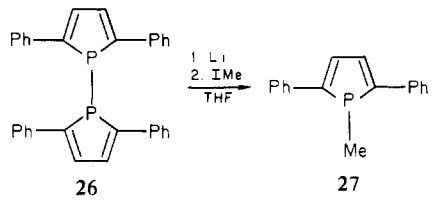


25

From all the experimental data gathered above, we can draw two conclusions: (a) Whereas the [2 + 2] dimerization of phosphaalkenes is a two-step dipolar process,[23] the [4 + 2] dimerization of 2*H*-phospholes is very probably a true concerted reaction under frontier-orbital control as the classical Diels–Alder reaction since it affords the least stable dimer with the same stereochemistry as the dimer of cyclopentadiene. (b) This thermal endo to exo conversion implies that, at around 100 °C, these [4 + 2] dimers are in equilibrium with the corresponding monomers. At still higher temperature, the exo dimer **24** in turn undergoes a new transformation: it loses hydrogen to give the 1,1′-biphospholyl **26**, which has been unambiguously characterized by comparison with an authentic sample[24] and through lithium cleavage and methylation. As discussed previously,[22] the



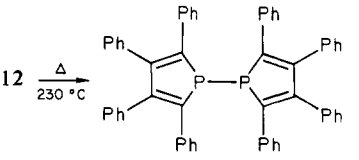
7a **7**



26 **27**

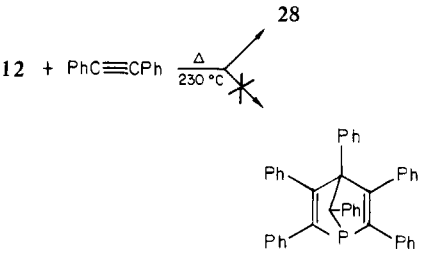
mechanism probably involves the transient 1*H*-phosphole **7**, which loses hydrogen through an homolytic cleavage of the P–H bond.

In contrast to dimers **10** and **11**, the "abnormal" dimer **12** is thermally very stable. However, when it is heated up to 230 °C, it loses hydrogen too and yields the 1,1′-biphospholyl **28**, which



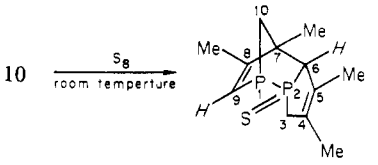
28

has been already mentioned in the literature but has not been characterized.[25] The mechanism of this dehydrogenation probably does not involve the transient 2*H*-phosphole **8a** since the same reaction performed in the presence tolan does not afford the expected 1-phosphanorbornadiene.



2*H*-Phosphole [4 + 2] Dimers as Sources of Monomers for Chemical Reactions. In the preceding paragraph, it has been unambiguously demonstrated that 2*H*-phosphole [4 + 2] dimers such as **10** and **11** (or **23** and **24**) are in equilibrium with the corresponding monomers **6a** and **7a** at around 100 °C. Thus, it is possible to study the chemistry of 2*H*-phospholes by using these [4 + 2] dimers as "in situ" generators. Some preliminary results on the Diels–Alder reactivity of **6a** have been described in our preliminary communication.[4] Hereafter, we give some additional data on the reactivity of **6a** and **7a**.

Before describing these new results, we want to comment briefly on the reaction of sulfur with the endo dimer **10**. At room temperature, a stoichiometric amount of sulfur reacts exclusively on the phosphorus at the junction demonstrating clearly that the nucleophilicity of the phosphorus at the bridgehead is markedly lower. The formula of **29** is easily established by comparing the



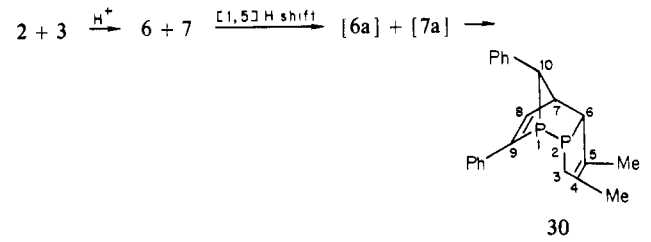
29

^{31}P and ^{13}C NMR spectra of **10** and **29**. Selective ^{31}P-decoupling experiments conducted on the ^1H NMR spectrum of **10** have shown that the phosphorus resonating at −63.1 ppm is coupled with the vinylic proton H_9 ($^2J(H_9–P_1)$ = 44 Hz) and the phosphorus resonating at −24.1 ppm with the proton at the junction H_6 ($^2J(H_6–P_2)$ = 28 Hz). Thus, the signals at −63.1 and −24.1 ppm are unambiguously assigned to P_1 (bridgehead) and P_2 (junction). The ^{31}P NMR spectrum of **29** shows two resonances at −55.1 and +83.5 ppm ($^1J(P_1–P_2)$ = 234 Hz) demonstrating that sulfur has reacted with the phosphorus at the junction. This conclusion is corroborated by the comparison of the various ^1J(C–P) coupling constants in **10** and **29**. They remain similar in the P_1-centered phospholene unit, whereas they increase sharply in the P_2-centered unit: $^1J(C_6–P_2)$ = 49 Hz in **29** vs. 27.3 Hz in **10**; $^1J(C_3–P_2)$ = 40 Hz in **29** vs. 19.0 Hz in **10**. This lower reactivity of the phosphorus at the bridgehead is perhaps connected with its very high stereochemical rigidity, which does not allow any sizable rehybridization when a reaction takes place at this center.

