Phospha[3]radialenes. Syntheses, Structures, Strain Energies, and Reactions

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Received July 5, 2000. Revised Manuscript Received September 29, 2000

Abstract: In situ-generated terminal phosphinidene complex PhPW(CO)$_5$ adds in a 1,2-fashion to the terminal double bond of tetramethylcumulene and cyclic 1,2,3-cyclodecatriene. The resulting alkenylidenephosphiranes **19A** and **20A**, which are three-membered phosphiranes containing an exocyclic allenic group, subsequently rearrange to the corresponding phospha[3]radiales **19B** and **20B**, which are phosphiranes having two exocyclic double bonds. All four organophosphorus compounds were characterized by single-crystal X-ray structure determinations. Bicyclic **20A** contains a significantly bent (171.5(7)°) and twisted (14.2(8)°) allenic unit in contrast to **19A**. The rearrangement to the thermodynamically favored radialenes is considered to occur by a phosphirane ring opening/closure sequence. On using a second equivalent of PhPW(CO)$_5$, insertion takes place into a PC bond of **20B**, but not of **19B**, to give two new phospha[4]radialene isomers, viz. *cis*-**20C** and *trans*-**20C**, both of which were characterized by crystal structure determinations. The PPCC ring in these systems is significantly puckered (∼150°), causing the olefinic bonds of the butadiene unit to be much twisted from planarity. Both phospha[3]radialenes undergo Diels−Alder reactions with methyl-1,2,4-triazole-3,5-dione (MTAD), resulting in the case of the acyclic cumulene in the expected addition product **19D** of which the phosphirane ring easily hydrolyzes. Cycloaddition of MTAD to **20B** does not occur at the radialene's diene unit but rather invokes one of its PC bonds, possibly in a concerted [$(\sigma^2 + \pi^2) + \pi^2$] mechanism, to give the unexpected adduct **20F**. Ab initio theoretical studies on the parent systems, using the G3(MP2) method, show phospha[3]radialene to be 3.6 kcal/mol more stable than ethenylidenephosphirane. Their strain energies (SE) are calculated to be 32.3 and 29.7 kcal/mol, respectively. The 22.2 kcal/mol SE of phosphirane increases by 5.9 kcal/mol on introducing one exocyclic double bond and by another 4.2 kcal/mol on introducing the second one. Still, the SE of phospha[3]radialene is less than the 39.0 kcal/mol of the more condensed phosphirene.

Introduction

The interplay of small rings with unsaturated bonds has yielded an array of intriguing hydrocarbons ranging from radialenes to spiroannelated rotanes and triangulanes.[1] The strain energy and electronic properties of the cyclopropane ring are prominent in these systems.[2] Far fewer systems are known that contain three-membered heterocycles.[3] This is especially the case for organophosphorus compounds despite the close relationship between carbon and phosphorus,[4] and even though the three-membered phosphiranes and the unsaturated phosphirenes are well accessible, particularly as transition metal stabilized complexes.[5] Recently, we reported on the synthesis and properties of phosphiranes containing one[6] and two spiroannelated rings[7] and those having one exocyclic double bond.[8] In the present study, we extend this work to phospha[3]radialenes and also report on new diphospha[4]radialenes.

So far, phospha[3]radialenes have been reported by three synthetic routes. Yoshifuji and co-workers[9] used the CCl$_2$ carbene addition to a heavily substituted terminal phosphacumulene to generate ethenylidenephosphirane **1A**, which rear-

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(1) See, for example: (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 317. (c) *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1987; 2 Vols. (d) Topical issue, Strained Organic Compounds. *Chem. Rev.* **1989**, *89* (5). (e) Pihlaja, K.; Taskinen, E. *Physical Methods in Heterocyclic Chemistry*; Academic Press: New York, 1978; Vol. 6, p 199. (f) *Houben-Weyl*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Vol. E, pp 17a−c.

(2) For a recent review, see: (a) de Meijere, A.; Kozhushkov, S. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Inc.: London, 1995: Vol. 4, pp 225−282. See also: (b) de Meijere, A.; Kozhushkov, S. I.; Khlebnikov, A. F. *Zh. Org. Khim.* **1996**, *32*, 1607; *Russ. J. Org. Chem. (Engl. Transl.)* **1996**, *32*, 1555. (c) Zefirov, N. S.; Kuznetsova, T. S.; Eremenko, O. V.; Kokoreva, O. V.; Zatonsky, G.; Ugrak, B. I. *J. Org. Chem.* **1994**, *59*, 4087. (d) Eaton, P. E.; Lukin, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 11370. (e) Fitjer, L.; Conia, J. M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 761.

(3) General three-ring heterocycles. Mathey, F. *Chem. Rev.* **1990**, *90*, 997.

(4) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998.

(5) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275.

(6) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786.

(7) Lammertsma, K.; Wang, B.; Hung, J.-T.; Ehlers, A. W.; Gray, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 11650.

(8) Krill, S.; Wang, B.; Hung, J.-T.; Horan, C. J.; Gray, G. M.; Lammertsma, K. *J. Am. Chem. Soc.* **1997**, *119*, 8432.

(9) Miyahara, I.; Hayashi, A.; Hirotsu, K.; Yoshifuji, M.; Yoshimura, H.; Toyota, K. *Polyhedron* **1992**, *11*, 385.

ranges to radialene **1B** (eq 1). Maercker and Brieden[10] used a
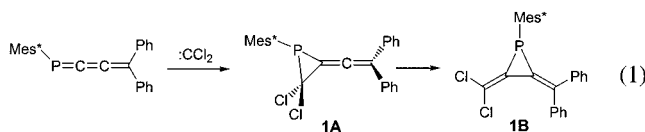
condensation route in which dichlorophosphines were reacted with a dynamic mixture[11] of dilithio 2,5-dimethylhexadienes and showed the ethenylidenephosphiranes to convert into the (symmetrically substituted) phospha[3]radialenes **2B**−**6B** (eq 2). A
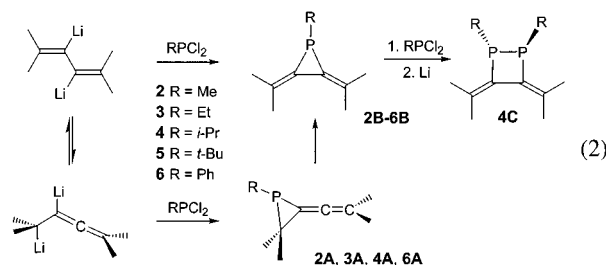
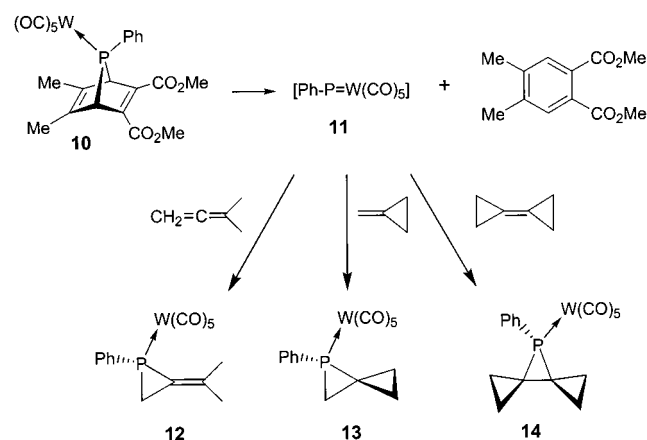transition metal decomplexation route leading directly to **7B** was recently described by Marjoral and co-workers (eq 3).[12] It
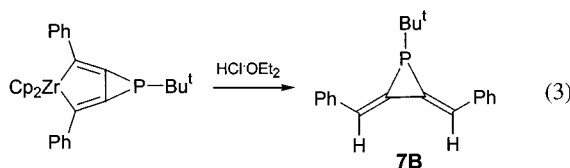
is noteworthy that the groups of both Yoshifuji and Maercker observed rearrangements to the phospha[3]radialenes whereas Breen and Stephan[13] did *not* report such a rearrangement for **8A**, which was synthesized from reaction of the nucleophilic phosphinidene **9**[14] with 1,4-dichloro-2-butyne (eq 4). It is evident
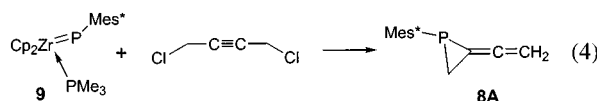

that these approaches are somewhat limited by the choice of starting materials. The only phospha[4]radialene we are aware of was reported by Brieden and Kellersohn,[15] who synthesized **4C** via **4A** and **4B** (eq 2) and thereby illustrated that access to the higher homologues is even more tedious.

Our approach toward the radialenes makes use of the carbene-like reactivity of PhPW(CO)$_5$ (**10**).[5a,16] This phosphinidene is generated in situ from thermal decomposition of phosphanorbornadiene **11** and adds to olefins to give phosphiranes in good yield.[17] Addition to cumulenes would then be a simple and effective way to generate the desired compounds. **10** and even the less electrophilic ^{i}Pr$_2$NPFe(CO)$_4$ also react with allenes.[18] An X-ray crystal structure was reported not only for methylenephosphirane **12**[8] but also for the strained phosphaspiropen-

(10) Maercker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933.

(11) Maercker, A.; Wunderlich, H.; Girreser, U. *Tetrahedron* **1996**, *52*, 6149.

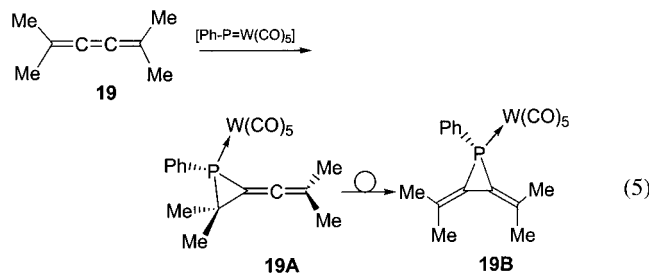(12) Mahieu, A.; Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P. *Organometallics* **1997**, *16*, 3086.

(13) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914.

(14) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158.