One of our first objectives when studying the Diels–Alder reactions of 2*H*-phospholes was to assess qualitatively the influence of the substitution pattern on the dienic and dienophilic reactivities of these species. This assessment has been obtained through cohydrolysis experiments. When hydrolyzing simultaneously a

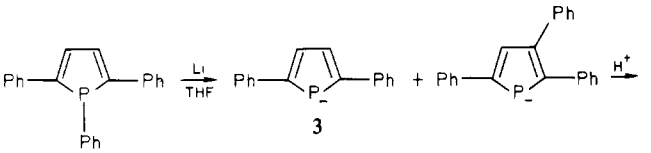
(23) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1982**, 569–570.
(24) Charrier, C.; Bonnard, H.; Mathey, F.; Neibecker, D. *J. Organomet. Chem.* **1982**, *231*, 361–367.
(25) Abel, E. W.; Towers, C. *J. Chem. Soc., Dalton Trans.* **1979**, 814. Abel, E. W.; Clark, N.; Towers, C. *Ibid.* **1979**, 1552.

1:1 mixture of the two anions **2** and **3**, the major product obtained is the mixed dimer **30**. That 3,4-dimethyl-2*H*-phosphole (**6a**)

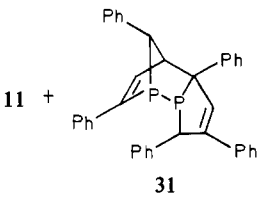


30

has acted as the dienophilic unit in the reaction leading to **30** is obvious from the inspection of the ^{13}C NMR spectrum of **30**. The carbon C_6 and the carbon C_3 appear respectively at 56.7 (J(C–P) = 28.3 Hz) and 31.4 ppm (J(C–P) = 22.6 and 3.5 Hz). The corresponding data for **10** are closely similar: δ 61.7 (J(C–P) = 27.3 Hz); 31.3 (J(C–P) = 19 and 2 Hz). We think that this apparent anomaly (**6a** acting as the dienophile and **7a** acting as the diene) means probably that steric factors are predominant in this dimerization, which leads to the less hindered dimer. When the two possible dimers are similarly hindered, the electronic factors dictate the course of the reaction. During the lithium cleavage of 1,2,5-triphenylphosphole, besides (2,5-diphenylphospholyl)lithium (**3**), some (2,3,5-triphenylphospholyl)lithium is also produced as demonstrated elsewhere.[24] Thus, the hydrolysis of this mixture produces some mixed dimer **31** together with the "normal" dimer **11**. Here, the triphenylphosphole is the dienophile as expected.



3



31

We have completed this work by a more conventional study of the reactivity of **7a** with 2,3-dimethylbutadiene and various acetylenes. The results are presented in Scheme I.

Experimental Section

All reactions were carried out under argon. Solvents, acid or basic aqueous solutions, and silica gel (70–230 mesh Merck) were used after being degassed with argon. NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13 MHz for ^1H, 32.435 MHz for ^{31}P, and 20.15 MHz for ^{13}C spectra. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4; ^1H and ^{13}C chemical shifts are internally referenced to Me_4Si and are positive for downfield shifts in all cases. Mass spectra were recorded on a Nermag R 10-10 spectrometer at 70 eV by Mr. Charrē (S.N.P.E.).

General Procedure for the Synthesis of 2*H*-Phosphole Dimers 9–11. A solution of 1-phenylphosphole for **9**, 1-phenyl-3,4-dimethylphosphole for **10**, or 1,2,5-triphenylphosphole for **11** (80 mmol) in 600 mL of dry THF with 1.12 g of lithium (162 mmol) was stirred at room temperature. The reaction was generally completed after 5 h, when the $^{31}P\{^1H\}$ NMR spectrum of the THF solution only showed the peak of the phospholyllithium, **1–3**. For **9** or **10**, a solution of 130 mL of water and 30 mL of acetic acid was added within 5 min; for **11** a solution of 80 mL of water and 80 mL of acetic acid was used. The mixture was stirred at room temperature for 5–10 h. After neutralization by an aqueous solution of $HNaCO_3$ (1 M), the product was extracted with ether (600 mL). The organic layer was dried and evaporated to give crude dimers **9**, **10**, and **11**.

4,5,7,8-Tetramethyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-4,8-decadiene (10, Endo). The crude tetramethyl-2*H*-phosphole dimer (**10**) was obtained in 60% yield. It can be purified by sublimation (50 °C, 1 torr) or recrystallization in chloroform, but a large part of the product was destroyed. The crude product was pure enough to be used without purification: mp 62 °C; ^1H NMR ($CDCl_3$) δ 1.5, 1.53, 1.81, 1.83 (CH_3), 1.5–2.3 (CH_2), 2.82 ($^2J_{H_6P_2}$ = 29 Hz, H_6), 5.69 ($^2J_{H_9P_1}$ = 44 Hz, H_9); ^{13}C NMR ($CDCl_3$) δ 16.6, 16.8, 18.0 and 22.5 (CH_3), 31.3 (J_{CP} = 19.0 Hz, J_{CP} = 2.0 Hz, C_3), 132.2 (C_4 and C_5), 61.5 (J_{CP} = 27.3 Hz, C_6), 63.2 (J_{CP} = 6.0, 2.0 Hz, C_7), 159.4 (J_{CP} = 4.0, 4.0 Hz, C_8), 124.1 (J_{CP} = 35.0, 5.0 Hz, C_9), 51.1 (J_{CP} = 9.0, 9.0 Hz, C_{10}); ^{31}P NMR ($CDCl_3$) δ −63.1 ($^1J_{P_1P_2}$ = 185 Hz, P_1), −24.1 (P_2).