(15) Brieden, W.; Kellersohn, T. *Chem. Ber.* **1993**, *126*, 845.

(16) Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-T. *Organometallics* **1988**, *7*, 1875.

Scheme 1

tane **13**[6] and phospha[3]triagulene **14**,[7] which result from the respective addition to alkylidenecyclopropane and bicyclopropylidene (Scheme 1). These compounds are surprisingly stable despite their significant strain energies (SE). Thus, calculations with the G2(MP2) ab initio method showed the parent uncomplexed, nonsubstituted **15** to be 10.6 kcal/mol more strained
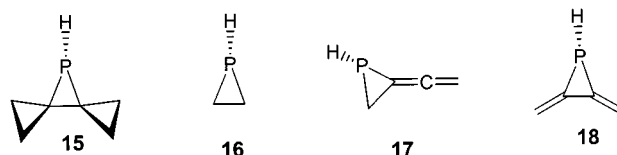
than the cumulative ring strain of the separate rings of which phosphirane **16** has an SE of 21.3 kcal/mol.[7] For parent phospha[3]radialene **18**, a larger SE of 35.8 kcal/mol has been reported, be it at the modest HF/6-31G* level of theory.[19] In the present study, we explore the reactivity of **11** toward cumulenes and address the effect of unsaturation on the phosphirane ring strain in **17** and **18** in more detail.

Results and Discussion

Two cumulenes were investigated, 2,5-dimethyl-2,3,4-hexatriene (**19**) and cyclic 1,2,3-cyclodecatriene (**20**). The cyclic system, which carries only two substituents, was considered to be of interest also because of its anticipated influence of the carbon ring-induced strain on the cumulenic unit. We first discuss the phosphinidene addition reaction to the cumulenes, then analyze the structures of the resulting organophosphorus compounds, discuss their strain energies, and last present insertion reactions, leading to 1,2-diphospha[4]radialenes and to Diels−Alder addition reactions. Structures, energies, and strain energies of parent systems (no substituents, no transition metal complex) are based on ab initio theoretical calculations. For clarity and consistency we label alkenylidenephosphiranes as **A**, phospha[3]radialenes as **B**, phospha[4]radialenes as **C**, and Diels−Alder products as **D**−**G**.

From Cumulene to Phospha[3]radialene. Reaction of terminal phosphinidene complex PhPW(CO)$_5$, generated in situ from 7-phosphanorbornadiene precursor **10** in toluene at 55 °C and catalyzed by CuCl,[17,20] with the tetramethyl derivative **19**

(17) (a) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. 6. (b) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484. (c) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456. (d) Hung, J.-T.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 1800.

(18) Wit, J. B. M.; van Eijkel, G. Th.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2596.

(19) Bachrach, S. M. *J. Phys. Chem.* **1993**, *97*, 4996.

gives in 70% isolated yield a 1:1 mixture of alkenylidenephosphirane **19A** and phopha[3]radialene **19B** (eq 5). Heating **19A**

(5)

in toluene at 100 °C for 2 h gives full conversion to **19B**. Likewise, reaction of **10** with the cyclic triene **20** gives in 46% isolated yield a 1:2 mixture of phospha[3]radialene **20B** and cyclic alkenylidenephosphirane **20A**, which also fully converts to the radialene on heating in toluene (eq 6). All products could

(6)
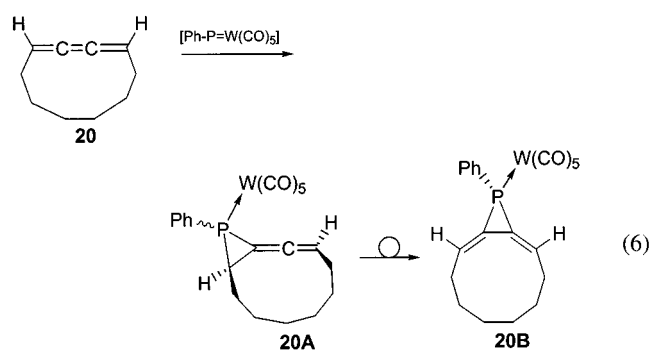
be separated by column chromatography, enabling spectroscopic characterization of the four structures including single-crystal X-ray structure determinations.

(1) Reactivities. The sequence of events indicates both **19A** and **20A** to be the kinetic products which subsequently rearrange to the corresponding radialenes **19B** and **20B** as the thermodynamically more stable products. The electrophilic phosphinidene apparently has a higher affinity for the terminal, conjugated unsaturated bonds of the cumulenes than for their central olefinic bonds. This intramolecular preference for a conjugated diene over an isolated double bond was recently also observed in the reaction of $^{i}Pr_2PFe(CO)_4$ with tetramethyldiallene, but the resulting vinylphosphirane **21** could not be isolated as it rearranges under the reaction conditions to phospholene **22** (eq 7).[18] Other examples of similar 1,3-sigmatropic shifts have been

(7)
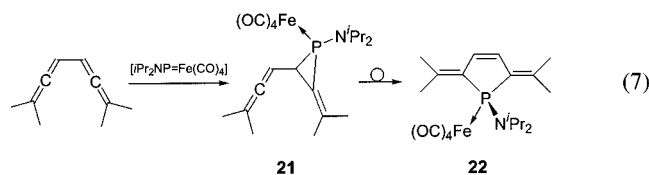
reported recently, either concerted or biradicaloid,[21] but such a process is not feasible for **19A** and **20A**. However, vinylphosphiranes have also been shown to epimerize at the P-center,[22] suggesting a CBP bond cleavage−closure sequence to give the thermodynamically more stable isomer. A related pathway may underlie the conversion of **A** into **B**.

Formation of radialenes from **19B** and **20B** would require rupture of the C(1)BP distal bond and subsequent closure of

Table 1. ^{31}P NMR Chemical Shifts of Alkenylidenephosphiranes (**A**) and Phospha[3]radialenes (**B**)

cmpd	P−R	R_1	R_2	R_3	R_4	M	A	B	ref
20	Ph	H	$-(CH_2)_6-$		H	$W(CO)_5$	−131.4	−153.0	*a*
19	Ph	Me	Me	Me	Me	$W(CO)_5$	−112.8	−155.0	*a*
1	Mes*	Cl	Cl	Ph	Ph		−60.5	−115.7	9
7	t-Bu	Ph	H	Ph	H			−131.1	12
6	Ph	Me	Me	Me	Me		−139.8	−183.4	10
5	t-Bu	Me	Me	Me	Me			−149.3	10
4	i-Pr	Me	Me	Me	Me		−124.5	−162.8	10
3	Et	Me	Me	Me	Me		−137.2	−177.7	10
2	Me	Me	Me	Me	Me		−152.8	−195.4	10
8	Mes*	H	H	H	H		−149.6		13

a This work.

the C(3)BP bond. Radialene **18** is indeed more stable than alkenylidenephosphirane **17** by 2.9 kcal/mol using the ab initio G3(MP2) method. This relative stability order is also in accord with the rearrangements of the uncomplexed systems of Yoshifuji[9] (**1A → 1B**) and of Maercker and Brieden[10] (**2A−6A** vs **2B−6B**, respectively). Breen and Stephan[13] synthesized by a rather different route alkenylidenephosphirane **8A**, which was well identified by its characteristic ^{31}P and ^{13}C NMR chemical shifts of δ −149.6 (P) and 200,5 (=C=) ppm, respectively, but they did not report the presence of any radialene in the reaction mixture.

(2) NMR Chemical Shifts. ^{31}P NMR spectroscopy is ideally suited for initial product identification and for monitoring the conversion of the alkenylidenephosphiranes to the more stable radialenes. Their ^{31}P NMR chemical shifts are compiled in Table 1 together with literature data on uncomplexed products.

The phosphorus chemical shifts of the alkenylidenephosphiranes are in all cases deshielded by an average of 40 ppm from those of the corresponding phospha[3]radialenes, which have smaller CPC angles and therefore have more shielded P-resonances. Only for **20** is this difference much less, i.e., 21.6 ppm, possibly indicating the presence of strain in **20A**; the $W(CO)_5$ complexed phospha[3]radialenes **19B** and **20B** have similar ^{31}P chemical shifts of ∼−154 ppm. For comparison, phosphirene complex **23** has a δ of −161.4 ppm.[17b] On the other
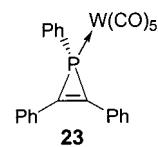
hand, the ^{31}P NMR resonance of **20A** of −112.8 ppm is at much lower field than the δ of −134.8 ppm for the related 2-isopropylidene-3,3-dimethylphosphirane (**12**-Me$_2$),[8] which may, however, illustrate an electronic effect of the allenic bond. The chemical shifts listed in Table 1 show a sensitivity to the nature of the P-substituent. Increasing its size from Me, Et, i-Pr, to t-Bu in the respective uncomplexed radialenes **2**, **3**, **4**, and **5** causes the phosphorus to deshield, by as much as 50 ppm. Resonance stabilization by a Ph group (**6**), on the other hand, has a significant shielding effect, while $W(CO)_5$ complexation (**2B**) causes a downfield shift of 30 ppm. Substituents at both the olefinic bonds and the phosphirane ring also influence the ^{31}P NMR chemical shift of **A**. We therefore decided to calculate the ^{31}P, ^{13}C, ^{1}H NMR chemical shifts (using the GIAO method) for the parent molecules **17** and **18** using MP2/6-31G* optimized

(20) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Chem. Soc. Chem. Commun.* **1984**, 45. Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.

(21) van Eis, M. J.; Nijbacker, T.; de Kanter, F. J. J.; de Wolf, W. H.; Lammertsma, K. Bickelhaupt, F. *J. Am. Chem. Soc.* **2000**, *122*, 3033.

(22) Wang, W.; Lake, C. H.; Lammertsma, K. *J. Am. Chem. Soc.* **1996**, *118*, 1690.
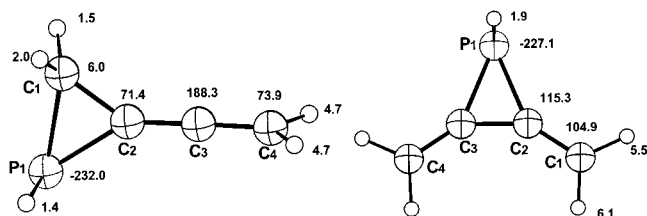
Figure 1. ^{31}P, ^{13}C, and ^{1}H NMR computed chemical shifts using MP2/6-31G* geometries for **17** (left) and **18**.
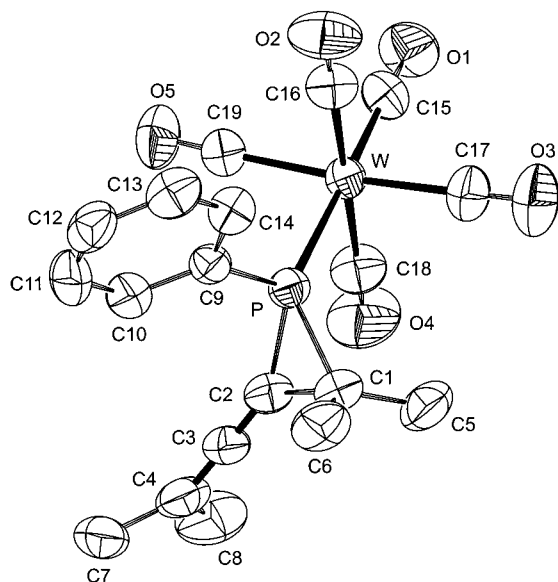

Figure 2. ORTEP presentation scaled to 50% probability ellipsoids of **19A**.

geometries and Me$_3$PO and Me$_4$Si as references, respectively. These data are displayed in Figure 1. They illustrate that the ^{31}P NMR chemical shifts of the parent systems are, as expected, at higher field but, maybe surprisingly, that they hardly differ from each other. The ^{31}P upfield shift of radialene **18** as compared to **2B** is due to the PBH vs PBMe substituent effect. We attribute the observed general downfield shift of ~40 ppm for the alkenylidene phosphiranes to the presence of substituents on the PCC ring. The calculated ^{13}C NMR chemical shift of 188 ppm for the allenic carbon (C(3)) of **17** agrees nicely with the δ of 200.5 ppm observed by Breen and Stephan for **8A**.

Alkenylidenephosphiranes. The single-crystal X-ray structures of **19A** and **20A** are the first of their kind. They are shown in Figures 2 and 3, respectively. Of the heterocyclic systems only a crystal structure of the sulfur analogue **24** has been
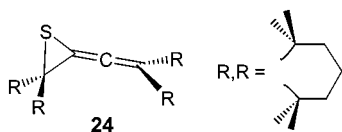
reported.[23] Selected bond lengths and angles are listed in Table 2, which also contains crystal structure data for **12**[8] and **13**[6] and MP2/6-31G* geometrical parameters of **17**, **25**, and C$_2$H$_5$P (**16**).

Structure **19A** has distinctly different PC bond lengths of which the 1.881(8) Å distal C(1)−P bond is ~0.1 Å longer than the proximal one; we refer to proximal P−C bonds as those attached to the allene unit and to distal PBC bonds as those

(23) Toyota, K.; Yoshimura, H.; Uesugi, T.; Yoshifuji, M. *Tetrahedron Lett.* **1991**, *32*, 6879.
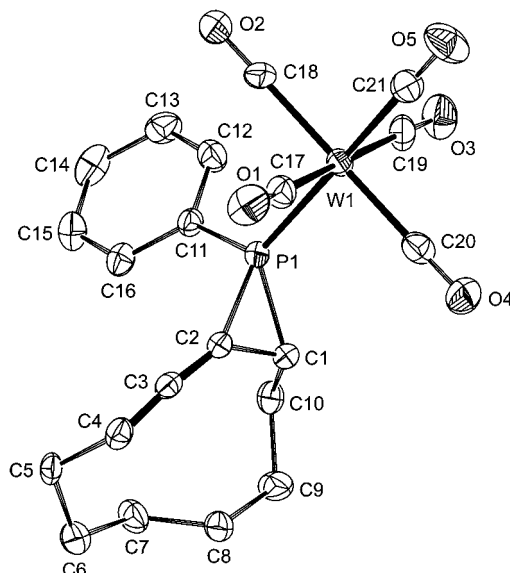

Figure 3. ORTEP presentation scaled to 50% probability ellipsoids of **20A**.

Table 2. Selected Bond Distances (in Å) and CPC Angles (in deg) for the X-ray Structures of **19A**, **20A**, **12**, and **13**, the Theoretical Structures of **17** and **25**, and the Microwave Structure of **16**

bond	19A	20A	12[a]	13[b]	17	25[a]	16[c]
P−C(1)	1.881(8)	1.855(6)	1.85(1)	1.855(7)	1.888	1.905	1.867
P−C(2)	1.784(8)	1.791(6)	1.776(8)	1.794(6)	1.824	1.818	1.867
C(1)−C(2)	1.505(12)	1.506(9)	1.47(1)	1.508(9)	1.466	1.460	1.502
C(2)−C(3)	1.291(11)	1.288(9)	1.31(1)	1.470(1) 1.475(10)	1.294	1.330	
C(3)−C(4)	1.303(12)	1.283(9)			1.315		
P−C(6)	1.818(7)	1.809(6)	1.799(7)	1.819(7)			
C(1)PC(2)	48.4(4)	48.8(3)	47.8(4)	48.6(3)	46.5	51.2	47.4

[a] Reference 8. [b] Reference 6. [c] Bowers, M.; Baudet, R. A.; Goldwhite, H.; Tang, R. *J. Am. Chem. Soc.* **1969**, *91*, 17.

that are not. This rather long and presumably weaker distal bond is fully in line with its suggested cleavage and subsequent C(3)−P bond formation sequence for the observed rearrangement that leads to **19B**. Slightly smaller differences in phosphirane PC bond lengths of ~0.07 Å were reported for **12** and **13**; the difference in SC bonds of **24** is 0.11 Å. MP2(fc)/6-31G* parent structure **17** also has a 0.064 Å longer distal than proximal PC bond; a similar difference in PC bond lengths of 0.087 Å for **25** has been explained to result from conjugative
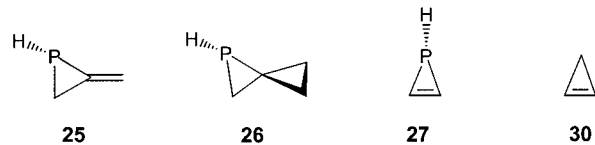
effects.[8] The olefinic bond lengths of **19A** are similarly as short as those calculated for **17**, but the experimental phosphirane C(1)BC(2) bond of 1.505(11) Å is distinctly longer (by ~0.05 Å) also compared to that of **12** (and its parent **25**).

Cyclic alkenylidenephosphirane **20A** has a strikingly different X-ray crystal structure, particularly with respect to the allenic C(2)=C(3)=C(4) unit, which is significantly bent at C(3) with an angle of 171.5(7)°, suggesting ring-induced strain. This bending contrasts the near allenic linearity in the acyclic structures **19A** (179.1(10)°), episulfide **24** (178.3°),[23] and several cyclopropane derivatives (178.0−179.4°).[24] Not only is the allene unit in **20A** bent, it is also twisted by 14.2(8)°; the dihedral angle between the C(1)C(2)C(3) and C(3)C(4)C(5) planes amounts to 75.8(8)°. Bending and twisting has been
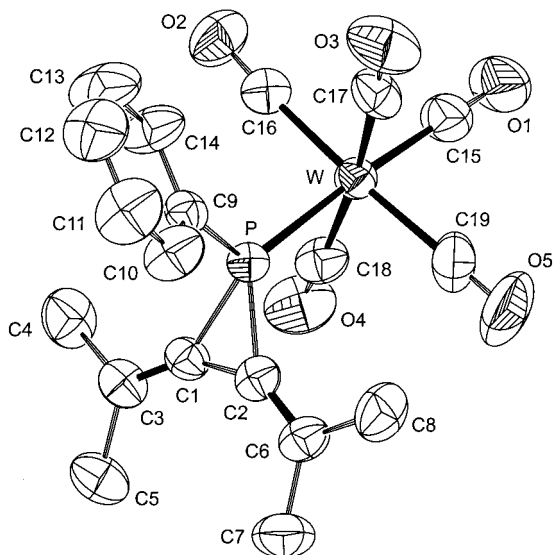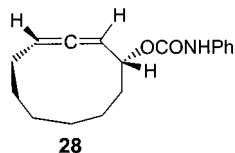
Phospha[3]radialenes

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Figure 4. ORTEP presentation scaled to 50% probability ellipsoids of **19B**.

recorded in the 10-membered ring allene **28**, which has a similar

28

bend angle of 170.7(4)°, but a smaller twist; its dihedral angle is 80.0(4)°.[25] These angles are larger in the corresponding 11-membered ring and smaller in the 9-membered ring, thereby illustrating the effect of ring strain.[25,26] On the basis of these arguments, we conclude that the strain in cyclic **20A** is higher than in acyclic **19A**. Additionally, this may also be reflected in the shorter olefinic bonds of **20A** and the reduced hyperconjugation with its PBC(1) bond, although these differences are within the experimental margins of error.

Phospha[3]radialenes. The single-crystal X-ray structures of **19B** and **20B** are shown in Figures 4 and 5, respectively. Selected bond lengths and angles are summarized in Table 3 together with those of the previously reported phospha[3]radialenes **1B** and **7B**, phosphatriangulene **14**, and phosphirene **23**.[17b] This table also contains MP2/6-31G* geometrical data for the parent **18** and phosphirene (**27**) structures. The data presented complements the already impressive set of diverse hetero[3]-radialenes, of which crystal structures have been reported for silicon,[27] germanium,[28] titanium,[29] and two sulfur[30] derivatives.