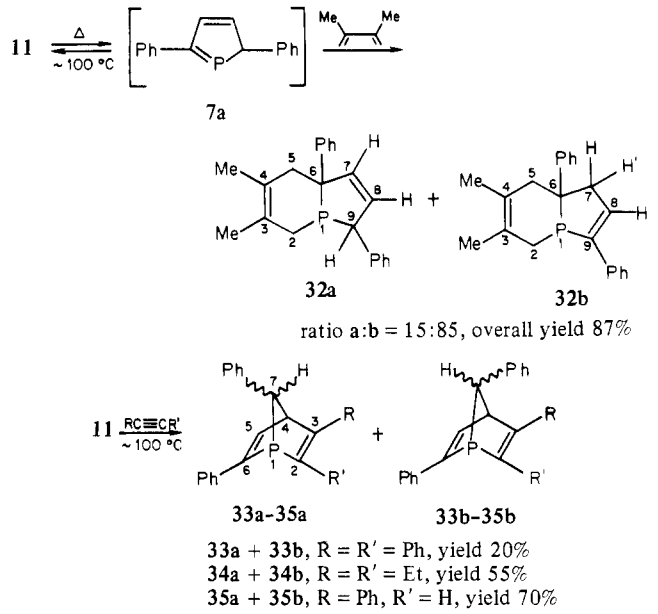
3,6,9,10-Tetraphenyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-3,8-decadiene (11, Endo). The crude dimer **11** was washed with acetone and recrystallized in cyclohexane to give a 9.5 g of pure **11** as a white solid (yield 50%): mp 177 °C; ^1H NMR ($CDCl_3$) δ 6.28 ($^3J_{H_4H_5}$ = 2.8, $^3J_{H_4H'_5}$ = 3.2, $^4J_{H_4P_1}$ = 2.0, $^3J_{H_4P_2}$ = 8.5 Hz, H_4), 2.87 ($^2J_{H_5H'_5}$ = 18.8, $^4J_{H_5P_1}$ = 2.5, $^3J_{H_5P_2}$ = 3.3 Hz, H_5), 3.37 ($^4J_{H_5P_1}$ = 2.9, $^3H_{H'_5P_2}$ = 1.8 Hz, H'_5), 4.27 ($^3J_{H_7H_8}$ = 3.9, $^3J_{H_7H_{10}}$ = 1.2, $^3J_{H_7P_1}$ = 7.0, $^3J_{H_7P_2}$ = 7.0 Hz, H_7), 6.93 (H_8, under phenyl group), 3.37 ($^2J_{H_{10}P_1}$ = 10.5, $^3J_{H_{10}P_2}$ = 3.5 Hz, H_{10}); ^{13}C NMR ($CDCl_3$) δ 133.8 (J_{CP} = 3.9, 1.9 Hz) and 132.0 (J_{CP} = 4.9, 4.9 Hz) (C_4 and C_8), 48.06 (J_{CP} = 0.8, 0.8 Hz, C_5), 61.3 (J_{CP} = 28.3, 0 Hz, C_6), 56.95 (J_{CP} = 12.6, 9.8 Hz, C_7), 68.8 (J_{CP} = 4.9, 1.9 Hz, C_{10}), ^{31}P NMR ($CDCl_3$) δ −25.9 ($^1J_{P_1P_2}$ = 200 Hz, P_1), +17.1 (P_2); mass spectrum (180 °C), *m/e* (relative intensity) 472 (M, 100) 236 (M/2, 100). Anal. Calcd for $C_{32}H_{26}P_2$: C, 81.34; H, 5.55; P, 13.11. Found: C, 81.11; H, 5.56; P, 13.03.

2,3,4,5-Tetraphenyl-1-(2′,3′,4′,5′-tetraphenylphospholyl)-2-phospholene (12). A solution of 1,2,3,4,5-pentaphenylphosphole (3.8 g, 8.2 mmol) and potassium (0.64 g, 16.4 mmol) in 70 mL of dry THF was refluxed for 3 h. Acetic acid (5 mL) was added at room temperature, and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (100 g) with toluene–hexane (20:80). The compound **12** was recovered with 51% yield (1.6 g) as an orange solid: mp 206 °C; ^1H NMR ($CDCl_3$) δ 4.69 ($^3J_{H_4H_5}$ = 9.0, $^3J_{H_4P_1}$ = 10.7, $^4J_{H_4P'}$ = 3.7 Hz, H_4), 4.38 ($^2J_{H_5P_1}$ = 2.2, $^3J_{H_5P'}$ = 5.4 Hz, H_5); ^{13}C NMR ($CDCl_3$) δ 64.4 (J_{CP} = 3.9, 0 Hz, C_4); 47.9 (J_{CP} = 15.6, 2.9 Hz, C_5); ^{31}P NMR ($CDCl_3$) δ −1.7 ($^1J_{P_1P'}$ = 370 Hz, P_1), +28.7 (P'); mass spectrum (180 °C), *m/e* (relative intensity) 776 (M, 98), 774 (M − 2 H, 100). Anal. Calcd for $C_{56}H_{42}P_2$: C, 86.58; H, 5.45; P, 7.97. Found: C, 85.81; H, 5.45; P, 7.89.

(2,3,4,5-Tetraphenylphosphole)pentacarbonyltungsten (14). A solution of 2,3,4,5-tetraphenylphospholylpotassium (2 mmol) in THF (17 mL) was cooled at −78 °C. Trifluoroacetic acid (2 mL) was added. The mixture was stirred for 5 min and was poured into a solution of $W(CO)_5$ THF [from $W(CO)_6$ (1.5 g, 4 mmol) irradiated for 1.5 h in 250 mL of THF] cooled at −78 °C. The mixture was allowed to stand for 2 h at room temperature. The solvent was evaporated and the complex was recrystallized in benzene–hexane, giving 1 g (70% yield) of **14** as a brown-red solid: mp 282 °C dec; ^1H NMR (C_6D_6) δ 6.68 ($^1J_{PH}$ = 338 Hz, P*H*); ^{13}C NMR (C_6D_6) δ 140.7 (J_{CP} = 37.9 Hz, C_2), 151.15 (J_{CP} = 14.6 Hz, C_3), 195.85 (J_{CP} = 7.3 Hz, CO cis), 198.4 (J_{CP} = 31.6 Hz, CO trans).