The phospha[3]radialenes **19B** and **20B** have slightly more contracted PC bonds (1.800(5)−1.815(6) Å) than **1B** (1.816 Å) and **7B** (1.826 Å) due to the stabilizing influence of the transition metal group. Also, the phosphorus substituents cause a significant reduction of the PC bond length, which is 1.845 Å at MP2/6-31G* for the parent molecule **18**. The phosphirane CC bond in **18** is consequently longer than in the experimental structures. Possible effects of strain from the hydrocarbon ring are not evident in cyclic **20B**. It is noteworthy that the P-phenyl of **20B** is oriented orthogonally to its PCC ring.

Figure 5. ORTEP presentation scaled to 50% probability ellipsoids of **20B**.

G3MP2 Strain Energies. To what extent does unsaturation increase the strain of the phosphirane ring? Recently, we evaluated the effect of spiroannulation (for **26** and **15**) and showed that the strain energy of 21.3 kcal/mol for the parent C_2H_5P system increases by 5.3 kcal/mol per spiro carbon as calculated with the G2(MP2) method.[7] Because of the electronic relationship between the cyclopropyl ring and the olefinic bond, a similar increase in SE may be anticipated for phosphiranes with exocyclic double bonds and this is indeed confirmed. SE values for **25**, **17**, and **18** of 28.1, 29,7, and 32.3 kcal/mol, respectively, are obtained with the more advanced G3(MP2) method[31,32] using the homodesmotic reactions a−c. At the same level of theory, phosphirane has a SE of 22.2 kcal/mol. Thus, its strain increases by 5.9 kcal/mol on introducing one exocyclic double bond and by another 4.2 kcal/mol on introducing the

(26) Interestingly, the bend (178.3(1)°) and twist (88.0(8)°) are hardly evident in the 10-membered allene **29**, which contains two carbonyl carbons. See: Carrell, H. L.; Glusker, J. P.; Covey, D. F.; Batzold F. H.; Robinson, C. H. *J. Am. Chem. Soc.*, **1978**, *100*, 4282.

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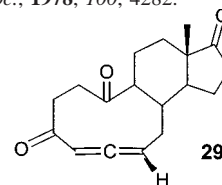
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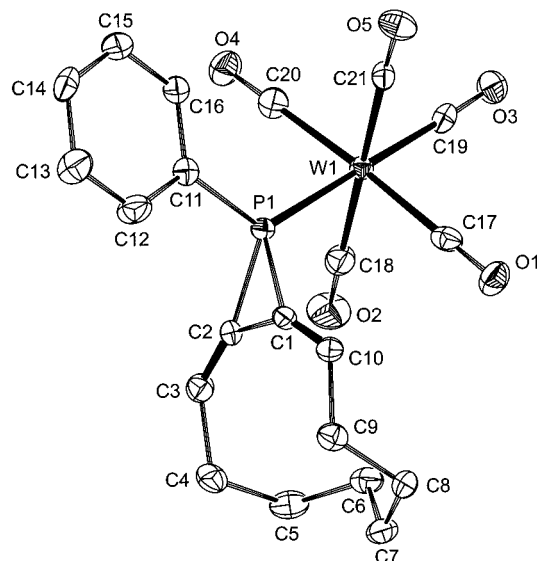(25) Luche, J.-L.; Damiano J.-C.; Cohen-Addad, C. *J. Am. Chem. Soc.* **1980**, *102*, 5370.

Table 3. Selected Bond Distances (in Å) and CPC Angles (in deg) for the X-ray Structures of **19B**, **20B**, **1B**, **7B**, **14**, and **23**, and the Theoretical Structures of **18** and **27**

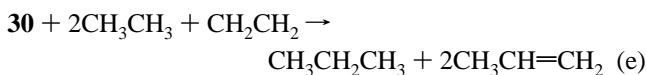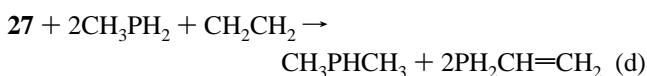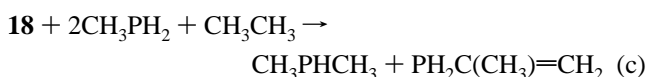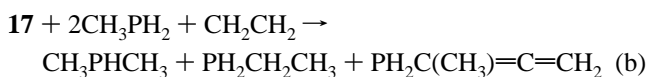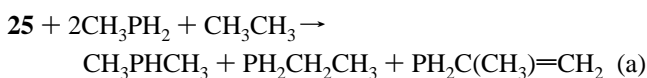| bond[a]	19B	20B	1B[b]	7B[c]	14[d]	23[e]	18	27
P−C(1)	1.815(6)	1.800(5)	1.816	1.827	1.807(8)	1.790(4)	1.845	1.845
P−C(2)	1.810(6)	1.809(6)	1.816	1.825	1.820(8)	1.787(4)	1.845	1.845
C(1)−C(2)	1.432(9)	1.434(6)	1.422	1.413	1.48(1)	1.307(6)	1.412	1.303
C(1)−C(α)	1.319(9)	1.334(7)	1.344	1.330	1.48(1)	1.453(6)	1.335	
					1.49(1)			
C(2)−C(β)	1.319(9)	1.327(6)	1.320	1.327	1.50(1)	1.474(6)	1.335	
					1.51(1)			
P−C(Ph)	1.822(6)	1.825(5)			1.833(8)	1.831(4)		
C(1)PC(2)	46.5(3)	46.8(2)	46.1	45.5	48.1(4)	42.8(2)	45.0	41.4
C(1)C(2)C(β)	148.0(6)	146.2(5)				150.0(4)	146.2	
C(2)C(1)C(α)	151.0(6)	146.7(5)				149.5(4)	146.2	
torsion	−1(2)	−10.9(14)	9.9		2.6(17)			
					3.7(16)			

^{a} C(α) and C(β) are respectively C(3) and C(6) for **19B** and C(10) and C(3) for **20B**. ^{b}Reference 9. ^{c}Reference 12. ^{d}Reference 7. ^{e}Reference 17b.

**Table 4.** G3MP2 Enthalpies (−au) and Strain Energies SE (kcal/mol)

structure	17	18	25	27
energy	495.966 00	495.970 58	457.956 20	418.707 15
SE[a]	29.3	32.3	28.3	39.0

^{a} The GMP2 enthalpies (−au) used in eqs a−e are as follows: CH_3PH_2, 381.923 20; CH_3CH_3, 79.646 71; CH_2CH_2, 78.430 77; CH_3PHCH_3, 421.162 24; $PH_2CH_2CH_3$, 421.155 35; $PH_2C(CH_3)CH_2$, 459.176 42; $PH_2C(CH_3)CH_2$, 497.188 85; PH_2CHCH_2, 419.942 15.

second double bond, rendering the incremental SE per unsaturated ring carbon slightly less than that for a spiro carbon. We reemphasize that ethenylidenephosphirane **17** is less strained (by 3.6 kcal/mol) than the thermodynamically more stable radialene **18**. It is further noteworthy that of the two three-membered rings with unsaturated ring carbons **18** has a 6.7 kcal/mol smaller SE than phosphirene **27** (39.0 kcal/mol, eq d). This difference is due not only to the 0.110 Å shorter ring CC bond of phosphirene but also to the unsaturation within the ring. This effect is further evident from the 14 kcal/mol difference in SEs between phosphirene and cyclopropene (**30**, 53 kcal/mol, eq e, same level) as the increase in SE on introducing an endocyclic C=C bond is less for phosphirane → phosphirene (ΔSE = 16.8 kcal/mol) than for cyclopropane → cyclopropene (ΔSE = 27 kcal/mol). For clarity, all ring SEs are summarized in Table 4.

$$25 + 2CH_3PH_2 + CH_3CH_3 \rightarrow$$
$$CH_3PHCH_3 + PH_2CH_2CH_3 + PH_2C(CH_3){=}CH_2 \text{ (a)}$$

$$17 + 2CH_3PH_2 + CH_2CH_2 \rightarrow$$
$$CH_3PHCH_3 + PH_2CH_2CH_3 + PH_2C(CH_3){=}C{=}CH_2 \text{ (b)}$$

$$18 + 2CH_3PH_2 + CH_3CH_3 \rightarrow$$
$$CH_3PHCH_3 + PH_2C(CH_3){=}CH_2 \text{ (c)}$$

$$27 + 2CH_3PH_2 + CH_2CH_2 \rightarrow$$
$$CH_3PHCH_3 + 2PH_2CH{=}CH_2 \text{ (d)}$$

$$30 + 2CH_3CH_3 + CH_2CH_2 \rightarrow$$
$$CH_3CH_2CH_3 + 2CH_3CH{=}CH_2 \text{ (e)}$$

B. 1,2-Diphospha[4]radialenes. Attempts to synthesize bis-phosphirylidenes **31** and spirodiphosphapentanes **32**, either from the cumulenes **19** and **20** directly or from their "primary" products **A** and **B**, respectively, proved to be unsuccessful. Instead, careful analysis of the above-discussed reaction of
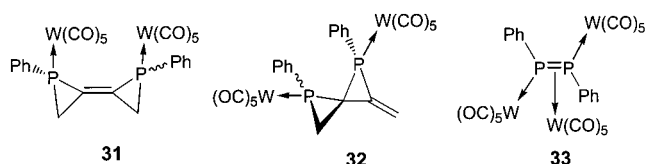
PhPW(CO)$_5$ with cyclic **20** (leading to **20A** and **20B**) showed
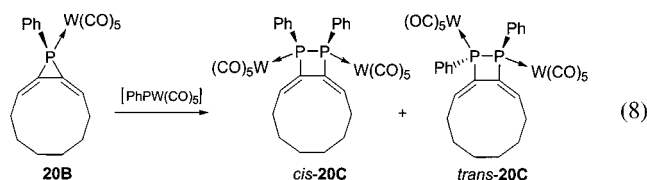
the formation of small amounts of the two unique 1,2-diphospha[4]radialenes, *cis*-**20C** and *trans*-**20C**. These also result from radialene **20B** (in addition to the common side product **33**)[33] but the corresponding products could not be identified in the reaction with acyclic **19** nor with **19B**. Repetitive chromatography and crystallization yielded the isomeric diphospha[4]-radialenes in pure form. We assume that these products are formed by a formal PhPW(CO)$_5$ insertion into a PC bond as was recently also observed in some, but not all, phosphirene complexes. The formation of the [4]radialenes was confirmed by determination of their single crystal X-ray structures, shown in Figures 6 and 7. We are aware of only one other crystal structure for a 1,2-diphospha[4]radialene, namely, uncomplexed *trans*-**4C**, reported by Brieden and Kellersohn.[15] Selected bond lengths and angles of these three crystal structures are summarized in Table 5.