(2,5-Diphenylphosphole)pentacarbonyltungsten (13). The same procedure as for **14** was used for 2,5-diphenylphospholyllithium. The complex **13** slowly decomposed at room temperature.

Scheme I. Diels-Alder Reactivity of 2,5-Diphenyl-2*H*-phosphole



7a

32a **32b**

ratio a:b = 15:85, overall yield 87%

33a-35a **33b-35b**

33a + 33b, R = R′ = Ph, yield 20%
34a + 34b, R = R′ = Et, yield 55%
35a + 35b, R = Ph, R′ = H, yield 70%

1-Methyl-2,3,4,5-tetraphenylphosphole Sulfide (15) and 1-Methyl-2,3,4,5-tetraphenyl-2-phospholene Sulfide (16). A mixture of compound **12** (1.1 g, 1.4 mmol) in 20 mL of dry THF and lithium (0.02 g, 2.9 mmol) was stirred at room temperature for 2 h. A solution of methyliodide (0.41 g, 2.9 mmol) in 2 mL of dry THF was added at room temperature. The mixture was stirred for 2 h. An excess of sulfur (0.2 g) was added and the medium was heated at reflux with stirring for 2 h. After evaporation, the residue was chromatographed on silica gel (100 g) first with hexane in order to remove the excess of sulfur and then with toluene; **15** was recovered first and then **16**.

15: mp 225 °C (0.41 g, 67% yield); ^{1}H NMR ($CDCl_3$) δ 1.98 ($^2J_{HP}$ = 13 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 19.57 (J_{CP} = 50.8 Hz, CH_3), 136.7 (J_{CP} = 73.2 Hz, C_2, C_5), 148.7 (J_{CP} = 24.4 Hz, C_3, C_4); ^{31}P NMR ($CDCl_3$) δ +51.9, mass spectrum (200 °C), *m/e* (relative intensity) 434 (M, 30). Anal. Calcd for $C_{29}H_{23}PS$: C, 80.18; H, 5.30; P, 7.14. Found: C, 80.20; H, 5.59; P, 6.80.

16: mp 276 °C (0.38 g, 62% yield); ^{1}H NMR ($CDCl_3$) δ 1.76 ($^2J_{HP}$ = 12.7 Hz, CH_3), 4.94 ($^3J_{H_4H_5}$ = 8.0, $^2J_{H_5P}$ = 27.3 Hz, H_5), 4.16 ($^3J_{H_4P}$ = 12.0 Hz, H_4); ^{13}C NMR ($CDCl_3$) δ 22.38 (J_{CP} = 54.7 Hz, CH_3), 51.94 (J_{CP} = 52.7 Hz, C_5), 60.25 (J_{CP} = 6.8 Hz, C_4); ^{31}P NMR ($CDCl_3$) δ +61.74; mass spectrum (200 °C), *m/e* (relative intensity) 436 (M, 100). Anal. Calcd for $C_{29}H_{25}PS$: C, 79.81; H, 5.73; P, 7.11. Found: C, 79.58; H, 5.79; P, 6.40.

4,5,7,8-Tetramethyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-4,8-decadiene (23, Exo). Compound **23** was obtained when **10** was heated at 80–100 °C for 2 h, but the transformation was not complete and the reaction mixture contained 75% of **10** and 25% of **23**: ^{13}C NMR ($CDCl_3$) δ 31.8 (J_{CP} = 20.5, 3.9 Hz, C_3), 135.0 and 131.0 (J_{CP} = 0 Hz, C_4 and C_5), 57.25 (J_{CP} = 25.3, 0 Hz, C_6), 61.94 (J_{CP} = 5.9, 3.9 Hz, C_7), 162.23 (J_{CP} = 9.7, 4.9 Hz, C_8), 128 (C_9), 41.9 (J_{CP} = 16.6, 0 Hz, C_{10}); ^{31}P NMR ($CDCl_3$) δ −56.4 ($^1J_{P_1P_2}$ = 185 Hz, P_1), −17.8 (P_2).

3,6,9,10-Tetraphenyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-3,8-decadiene (24, Exo). Compound **24** was obtained quantitatively when **11** was heated at 110 °C in toluene for 3 h: mp 185 °C; ^{1}H NMR ($CDCl_3$) δ 6.59 ($^3J_{H_4H'_5} \simeq {}^3J_{H_4H'_5}$ = 2.9, $^4J_{H_4P_1}$ = 1.9, $^3J_{H_4P_2}$ = 7.9 Hz, H_4), 3.34 ($^4J_{H_5P_1} \simeq {}^4J_{H'_5P_1}$ = 5.2, $^3J_{H_5P_2} \simeq {}^3J_{H'_5P_2}$ = 2.9 Hz, H_5 and H'_5), 3.94 ($^3J_{H_7H_8}$ = 3.6, $^3J_{H_7H_{10}}$ = 1.5, $^3J_{H_7P_1}$ = 9, $^3J_{H_7P_2}$ 7.8 Hz, H_7), 6.23 ($^3J_{H_8P_1}$ = 7.4, $^4J_{H_8P_2}$ = 3.6 Hz, H_8), 3.75 ($^2J_{H_{10}P_1}$ = 9.2, $^3J_{H_{10}P_2}$ = 1.3 Hz, H_{10}); ^{13}C NMR ($CDCl_3$) δ 134.1 (J_{CP} = 5.9, 3.7 Hz) and 137.45 (J_{CP} = 9.8, 0 Hz) (C_4 and C_8), 51.36 (J_{CP} = 1.2, 0.8 Hz, C_5), 63.0 (J_{CP} = 21.5, 0 Hz, C_6), 54.12 (J_{CP} = 17.6, 0 Hz, C_7), 68.4 (J_{CP} = 5.8, 2.9 Hz, C_{10}); ^{31}P NMR ($CDCl_3$) δ −22.6 ($^1J_{P_1P_2}$ = 211 Hz, P_1), + 22.8 (P_2); mass spectrum (180 °C), *m/e* (relative intensity) 472 (M, 100); 236 (M/2, 100). Anal. Calcd for $C_{32}H_{26}P_2$: C, 81.34; H, 5.55; P, 13.11. Found: C, 81.22; H, 5.64; P, 12.77.

3,6,9,10-Tetraphenyl-1,2-diphosphapentacyclo[5.2.1.0^{2,6}.0^{3,9}.0^{4,8}]decane (25). The endo compound **11** (1 g, 2.12 mmol) in 250 mL of dry THF was irradiated by a medium-pressure mercury lamp (125 W) at −30 °C for 15 min. The solvent was evaporated and the residue chromatographed on silica gel (40 g) with toluene–hexane (20:80). After recrystallization in ether, **25** was recovered with 60% yield (0.6 g): mp 165 °C; ^{1}H NMR ($CDCl_3$) δ 3.83 ($^3J_{H_4H_5}$ = 1.9, $^3J_{H_4H'_5}$ = 1.2, $^3J_{H_4H_8}$ = 6.1, $^3J_{H_4P_2} \simeq$ 0.3, $^4J_{H_4P_1}$ = 0 Hz, H_4), 2.67 ($^2J_{H_5H'_5}$ = 12.5, $^4J_{H_5P_1}$ = 0, $^3J_{H_5P_2}$ = 16.5 Hz, H_5), 2.42 ($^4J_{H'_5P_1}$ = 0, $^3J_{H'_5P_2}$ = 5.6 Hz, H'_5), 4.18 ($^3J_{H_7H_8}$ = 6.3, $^3J_{H_7H_{10}}$ = 0.5, $^3J_{H_7P_1}$ = 9.0, $^3J_{H_7P_2}$ = 1.2 Hz, H_7), 3.53 ($^3J_{H_8P_1}$ = 0, $^4J_{H_8P_2}$ = 0 Hz, H_8), 4.24 ($^2J_{H_{10}P_1}$ = 7.6, $^3J_{H_{10}P_2}$ = 0.8 Hz, H_{10}); ^{13}C NMR ($CDCl_3$) δ 62.75 (J_{CP} = 7.8, 4.9 Hz), 64.20 (J_{CP} = 29.3, 0 Hz) and 55.80 (J_{CP} = 0.5, 0.5 Hz) (C_3, C_6, and C_9), 46.8 (J_{CP} = 0.4, 0.4 Hz), 53.8 (J_{CP} = 4.9, 0 Hz), 60.5 (J_{CP} = 26.4, 0 Hz) and 67.11 (J_{CP} = 3.9, 2.9 Hz) (C_4, C_7, C_8 and C_{10}), 47.55 (J_{CP} = 12.7, 0 Hz, C_5)f ^{31}P NMR ($CDCl_3$) δ −13.6 ($^1J_{P_1P_2}$ = 73.2 Hz, P_1), −4.5 (P_2); mass spectrum (170 °C), *m/e* (relative intensity) 472 (M, 20), 236 (M/2, 100). Anal. Calcd for $C_{32}H_{26}P_2$: C, 81.34; H, 5.55; P, 13.11. Found: C, 80.91; H, 5.52; P, 13.14.

2,2′,3,3′,4,4′,5,5′-Octaphenyl-1,1′-biphospholyl (28). Compound **12** heated in a sealed tube at 230 °C for 24 h yields 72% of **28**, which was purified by chromatography on silica gel with toluene–hexane (20:80); **28** is an orange solid: mp 142 °C; ^{13}C NMR ($CDCl_3$) δ 148.0 (pseudo t; C cycle), 143.3 (pseudo t, C cycle), 137.5–125.2 (phenyl); ^{31}P NMR ($CDCl_3$) δ −14.6; mass spectrum (150 °C), *m/e* (relatively intensity) 774 (M, 60). Anal. Calcd for $C_{56}H_{40}P_2$: C, 86.82; H, 5.17; P, 8.01. Found: C, 86.58; H, 5.18; P, 7.89.

4,5,7,8-Tetramethyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-4,8-decadiene 2-Sulfide (29). Crude compound **10** was stirred in benzene with 1 equiv of sulfur at room temperature for 3 h. After evaporation of the solvent, the residue was chromatographed on silica gel (40 g of silica gel/g of product) with benzene–ethyl acetate (90:10). The monosulfide **29** was recovered with 60% yield: mp 156 °C; ^{1}H NMR ($CDCl_3$) δ 5.68 ($^2J_{H_9P_1}$ = 47 Hz, H_9); ^{13}C NMR ($CDCl_3$) δ 17.3, 17.3, 18.6, and 22.2 (4 CH_3), 43.2 (J_{CP} = 40, 3.9 Hz, C_3), 130.8 (J_{CP} = 9.8, 0 Hz) and 132.2 (J_{CP} = 0 Hz) (C_4 and C_5), 62.4 (J_{CP} = 49.0, 0 Hz, C_6), 60.7 (J_{CP} = 7.0, 7.0 Hz, C_7), 164.5 (J_{CP} = 11.7, 3.9 Hz, C_8), 121.9 (J_{CP} = 29.3, 9.8 Hz, C_9), 50.4 (J_{CP} = 12.6, 11.8 Hz, C_{10}); ^{31}P NMR ($CDCl_3$) δ −55.1 ($^1J_{P_1P_2}$ = 234 Hz, P_1), + 83.5 (P_2); mass spectrum (160 °C), *m/e* (relative intensity) 256 (M, 67).