The central four-membered ring in the 1,2-diphospha[4]-radialenes are similarly puckered with angles (defined by the P(1)P(2)C(1) and P(2)C(2)C(1) planes) of 148.3(3)° and 129.6-(4)° for *trans*-**20C** and *cis*-**20C**, respectively. The extend of puckering appears not to be influenced by the two transition metal groups as the P(1)C(1)C(2)P(2) torsion angles of 26.0-(3)° for *cis*-**20C** and 27.7(3)° for *trans*-**20C** are similar to the 23.2° angle for uncomplexed *trans*-**4C**. As a result of ring puckering, the butadiene unit is rather twisted with a dihedral angle of 47.0(10)° for *cis*-**20C** and a still larger angle of 61.9-(9)° for *trans*-**20C**. Also phospha[3]radialene **20B** shows torsion between the double bonds of the butadiene unit, be it only by −10.9(14)°, which in this case is solely due to the 10-membered ring-induced conformational twist. It is then not surprising that

(33) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.
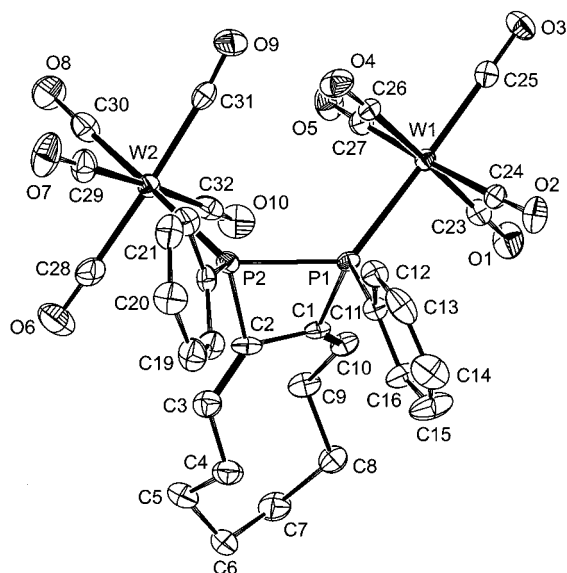
Phospha[3]radialenes

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Figure 6. ORTEP presentation scaled to 50% probability ellipsoids of cis-**20C**.

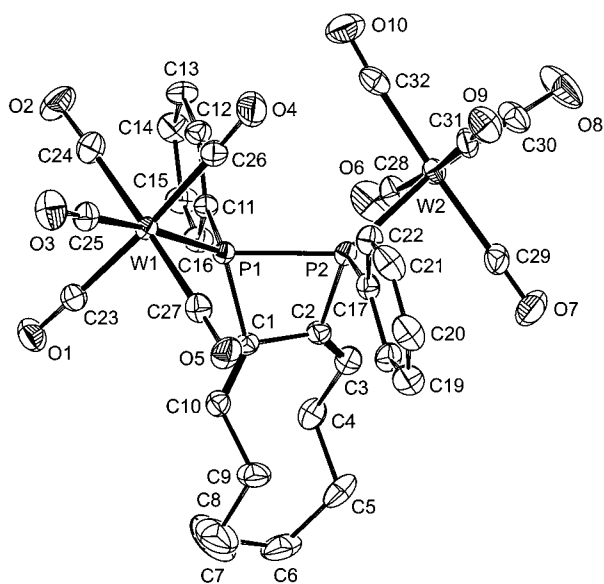**Figure 7.** ORTEP presentation scaled to 50% probability ellipsoids of trans-**20C**.

the endocyclic CC bond of the PCC ring in **20B** (1.434(6)°) and of the PPCC ring in *cis*-**20C** (1.475(8)°) and *trans*-**20C** (1.487(7)°) appears to increase with increased twisting of the butadiene component.

The ^{31}P NMR spectrum of the trans isomer shows a single resonance at 63.4 ppm suggesting a C_2-like symmetrical (or rapidly equilibrating) structure, but we were unable to confirm this by ^{13}C NMR due to a lack of adequate pure material. The crystal structure, however, gives slightly different PC bond lengths, albeit within the margins of error. Due to the ring puckering, the ^{31}P NMR spectrum of the cis isomer shows two dissimilar and more shielded resonances (δ = 58.2 and 37.1 ppm, $^1J_{PP}$ = 55 Hz), which compare well with those of di-W(CO)$_5$ complexed 1,2-dihydro-1,2-diphosphetes.

The ^{31}P NMR spectrum of the reaction mixture of **20C** also contains small resonances δ 24.1 (d), 10.3 (d), and −27.9 ppm (t, $^1J_{PP}$ = 240 Hz), which we speculatively attribute to the presence of a minute amount of a triphospha[5]radialene.

C. Diels−Alder Reactions. Phospha[3]radialenes contain a diene unit and hence could be susceptible to [2+4] Diels−Alder

(DA) cycloadditions as was demonstrated by Ando for the reactions of the sila- and germa[3]radialenes **34** with 4-methyl- and 4-phenyl-1,2,4-triazoline-3,5-dione (MTAD, PTAD) (eq 9).[27,28] To examine whether the phospha derivatives **19B** and

(9)

(10)

19B $R_1 = R_2 = R_3 = R_4 = $ Me
20B $R_1 = R_3 = $ H; R_2-$R_3 = $ -(CH$_2$)$_6$-
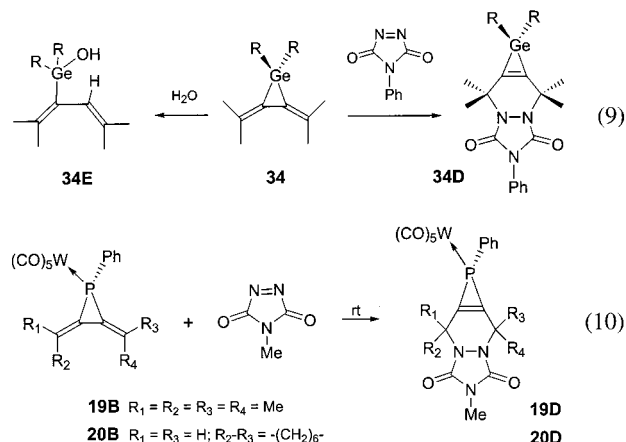
20B behave analogously, we used MTAD for the DA reactions (eq 10).

Reaction in benzene of acyclic **19B** with the reddish MTAD occurs with rapid loss of color to give the expected tricyclic phosphirene **19D**. Characteristic are the ^{31}P and ^{13}C NMR chemical shifts of the phosphirene ring atoms at −75.9 and 144.0 ppm, respectively. This DA product, however, reacts with the moisture in chloroform over a period of 2 weeks at 5 °C to fully convert into **19E**, which was identified by its ^{31}P, ^{13}C,
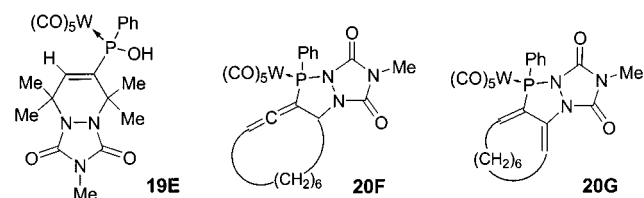
and ^{1}H NMR and HRMS spectroscopic data. Characteristic are its olefinic CH=C group and its phosphine ^{31}P NMR resonance at 114 ppm. This H$_2$O induced ring-opened product **19E** is similar to **34E**, which Ando reported to result from hydrolysis of a germa[3]radialene (eq 9).[28] Also Marinetti and Mathey[34] reported similar nucleophilic-induced ring openings of substituted phosphirenes.

The reaction of cyclic **20B** with MTAD is slower and behaves differently. The ^{31}P NMR spectrum of the reaction mixture showed the appearance of two new resonances at 52.6 and −84.1 ppm in a ratio of 9 to 1. We assume the minor product to be tricyclic structure **20D**, because of the similarity of its ^{31}P NMR resonance to that of **19D**, but too little material was obtained to establish this with certainty. However, the major product could be isolated, and on the basis of its ^{31}P, ^{13}C, and ^{1}H NMR data with supporting APT and CH-COSY measurements and a HRMS exact mass measurement, we assign it tricyclic structure **20F**; characteristic is its allenic ^{13}C NMR resonance at δ 204 ppm. While selected phosphiranes and azaphosphiranes are known to react with alkenes[17b] and imines[35] to give stable five-membered ring structures, we are unaware of a similar process for phosphirenes. Product **20F** must result from an interaction of the N=N bond of MTAD with the phosphirene ring, but a

(34) Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061. Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700.

(35) Huy, N. H. T.; Ricard, L.; Mathey, F. *Heteroatom Chem.* **1998**, *9*, 597.

Table 5. Selected Bond Distances (in Å) and CPC Angles (in deg) for the X-ray Structures of 1,2-diphospha[4]radialenes *cis*-**20C**, *trans*-**20C**, and **4C**

	cis-**20C**	*trans*-**20C**	*trans*-**4C**[a]		*cis*-**20C**	*trans*-**20C**	*trans*-**4C**
P1−C1	1.835(5)	1.840(5)	1.847(3)	P1−C1−C2	101.1(4)	100.0(3)	100.1(2)
P2−C2	1.820(6)	1.825(5)	1.847(3)	C1−C2−P2	99.8(4)	99.9(4)	100.1(2)
C1−C2	1.475(8)	1.487(7)	1.468(3)	C2−P2−P1	76.4(2)	75.99(18)	76.6(1)
P1−P2	2.284(2)	2.2891(18)	2.245(1)	P2−P1−C1	74.89(19)	75.20(17)	76.6(1)
C=C1	1.334(8)	1.321(7)	1.336(4)	Σ∠(4-ring)	352.2	351.1	352.4
C2=C	1.335(8)	1.333(8)	1.336(4)	C=C1−C2=C	47.0(10)	61.9(9)	57.8(3)
				P1−C1−C2−P2	26.0(3)	27.7(3)	23.2(1)

[a] Reference 15.

direct PC insertion would, however, result in **20G**, in analogy with the insertion of phosphinidenes to give 1,2-dihydro-1,2-diphosphetes.[36] The unexpected formation of **20F** suggests a MTAD-induced (nucleophilic) ring opening of phospha[3]-triangulene **20B** with subsequent ring closure to the apparently thermodynamically more stable **20F**. However, **20F** can also be explained to result from a concerted $[(\sigma^2 + \pi^2) + \pi^2]$ mechanism. Such a mechanism has been extensively investigated by Pasto for the cycloaddition reactions of alkenylidenecyclopropanes with dienophiles such as MTAD to give related five-membered ring structures.[37] We conclude that the difference in reactivity between **19B** and **20B** for cycloaddition has its origin in the torque of the diene unit of the cyclic radialene enabling it to follow a different cycloaddition path.

Conclusions

Phospha[3]radialenes can be conveniently synthesized from the 1,2-cycloaddition of in situ-generated phosphinidene complex PhPW(CO)$_5$ to readily available cumulenes. Alkenylidene-phosphiranes are obtained as intermediate products as PhPW-(CO)$_5$ has a preference for the terminal double bond of the cumulene. However, these products cleanly rearrange to the phospha[3]radialene complexes, supposedly by a phosphirane ring opening/closure sequence. The reaction has been demonstrated for the simple tetramethylcumulene and the strained cyclic 1,2,3-cyclodecatriene. Single-crystal X-ray structures were obtained both for the kinetic products **19A** and **20A** and for the thermodynamically preferred radialenes **19B** and **20B**. The structural and NMR spectroscopic properties of the radialenes compare well with literature data on related systems. The crystal structures of **19A** and **20A** are the first of their kind. They show the distal PC bond to the allenic group to be significantly elongated. The higher reactivity of the more strained bicyclic **20A** is evident from the significant bending (172.1°) and twisting (15°) that is present in its allenic unit.

Phosph[4]radialenes result from the reaction of an additional equivalent of PhPW(CO)$_5$ with phospha[3]radialene **20B**. Two isomers are formed, i.e., *cis*-**20C** and *trans*-**20C**. X-ray crystal structures were obtained for both, which is also a first. Both isomers have puckered PPCC rings (∼150°), and as a result, the olefinic bonds of their butadiene units are substantially twisted from planarity. No phospha[4]radialenes are obtained in the reaction of PhPW(CO)$_5$ with **19B**. The higher reactivity of **20B** toward the phosphinidene is considered to originate from the influence of the 10-membered hydrocarbon ring on the phosphirane ring.

Phospha[3]radialenes **19B** and **20B** undergo different Diels−Alder reactions with methyl-1,2,4-triazole-3,5-dione. The "normal" 4+2 cycloaddition product **19D** is formed in the reaction with the acyclic radialene **19B**. The ring-induced strain in this compound is evident from the rather high sensitivity of the phosphirane ring toward hydrolysis, resulting in **19E**. An alternative $[(\sigma^2 + \pi^2) + \pi^2]$ cycloaddition occurs with cyclic radialene **20B** that involves the participation of one of its PC bonds. Because of the presence of an allenic unit, **20F** cannot be formed by a simple insertion of MTAD into the phosphirane ring. The formation of product **20F** is reminiscent to the similar reactions of alkenylidenecyclopropanes with dienophiles such as TMAD.

Ab initio theoretical studies on the parent systems, using the G3(MP2) method, show phospha[3]radialene to be 3.6 kcal/mol more stable than ethenylidenephosphirane. Their strain energies are 32.3 and 29.7 kcal/mol, respectively, as obtained from isodesmic equations using G3(MP2) calculated heats of formation for the molecules of these equations. Phospha[3]-radialene illustrates that the SE of 22.2 kcal/mol of phosphirane increases by 5.9 and 4.2 kcal/mol on subsequently introducing exocyclic double bonds. Still, the SE of phospha[3]radialene is less than the 39.0 kcal/mol of the more condensed phosphirene.

Optimized MP2(fc) geometries of the parent molecules compare well with the X-ray crystal structures of **19A** and **19B**, taking substituent effects into account. Their GIAO calculated ^{13}C and ^{31}P NMR chemical shifts compare well with available literature data on derivatized uncomplexed systems.

Experimental Section

NMR spectra were recorded on a Bruker MSL 400 and a Bruker AC 200. Chemical shifts are referenced in ppm to internal Me$_4$Si for the ^{1}H and ^{13}C NMR spectra and to external 85% H$_3$PO$_4$ for the ^{31}P NMR spectra. Downfield shifts are reported as positive. Toluene was dried by distillation from sodium and Et$_2$O from LiAlH$_4$. The oxygen-sensitive 2,5-dimethyl-2,3,4-hexatriene (**2**)[38] was prepared from the reaction of 3,4-diiodo-2,5-di-methyl-2,4-hexadiene[39] (synthesized from 2,5-dimethyl-3-hexyne-2,5-diol with hydriodic acid) and butyllithium in diethyl ether at −50 °C. 1,2,3-Cyclodecatriene (**20**)[40] was synthesized from cyclooctene in a four steps, starting with its conversion into 1,2-cyclononadiene[41] via a dibromocarbene addition (by means of phase-transfer catalysis in aqueous medium)[42] followed by treatment with MeLi in diethyl ether at −40 °C. Repetition of the carbene addition and the ring expansion reactions gives the very oxygen sensitive 1,2,3-cyclodecatriene via 10,10-dibromobicyclo[7.1.0]decene. Each compound was purified by a vacuum distillation, except for 1,2,3-

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Phospha[3]radialenes

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cyclodecatriene. The synthesis of the phosphinidene precursor **10** is described in ref 17. The reaction of **10** with the cyclic cumulene is described first because of its more diverse product composition.

PhPW(CO)₅ Addition to 1,2,3-Cyclodecatriene (20). Freshly prepared and carefully dried **20** (0.8 g, 6 mmol) and **10** (3.5 g, 5.4 mmol) were heated for 3 h at 55 °C in 15 mL of toluene with CuCl (0.11 g). Monitoring of the reaction mixture, using ^{31}P NMR, showed the appearance of both alkenylidenephosphirane **20A** (δ −131.4 ppm) and phospha[3]radialene **20B** (δ −153.0 ppm) in a ratio of ∼1:2. The reaction mixture was evaporated to dryness and chromatographed on silica gel with hexane. The first fraction (0.3 g, 10%) contains mostly alkenylidenephosphirane **20A** (**20A**:**20B** = 3:1), fractional crystallization from hexane gave **20A** as colorless crystals. The second fraction (1.1 g, 36%), a mixture of alkenylidenephosphirane **20A** and phospha-[3]radialene **20B** (**20A**:**20B** = 1:3), was converted completely to **20B** by heating in toluene at 100 °C during 2 h. Crystallization from hexane gave **20B** as colorless crystals. Minor amounts of yellow-green crystals *trans*-**20C** and *cis*-**20C** were obtained from fractions 3 and 4, respectively.

20A: mp 118 °C; ^{31}P NMR (C₆D₆) δ −131.4 ($^1J_{PW}$ = 250.5 Hz); ^{13}C NMR (C₆D₆) δ 25.7 (d, J_{CP} ≤ 2.5 Hz, CH₂), 26.0 (d, J_{CP} = 4.8 Hz, CH₂), 26.9 (s, CH₂), 27.3 (s, CH₂), 27.5 (d, J_{CP} = 8.9 Hz, CH₂), 30.4 (d, JCP = 2.8 Hz, C=C=CH-CH₂), 30.8 (d, $^2J_{CP}$ = 10.5 Hz, CH-ring), 83.3 (d, $^1J_{CP}$ = 7.4 Hz, C=C=CH), 95.4 (d, $^3J_{CP}$ = 6.9 Hz, C=C=CH), 128.8 (d, $^3J_{CP}$ = 10.0 Hz, *m*-Ar), 130.7 (d, $^4J_{CP}$ ≤ 2 Hz, *p*-Ar), 132.5 (d, $^2J_{CP}$ = 12.0 Hz, *o*-Ar), 132.2 (d, $^1J_{CP}$ = ± 24 Hz, *i*-Ar), 195.9 (d, $^2J_{CP}$ = 7.9 Hz, *cis*-CO), 198.3 (d, $^2J_{CP}$ = 30.2 Hz, *trans*-CO), 202.0 (s, C=C=C); ^{1}H NMR (C₆D₆) δ 0.82−1.23 (m, 7H, CH₂), 1.38−1.5 (m, 2H, CH₂), 1.55−1.7 (m, 1H, C=C=CH−CH₂), 1.7−1.8 (m, 1H, CH₂) 2.05−2.15 (m, 1H, C=C=CH−CH₂), 2.15−2.22 (m, 1H CH-ring), 5.3−5.4 (d pseudo q, $^{3+3+5}J_{HH}$ = 7.5 and $^4J_{HP}$ = 4.7, 1H, C=C−H), 6.85−6.98 (m, 3H, Ar−H), 7.35−7.45 (m, 2H, *o*-Ar−H).