4,5-Dimethyl-9,10-diphenyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-4,8-decadiene (30). 3,4-Dimethylphospholyllithium was prepared from 1-phenyl-3,4-dimethylphosphole (3.3 g, 17.6 mmol) with lithium (0.35 g) in 55 mL of dry THF. 2,5-Diphenylphospholyllithium was prepared from 1,2,5-triphenylphosphole (5.5 g, 17.6 mmol) with lithium (0.35 g) in 135 mL of dry THF. The reactions were complete after 2 h. The mixture of both phospholyllithium reagents was poured within 1 h into acetic acid (80 mL). The reaction mixture was stirred at room temperature for 3 h. Solvents were evaporated under vacuum, and the residue was chromatographed on silica gel (40 g silica gel/g of product) with toluene–hexane (20:80). The product **30** was recovered as a yellow oil with 57% yield (3.5 g): ^{1}H NMR (C_6D_6) δ 3.4 ($^3J_{H_6H_7}$ = 5.3 Hz, H_6), 4.03 ($^3J_{H_7H_8}$ = 3.9, $^3J_{H_7H_{10}}$ = 1.4, $^3J_{H_7P_1}$ = 13.3, $^3J_{H_7P_2}$ = 7.9 Hz, H_7), 6.59 ($^3J_{H_8P_1}$ = 6.3, $J_{H_8P_2}$ = 0.5 Hz, H_8), 3.15 ($^2J_{H_{10}P_1}$ = 8.6, $^3J_{H_{10}P_2}$ = 5.0 Hz, H_{10}); ^{13}C NMR (C_6D_6) δ 31.4 (J_{CP} = 22.6, 3.5 Hz, C_3), 5 6.7 (J_{CP} = 28.3, 0 Hz, C_6), 58.6 (J_{CP} = 4.9, 3.0 Hz, C_7), 134.97 (J_{CP} = 4.8, 0.8 Hz, C_8), 60.11 (J_{CP} = 10.5, 9.8 Hz, C_{10}), 16.9 (CH_3), 17.25 (J_{CP} = 1.9, 1.9 Hz, CH_3); ^{31}P NMR (C_6D_6) δ −46.03 ($^1J_{P_1P_2}$ = 200 Hz, P_1), −28.61 (P_2).

3,4,6,9,10-Pentaphenyl-1,2-diphosphatricyclo[5.2.1.0^{2,6}]-4,8-decadiene (31). When the solution of 2,5-diphenylphospholyllithium in THF was stirred at room temperature for 20 h, the phenyllithium slowly reacted with it to give about 10% of 2,3,5-triphenylphospholyllithium.[24] After following the same procedure as for **11**, the residue was chromatographed on silica gel (40 g silica gel/g of product) with toluene–hexane (30:70). Compound **11** was recovered first and then **31** with 10% yield: mp = 139 °C; ^{1}H NMR ($CDCl_3$) δ 4.75 ($^4J_{H_3H_5}$ = 1.7, $^3J_{H_3P_1}$ = 9.8, $^2J_{H_3P_2}$ = 2.7 Hz, H_3), 6.71 ($^4J_{H_5P_1}$ = 0, $^3J_{H_5P_2}$ = 6.4 Hz, H_5), 4.24 ($^3J_{H_7H_8}$ = 3.6, $^3J_{H_7H_{10}}$ = 1.6, $^3J_{H_7P_1}$ = 7.3, $^3J_{H_7P_2}$ = 7.3 Hz, H_7), 5.51 ($^3J_{H_8P_1}$ = 7.5, $^4J_{H_8P_2}$ = 3.9 Hz, H_8), 3.85 ($^2J_{H_{10}P_1}$ = 9.0, $^3J_{H_{10}P_2}$ = 1.7 Hz, H_{10}); ^{13}C NMR ($CDCl_3$) δ 48.9 (J_{CP} = 24.4, 3.9 Hz, C_3), 136.6 (J_{CP} = 0, C_5), 70.58 (J_{CP} = 26.3, 0 Hz, C_6), 51.1 (J_{CP} = 16.6, 1.0 Hz, C_7), 139.0 (J_{CP} = 8.8, 0 Hz, C_8), 63.86 (J_{CP} = 3.9, 1.3 Hz, C_{10}); ^{31}P NMR ($CDCl_3$) δ −20.37 ($^1J_{P_1P_2}$ = 213 Hz, P_1), +18.35 (P_2); mass spectrum (140 °C), *m/e* (relative intensity) 548 (M, 70). Anal. Calcd for $C_{38}H_{30}P_2$: C, 83.19; H, 5.51; P, 11.29. Found: C, 82.66; H, 5.50; P, 11.21.

3,4-Dimethyl-6,9-diphenylphosphabicyclo[4.3.0]-3,8-nonadiene (32). Diphenyl-2*H*-phosphole dimer (**11**) (0.5 g) and 2,3-dimethyl-1,3-butadiene (5 mL) were heated at 100 °C in a sealed tube for 20 h. After evaporation of the excess of 2,3-dimethyl-1,3-butadiene, the residue was chromatographed on silica gel (40 g) with toluene–hexane (20:80), giving impure **32a** and pure **32b** (ratio 15:85) (87% yield, 0.58 g).

32a: ^{1}H NMR ($CDCl_3$) δ 1.55 and 1.61 (2 CH_3), 1.8–2.5 (H_2,H'_2 and H_5,H'_5), 5.74 and 5.79 ($^3J_{H_7H_8}$ = 7.0, $J_{H_7P} \simeq J_{H_8P} \simeq$ 6.1 Hz, H_7 and H_8), 3.8 ($^2J_{H_9P}$ = 4.9 Hz, H_9); ^{31}P NMR ($CDCl_3$) δ +24.2.

32b: mp 131 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 and 1.61 (2 CH_3), 1.8–2.5 (H_2,H'_2 and H_5,H'_5), 3.12 and 3.00 ($^2J_{H_7H'_7}$ = 18.5, $^3J_{H_7H_8} \simeq {}^3J_{H'_7H_8}$ = 2.9, $^3J_{H_7P} \simeq {}^3J_{H'_7P}$ = 2.7 Hz, H_7 and H'_7), 6.39 ($^3J_{H_8P}$ = 9.5 Hz, H_8); ^{13}C NMR ($CDCl_3$) δ 20.44 and 21.26 (2 CH_3), 26.45 (J_{CP} = 25.4 Hz, C_2), 46.85 (J_{CP} = 3.0 Hz) and 50.49 (J_{CP} = 1.0 Hz) (C_5 and C_7), 52.96 (J_{CP} = 11.7 Hz, C_6), 132.71 (J_{CP} = 6.8 Hz, C_8); ^{31}P NMR ($CDCl_3$) δ +13.27; mass spectrum (130 °C), *m/e* (relative intensity) 318 (M, 100). Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.29; P, 9.72. Found: C, 82.57; H, 7.39; P, 9.17.

2,3,6,7-Tetraphenyl-1-phosphanorborna-2,5-diene (33). Diphenyl-2*H*-phosphole dimer **11** (0.5 g) and tolan (3.8 g) were heated at 100 °C in a sealed tube for 48 h. After chromatography with toluene–hexane (20:80), both isomers **33a** (pure) and **33b** (impure) were recovered with 20% yield (ratio 1:1).

33a: ^{1}H NMR ($CDCl_3$) δ 4.78 ($^3J_{H_4H_5}$ = 3.9, $^3J_{H_4H_7}$ = 1.9, $^3J_{H_4P}$ = 3.9 Hz, H_4), 7.90 ($^3J_{H_5P}$ = 6.0 Hz, H_5), 3.91 ($^2J_{H_7P}$ = 8.8 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 68.15 (J_{CP} = 4.9 Hz, C_4), 144.20 (J_{CP} = 2.0 Hz, C_5), 76.66 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ +12.67; mass spectrum (140 °C), *m/e* (relative intensity) 414 (M, 100). Anal. Calcd for $C_{30}H_{23}P$: C, 86.93; H, 5.59; P, 7.48. Found: C, 87.28; H, 5.63; P, 7.11.

33b: ^{1}H NMR ($CDCl_3$) δ 4.78 ($^3J_{H_4H_5}$ = 3.8, $^3J_{H_4H_7}$ = 1.7, $^3J_{H_4P}$ = 3.9 Hz, H_4), 7.65 ($^3J_{H_5P}$ = 6.5 Hz, H_5), 4.27 ($^2J_{H_7P}$ = 9.3 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 68.15 (J_{CP} = 4.9 Hz, C_4), 141.26 (J_{CP} = 0 Hz, C_5), 76.61 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ +11.46.

2,3-Diethyl-6,7-diphenyl-1-phosphanorborna-2,5-diene (34). Diphenyl-2*H*-phosphole dimer **11** (0.5 g) and 3-hexyne (4.5 g) were heated at 100 °C in a sealed tube for 3 days. After chromatography with toluene–hexane (20:80), both isomers were recovered together with 55% yield as a yellow oil (ratio **a**:**b** = 2:3).

34a: ^{1}H NMR ($CDCl_3$) δ 4.03 ($^3J_{H_4H_5}$ = 3.9, $^3J_{H_4H_7}$ = 2.0, $^3J_{H_4P}$ = 4.0 Hz, H_4) (H_5 under phenyl group), 3.75 ($^2J_{H_7P}$ = 8.8 Hz, H_7); ^{13}C

NMR ($CDCl_3$) δ 64.7 (J_{CP} = 3.9 Hz, C_4), 142.11 (J_{CP} = 2.0 Hz, C_5), 77.95 (J_{CP} = 0, C_7); ^{31}P NMR ($CDCl_3$) δ −1.55.

34b: ^1H NMR ($CDCl_3$) δ 4.00 ($^3J_{H_4H_5}$ = 3.9, $^3J_{H_4H_7}$ = 2.0, $^3J_{H_4P}$ = 4.0 Hz, H_4), 7.42 ($^3J_{H_5P}$ = 5.9 Hz, H_5), 3.66 ($^2J_{H_7P}$ = 8.8 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 64.85 (J_{CP} = 3.9 Hz, C_4), 145.46 (J_{CP} = 2.0 Hz, C_5), 76.98 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ −1.85; mass spectrum (140 °C), *m/e* (relative intensity) 318 (M, 100). Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.29; P, 9.72. Found: C, 83.11; H, 7.37; P, 9.51.

3,6,7-Triphenyl-1-phosphanorborna-2,5-diene (35). Diphenyl-2*H*-phosphole dimer **11** (0.5 g) and phenylacetylene (5 mL) were heated at 100 °C in a sealed tube for 16 h. After chromatography with toluene–hexane (20:80), both isomers **35a** (pure) and **35b** (impure) were recovered wth 70% yield (ratio **a**:**b** = 90:10).