20B: mp 110 °C; ^{31}P NMR (C₆D₆) δ −153.0 ($^1J_{PW}$ = 248.2 Hz); ^{13}C NMR (C₆D₆) δ 27.1 (s, CH₂), 30.1 (s, CH₂), 32.1 (d, $^4J_{CP}$ = 11.0 Hz, C=C−CH₂), 122.3 (s, C=CH), 128.9 (d, $^3J_{CP}$ = 10.7 Hz, *m*-Ar), 130.6 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ar), 131.7 (d, $^2J_{CP}$ = 14.3 Hz, *o*-Ar), 134.0 (s, C=CH), 135.0 (d, $^1J_{CP}$ = 18.5 Hz, *i*-Ar), 196.0 (d, $^2J_{CP}$ = 8.1 Hz, *cis*-CO), 198.4 (d, $^2J_{CP}$ = 28.8 Hz, *trans*-CO); ^{1}H NMR (C₆D₆) δ 1.4−1.78 (m, 8H, CH₂), 2.5−2.65 (m, 4H, C=C−CH₂), 6.49−6.60 (d t, $^3J_{HP}$ = 17.5 Hz and $^3J_{HH}$ = 7.7 Hz, 2H, C=C−H), 7.35−7.42 (m, 3H, Ar−H), 7.48−7.57 (m, 2H, o-Ar−H); HRMS (EI) (*m/e*) for C₂₁H₁₉-PO₅182W₂: calcd 564.0453, found 564.0454 ± 0.0010.

***trans*-20C:** mp 248 °C (dec); ^{31}P NMR (C₆D₆) δ 63.4 (s, $^1J_{PW}$ = 201.6 Hz); ^{1}H NMR (C₆D₆) δ 1.05−1.24 (m, 4H, CH₂), 1.50−1.70 (m, 4H, CH₂), 1.55−1.92 (m, 2H, CH₂), 2.22−2.35 (m, 2H, CH₂), 6.18−6.28 (m, 2H, C=C−H), 7.06−7.14 (m, 2H, Ar−H), 7.22−7.28 (m, 4H, Ar−H), 7.62−7.72 (m, 4H, Ar−H); HRMS (EI) (*m/e*) for C₃₂H₂₄P₂O10184W₂: calcd 997.9865, found 997.986 ± 0.003.

***cis*-20C:** mp 210 °C (dec); ^{31}P NMR (C₆D₆) δ 58.22 (d, $^1J_{PP}$ = 55 Hz), 37.05 (d, $^1J_{PP}$ = 55 Hz); ^{1}H NMR (C₆D₆) δ 1.23−1.58 (m, 8H, CH₂), 2.02−2.26 (m, 4H, CH₂), 5.9−6.3 (m, 2H, C=C−H), 6.76−6.68 (m, 4H, Ar−H), 6.86−6.76 (m, 2H, Ar−H), 6.86−6.96 (m, 4H, Ar−H); HRMS (EI) (*m/e*) for C₃₂H₂₄P₂O₁₀184W₂: calcd 997.9865, found 997.986 ± 0.005.

PhPW(CO)₅ Addition to 2,5-Dimethyl-2,3,4-hexatriene (19). The reaction was executed as described for **20** giving a crude mixture of alkenylidenephosphirane **19A** and phospha[3]radialene **19B** in a 1:1 ratio. After column chromatography, a 370 mg (70%) yield of a colorless solid was obtained containing mostly alkenylidenephosphirane **19A** and a small amount of phospha[3]radialene **19B**; fractional crystallization from hexane gave **19A** as colorless crystals. Part of the crude mixture of **19A** and **19B** was converted completely to **19B** by heating in toluene at 100 °C during 2 h. Crystallization from hexane gave **19B** as colorless crystals.

19A: mp 93−94 °C; ^{31}P NMR (CDCl₃) δ −112.8 ($^1J_{PW}$ = 279.1 Hz); ^{13}C NMR (C₆D₆) δ 20.7 (d, $^2J_{CP}$ = 3.8 Hz, CH₃), 21.1 (d, $^2J_{CP}$ = 3.9 Hz, CH₃), 22.6 (d, $^5J_{CP}$ = 2.5 Hz, CH₃), 26.3 (d, $^5J_{CP}$ = 5.6 Hz, CH₃), 32.2 (d, $^1J_{CP}$ = 10.6 Hz, P*C*Me₂) 88.7 (s, C=C=*C*Me₂), 101.6 (d, $^3J_{CP}$ = 7.3 Hz, C=C=*C*Me₂), 128.5 (d, $^3J_{CP}$ = 9.7 Hz, *m*-Ar), 130.2 (d, $^4J_{CP}$ = 2.2 Hz, *p*-Ar) 132.2 (d, $^2J_{CP}$ = 11.7 Hz, *o*-Ar), 134.9 (d, $^1J_{CP}$ = 21.6 Hz, *i*-Ar), 195.2 (s, C=*C*=C), 195.8 (d, $^2J_{CP}$ = 8.0 Hz,

cis-CO), 198.3 (d, $^2J_{CP}$ = 29.9 Hz, *trans*-CO); ^{1}H NMR (C₆D₆) δ 1.08 (d, $^3J_{HP}$ = 13.1 Hz, 3H, CH₃), 1.46 (d, $^3J_{HP}$ = 19.4 Hz, 3H, CH₃), 1.79 (d, $^5J_{HP}$ = 4.9 Hz, 3H, C=C−CH₃), 1.85 (d, $^5J_{HP}$ = 5.0 Hz, 3H, C=C−CH₃), 7.29−7.47 (m, 5H, Ar−H); MS (*m/e*; relative intensity) 540 (M⁺, 35.0), 512 (M − CO, 2.0), 484 (M − 2CO, 13.8), 456 (M − 3CO, 25.2), 428 (M − 4CO, 17.1), 400 (M − 5CO, 100), 348 (PhP − W(CO)₂, 33.4), 320 (PhPW(CO), 56.8), 292 (PhPW, 51.4), 108 (C₈H₁₂, 24.3), 77 (C₆H₅, 79.2).

19B: mp 110−111 °C; ^{31}P NMR (CDCl₃) δ −155.0 ($^1J_{PW}$ = 246.2 Hz); ^{13}C NMR (CDCl₃) δ 24.4 (d, $^3J_{CP}$ = 10.3 Hz, CH₃), 25.5 (d, $^3J_{CP}$ = 8.8 Hz, CH₃), 116.6 (s, *C*=CMe₂), 128.5 (d, $^3J_{CP}$ = 10.4 Hz, *m*-Ar), 129.9 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ar), 131.0 (d, $^2J_{CP}$ = 13.9 Hz, *o*-Ar), 133.9 (d, $^2J_{CP}$ = 2.2 Hz, C=*C*Me₂), 135.2 (d, $^1J_{CP}$ = 17.9 Hz, *i*-Ar), 195.7 (d, $^2J_{CP}$ = 8.0 Hz, *cis*-CO), 198.2 (d, $^2J_{CP}$ = 28.2 Hz, *trans*-CO); ^{1}H NMR (CDCl₃) δ 2.12 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 7.32−7.50 (m, 5H, ArH); MS (*m/e*; relative intensity) 540 (M⁺, 29.4), 512 (M − CO, 2.5), 484 (M −2CO, 11.8), 456 (M − 3CO, 26.6), 428 (M − 4CO, 16.6), 348 (PhP − W(CO)₂, 31.2), 320 (PhPW(CO), 60.1), 292 (PhPW, 51.4), 108 (C₈H₁₂, 18.8), 77 (C₆H₅, 76.9). Anal. Calcd for C₁₆H₁₃-PWO₅: C, 42.25; H, 3.17. Found: C, 42.22; H, 3.04.

Phospha[4]radialenes 20C. Phospha[3]radialene **20B** (0.18 g, 0.3 mmol) and **10** (0.2 g, 0.3 mmol) were heated for 3 h at 55 °C in 2 mL of toluene with CuCl (0.11 g). Monitoring of the reaction mixture using ^{31}P NMR showed the appearance of phospha[4]radialene *cis*-**20C** and **33**.[33] Extra phosphinidene precursor (0.15 g) was added, and the reaction mixture was heated until no starting materials were detected by monitoring with ^{31}P NMR. The reaction mixture was evaporated to dryness and purified by column chromatography on silica gel with pentane/benzene (4:1). The first fraction (0.12 g) contains, according to the ^{31}P NMR spectrum, both phospha[4]radialene *cis*-**20C** (δ = 63.9 ppm (s), $^1J_{PW}$ = 201.6 Hz) and triphospholane (δ = 24.1 ppm (d), 10.3 ppm (d), −27.9 ppm (t), $^1J_{PP}$ = 240 Hz, 5:3). These products could not be separated, and it was not possible to convert the mixture completely to the triphospholane. The second fraction was diphosphene **33**.

Reaction of 19B with MTAD. To a solution of 27.5 mg (0.05 mmol) of **19B** in benzene was added 6.1 mg (0.05 mmol) of MTAD. The reaction mixture was stirred at room temperature until it fully decolorized. The solution was filtered, and the solvent was removed in vacuo. The crude product was dissolved in CDCl₃.

19D: ^{31}P NMR (CDCl₃) δ −75.9 ($^1J_{PW}$ = 284.1 Hz); ^{13}C NMR (CDCl₃) δ 23.7 (s, CH₃), 24.4 (s, CH₃), 25.3 (s, NCH₃), 62.7 (d, $^2J_{CP}$ = 5.8 Hz, *C*Me₂), 129.1 (d, $^3J_{CP}$ = 10.7 Hz, *m*-Ar), 131.2 (d, $^2J_{CP}$ = 16.9 Hz, *o*-Ar), 131.9 (d, $^4J_{CP}$ = 2.3 Hz, *p*-Ar), 139.3 (d, $^1J_{CP}$ = 5.6 Hz, *i*-Ar), 144.0 (s, $^1J_{CP}$ = 7.1 Hz, *C*=C), 153.9 (s, N-*C*=O), 195.9 (d, $^2J_{CP}$ = 8.4 Hz, *cis*-CO), 197.0 (d, $^2J_{CP}$ = 33.6 Hz, *trans*-CO); ^{1}H NMR (CDCl₃) δ 1.75 (s, 6H, CH₃), 1.80 (s, 6H, CH₃), 3.08 (s, 3H, NCH₃) 7.42−7.56 (m, 5H, ArH); HRMS (EI) (*m/e*) for C₂₂H₂₀N₃O₇P182W: calcd 653.0549 found 653.0550 ± 0.0002.