34a: mp 112 °C; ^1H NMR ($CDCl_3$) δ 6.81 ($^4J_{H_2H_4}$ = 0.9, $^2J_{H_2P}$ = 45.6 Hz, H_2), 4.87 ($^3J_{H_4H_5}$ = 4.1, $^3J_{H_4H_7}$ = 1.8, $^3J_{H_4P}$ = 5.1 Hz, H_4), 7.73 ($^3J_{H_5P}$ = 5.9 Hz, H_5), 4.01 ($^2J_{H_7P}$ = 8.3 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 61.61 (J_{CP} = 4.9 Hz, C_4), 142.68 (J_{CP} = 2.8 Hz, C_5), 78.2 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ −3.89; mass spectrum (120 °C), *m/e* (relative intensity) 338 (M, 100). Anal. Calcd for $C_{24}H_{19}P$: C, 85.20; H, 5.62; P, 9.18. Found: C, 85.64; H, 5.61; P, 8.48.

35b: ^1H NMR ($CDCl_3$) δ 4.87 ($^4J_{H_4H_2}$ = 0.9, $^3J_{H_4H_5}$ = 4.1, $^3J_{H_4H_7}$ = 1.8, $^3J_{H_4P}$ = 5.1 Hz, H_4) (H_2 and H_5 under phenyl groups), 4.01 ($^2J_{H_7P}$ = 8.3 Hz, H_7); ^{31}P NMR ($CDCl_3$) δ −7.58.

Registry No. 1, 55219-61-9; **2**, 87319-14-0; **3**, 87319-15-1; **4**, 87319-16-2; **5**, 288-01-7; **6**, 87319-17-3; **7**, 82476-30-0; **8**, 82476-27-5; **9**, 87319-18-4; **10**, 87392-50-5; **11**, 87319-19-5; **12**, 87319-20-8; **14**, 87319-35-5; **15**, 87319-21-9; **16**, 87319-22-0; **23**, 87391-90-0; **25**, 87319-23-1; **28**, 87319-24-2; **29**, 87319-25-3; **30**, 87319-26-4; **31**, 87319-27-5; **32a**, 87319-28-6; **32b**, 87319-32-2; **33a**, 87319-29-7; **33b**, 87319-33-3; **34a**, 87319-30-0; **34b**, 87319-34-4; **35a**, 87319-31-1; **35b**, 87391-91-1; $W(CO)_5$, 30395-19-8; S, 7704-34-9; EtC≡CEt, 928-49-4; PhC≡CH, 536-74-3; 2,3-dimethylbutadiene, 513-81-5; tolan, 501-65-5.

Palladium-Catalyzed Oxidation of Amino Alkenes to Cyclic Imines or Enamines and Amino Ketones

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Abstract: Amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ (n = 3, 4) are cyclized to pyrrolines or piperideines under "Wacker process" conditions. Amino alkenes with a secondary amino group yield the corresponding cyclic enamines, while tertiary amino alkenes give amino ketones.

Much work has been done on the palladium-promoted amination of alkenes.[1-7] The reaction proceeds through a trans attack of the amine at the coordinated double bond.[8] However, most of these reactions cannot be catalytic, as amines usually displace alkenes coordinated to palladium(II). Known exceptions are the catalytic cyclization of *o*-allylanilines[4] and olefinic tosamides.[5]

It is known that in water most palladium–alkene complexes decompose to palladium metal, HCl, and oxidized organic products (e.g., aldehydes or ketones).[9,10] Smidt and co-workers[10] found that the palladium metal formed can easily be reoxidized by air using, e.g., copper(II) as an oxidation transfer catalyst, thus making a continuous oxidation reaction of alkenes possible. It is now shown that "Wacker process" conditions[10] can be used for the catalytic cyclization of a wide range of amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ (n = 3, 4).

Results and Discussion

The Reaction. The addition of 1 equiv of pent-4-enylamine (**3**) to a weakly acidic solution of $PdCl_4^{2-}$ results in a slow precipitation of palladium metal, and 2-methyl-1-pyrroline (**4**) can be isolated from the reaction mixture. If the reaction is run under an oxygen atmosphere and some copper(II) is added, it can be made catalytic with regard to palladium and copper.

To investigate the scope of this reaction, a series of amino alkenes were allowed to react at 60 °C under nonoptimized standard conditions, i.e., $[PdCl_2]$ = 0.005 M, $[CuCl_2]$ = 0.01 M, [NaCl] = 0.1 M, and [HCl] = 0.2 M (see Table I). Except for the reaction with a 100-fold excess of pent-4-enylamine, all reactions were run with 20 equiv of aminoalkene/mol of palladium ([amino alkene] = 0.1 M).

Table I shows that primary amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ give cyclic imines, if n = 3 and 4. But-3-enylamine (**1**, n = 2) is only oxidized to aminobutan-3-one (**2**) and does not cyclize under these conditions. Aminobutan-3-one (**2**) was characterized by ^1H NMR in the reaction mixture as it polymerizes on the GC column.

In the acidic reaction mixture, *N*-methylpent-4-enylamine (**5**), a secondary amino alkene, yields the stable 1,2-dimethyl-1-pyrrolinium ion (**6**), which was characterized in situ by ^1H NMR and can be deprotonated to the corresponding unstable enamine **6b**,[11,12] which was characterized by reduction to 1,2-dimethylpyrrolidine (**6c**) with H_2/Pd/C. The oxidation of tertiary amino alkenes gives only the corresponding amino ketones. The product mixtures obtained from some of the reactions indicate that double-bond isomerization must have occurred before oxidation.

Double-Bond Isomerization. It is known, that palladium(II) is a very effective catalyst for isomerization of double bonds, particularly of terminal alkenes.[13] As can be seen in Table I,

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