19E: ^{31}P NMR (CDCl₃) δ 114.0 ($^1J_{PW}$ = 280.8 Hz); ^{13}C NMR (CDCl₃) δ 23.6 (s, CH₃), 24.0 (s, CH₃), 24.4 (s, CH₃), 24.9 (s, NCH₃), 25.2 (s, CH₃), 58.8 (d, $^3J_{CP}$ = 16.7 Hz, *C*Me₂), 63.3 (d, $^2J_{CP}$ = 4.2 Hz, *C*Me₂), 128.0 (d, $^2J_{CP}$ = 13.5 Hz, *o*-Ar), 128.5 (d, $^3J_{CP}$ = 10.0 Hz, *m*-Ar), 130.4 (d, $^4J_{CP}$ = 2.3 Hz, *p*-Ar), 130.7 (d, $^1J_{CP}$ = 31.8 Hz, *i*-Ar), 141.7 (s, $^1J_{CP}$ = 7.1 Hz, H−C=C), 145.9 (s, $^2J_{CP}$ = 29.2 Hz, H-*C*=C), 153.5 (s, N-*C*=O), 153.7 (s, N-*C*=O), 196.5 (d, $^2J_{CP}$ = 7.5 Hz, *cis*-CO), 198.5 (d, $^2J_{CP}$ = 33.6 Hz, *trans*-CO); ^{1}H NMR (CDCl₃) δ 1.45 (s, 3H, CH₃), 1.55 (s, 3H, CH₃), 1.65 (s, 3H, CH₃) 1.79 (s, 3H, CH₃), 2.79 (s, 3H, NCH₃), 6.30 (d, $^3J_{HP}$ = 23.6 Hz, 1H, H−C=C), 7.4−7.6 (m, 5H, ArH); HRMS (EI) (*m/e*) for C₂₂H₂₂N₃O₈P182W: calcd 671.0654, found 671.0654 ± 0.0003.

Reaction of 20B with MTAD. The reaction was executed on a 0.20-mmol scale in a fashion similar to that described for **19B**. The ^{31}P NMR spectrum of the crude reaction mixture showed two resonances at 52.6 and −84.1 ppm (9:1). The main product (**20F**) was isolated as a yellow solid by means of column chromatography (pentane/benzene) in a yield of 59% (79.6 mg).

20F: ^{31}P NMR (CDCl₃) δ 52.6 ($^1J_{PW}$ = 288.5 Hz); ^{13}C NMR (CDCl₃) δ 19.7 (s, CH₂), 21.2 (s, CH₂), 24.5 (s, CH₂), 24.9 (s, CH₂), 25.6 (s, NCH₃), 26.9 (d, $^3J_{CP}$ = 1.4 Hz, N−CH−CH₂), 27.0 (d, $^4J_{CP}$ = 4.3 Hz, C=C=CH−CH₂), 60.2 (s, N−CH), 101.2 (d, $^3J_{HP}$ = 12.8 Hz, C=C=

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Table 6. Crystal Data and Data Collection Procedures for **19A**, **19B**, **20A**, **20B**, *cis*-**20C**, and *trans*-**20C**

	19A	**19B**	**20A**	**20B**	*cis*-**20C**	*trans*-**20C**
formula	$C_{19}H_{17}O_5PW$	$C_{19}H_{17}O_5PW$	$C_{21}H_{19}O_5PW$	$C_{21}H_{19}O_5PW$	$C_{32}H_{24}O_{10}P_2W_2$	$C_{32}H_{24}O_{10}P_2W_2$
fw	540.15	540.15	566.18	566.18	998.15	998.15
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
space gp	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	7.031(2)	8.541(2)	9.910(3)	10.8902(12)	10.2375(11)	9.5208(4)
b (Å)	9.599(2)	10.498(2)	31.360(10)	9.8451(11)	10.6317(9)	11.1008(7)
c (Å)	15.959(3)	12.943(3)	6.826(3)	20.6783(17)	15.3774(15)	16.0527(12)
α (deg)	86.30(2)	66.21(2)	90	90	85.707(7)	90.116(6)
β (deg)	78.29(2)	81.63(2)	103.95(3)	112.802(7)	86.277(9)	95.543(5)
γ (deg)	83.37(2)	72.12(2)	90	90	82.092(8)	97.452(4)
V (Å)^3	1046.7(4)	1010.3(4)	2058.8(12)	2043.8(4)	1650.6(3)	1674.21(18)
Z	2	2	4	4	2	2
density (g/cm^3)	1.714	1.776	1.827	1.840	2.008	1.980
μ (mm^{-1})	5.62	5.82	5.72	5.76	7.12	7.02
cryst color	colorless	colorless	colorless^a	colorless	yellowish	yellowish
cryst size (mm^{-3})	$0.49 \times 0.30 \times 0.23$	$0.47 \times 0.29 \times 0.17$	$0.53 \times 0.18 \times 0.18$	$0.33 \times 0.25 \times 0.25$	$0.50 \times 0.37 \times 0.25$	$0.45 \times 0.30 \times 0.18$
transmission	0.11−0.58	0.12−0.59	0.12−0.59	0.30−0.74	0.28−0.72	0.24−0.70
$\sin(\theta/2\theta)_{max}$	0.65	0.65	0.65	0.65	0.63	0.65
refl measd/unique	5349/4804	4971/4618	8685/4716	4878/4669	6523/6278	9358/7684
R_{int}	0.068	0.048	0.107	0.042	0.040	0.034
params/restraints	239/0	239/0	261/0	253/0	415/0	415/0
R (obs/all refl)	0.0468/0.0660	0.0378/0.0532	0.0448/0.0585	0.0314/0.0470	0.0309/0.0391	0.0340/0.0449
wR2 (obs/all refl)	0.1202/0.1289	0.0949/0.1013	0.1104/0.1187	0.0623/0.0669	0.0714/0.0748	0.0788/0.0838
GooF	1.058	1.057	1.030	1.038	1.040	1.030
resid e density (e/A^3)	−2.13/1.34	−1.68/1.46	−2.63/2.23	−0.81/0.65	−2.38/2.35	−1.86/2.17

^{a} Crystal turns orange during X-ray exposure.

*C*H), 108.3 (d, $^1J_{CP} = 50.0$ Hz, P−*C*≡C≡C), 127.7 (d, $^2J_{CP} = 13.5$ Hz, *o*-Ar), 128.8 (d, $^3J_{CP} = 10.2$ Hz, *m*-Ar), 131.1 (d, $^4J_{CP} = 2.1$ Hz, *p*-Ar), 137.9 (d, $^1J_{CP} = 32.8$ Hz, *i*-Ar), 150.8 (d, $^3J_{CP} = 5.2$ Hz, P−N−N−*C*=O), 152.7 (s, P−N−*C*=O), 194.8 (d, $^2J_{CP} = 7.4$ Hz, *cis*-CO), 197.5 (d, $^2J_{CP} = 30.2$ Hz, *trans*-CO), 204.2 (d, $^2J_{CP} = 16.0$ Hz, *C*≡*C*≡C); ^{1}H NMR (CDCl$_3$) δ 0.7−2.4 (m, 12H, CH$_2$), 3.10 (s, NCH$_3$), 4.78 (dddd, $^3J_{HP} = 5.8$ Hz, $^3J_{HH} = 3.8$ Hz, $^3J_{HH} = 3.7$ Hz, $^5J_{HH} = 4.0$ Hz, 1H, N−C−H), 5.98 (dddd, $^4J_{HP} = 9.8$ Hz, $^3J_{HH} = 6.8$ Hz, $^3J_{HH} = 4.0$ Hz, $^5J_{HH} = 4.0$ Hz, 1H, C=C−H), 7.41−7.48 (m, 5H, Ar−H); HRMS (EI) (*m/e*) for $C_{24}H_{22}N_3O_7P^{182}W$: calcd 679.0705, found 679.0704 ± 0.0003.

Computations. All electronic structure calculations were carried out using the GAUSSIAN 98 suite of programs.[32] Geometries were optimized at the HF and MP2(fc) levels of theory using the 6-31G* basis set. The Hessian index, which is the number of negative eigenvalues of the force constant matrix, was determined for all species at the SCF level to be 0. Geometrical MP2(fc) parameters for selected systems are shown in Figure 1. This figure also shows the ^{31}P and ^{13}C NMR chemical shifts for structures **17** and **18** as calculated with the GIAO method at MP2(fc)/6-31G* and referenced against Me$_3$PO and Me$_4$Si, respectively. G3(MP2) theory was used to obtain more accurate absolute energies for the optimized structures. Heats of formation (ΔH_f^{298}) for the systems in eqs a−e were estimated from their heats of atomization calculated at G3MP2.[31] The resulting strain energies are listed in Table 4 together with the ΔH_f^{298} values and absolute energies for selected molecules.

X-ray Crystal Structure Determination of 19A and 19B. Diffraction data of single crystals, mounted on a glass fiber with epoxy cement, were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å, sealed tube, graphite monochromator). Data reduction was performed with the HELENA program.[43] The structures were solved using the MolEN package.[44] Refinement was done on F^2 of all reflections using SHELXL-97.[45] Absorption correction (routine DELABS), checking for higher symmetries, and structure calculations were performed with the

PLATON package.[46] Details of the crystal data and structure solution procedures are summarized in Table 6.

X-ray Crystal Structure Determination of 20A, 20B, *cis*-20C, and *trans*-20C. Diffraction data of single crystals, mounted on a glass fiber with perfluoropolyether oil, were collected at a temperature of 150 K on an Enraf-Nonius CAD4T diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å, rotating anode, graphite monochromator). Data reduction was performed with the HELENA program.[43] The structures were solved with Patterson methods using the program DIRDIF.[47] Refinement was done on F^2 of all reflections using SHELXL-97.[45] In structure *trans*-**20C**, the disorder of atoms C7 and C8 could not be resolved. Absorption correction (routine DELABS), checking for higher symmetries and structure calculations were performed with the PLATON package.[46] Details of the crystal data and structure solution procedures are summarized in Table 6.

Supporting Information Available: Position and thermal parameters and a complete listing of bond lengths, angles, and torsion angles for **19A**, **19B**, **20A**, **20B**, *cis*-**20C**, *trans*-**20C** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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